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Geochemical methods for interpreting groundwater flow around Tono and their generic relevance to site selection, site characterization and Performance Assessment

(A final report)

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Tono Geoscience Center

Japan Nuclear Cycle Development Institute

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JAPAN NUCLEAR CYCLE DEVELOPMENT INSTITUTE

Geochemical methods for interpreting groundwater flow around Tono and their generic relevance to site selection, site characterisation and Performance Assessment

A Final Report on a JNC International Fellowship by

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PREFACE

This report presents work undertaken by Richard Metcalfe, during a JNC International Fellowship, between 1st March 1999 and 28th February 2002.

During this period, the main purpose of the work was continuous review and appraisal of geochemical studies being done by the Japan Nuclear Cycle Development Institute (JNC) and contribution to a range of specific geochemical studies.

This involved working closely with Japanese colleagues at Tono Geoscience Center (TGC) and included the following major activities:

- assistance with the production of the English language version of the Second Progress Report (H12);
- contribution to the construction of a geochemical database for the Tono area;
- interpretation of groundwater and mineralogical chemical data from the Tono area;
- interpretation of rock chemical and mineralogical data from the Tsukiyoshi Fault zone;
- development of a new statistical method for investigating groundwater mixing;
- review of investigations in a new, inclined deep borehole (MIU-4);
- contribution to planning the Mizunami Underground Laboratory (MIU);
- publication of results (two papers in press at the time of completion);
- dissemination of results at conferences.

These activities were very broad in scope and produced a wide range of different outputs. However, a dominant theme was the application of geochemical information to understand past and present groundwater flow. The present report aims to compile those outputs from the Fellowship that deal with this theme.

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1. INTRODUCTION

1.1 Purpose of this report

This report describes work done by Richard Metcalfe, during a Japan Nuclear Cycle Development Corporation (JNC) International Fellowship (henceforth 'Fellowship'). This Fellowship began on 1st March 1999 and was completed on 28th February 2002.

1.2 Purpose of the Fellowship

The Tono Geoscience Center (TGC) of JNC is developing generic methods for investigating deep groundwater systems, during on-going research in the Tono area of Gifu-ken, central Honshu. The work focuses on the Cretaceous Toki Granite and on overlying Miocene and Pliocene to Pleistocene sedimentary rocks.

The Fellowship aimed to determine how this research could produce generic geochemical methods for investigating past/present groundwater flow near possible future sites for the deep geological disposal of high level radioactive waste (HLW) elsewhere in Japan.

To meet this general goal, subsidiary goals of the Fellowship were to:

- summarise how previous geochemical research in the Tono investigations is useful;
- suggest how future investigations in the Tono area could:
  - ⇒ demonstrate the applicability of geochemical methods developed elsewhere;
  - ⇒ develop new generic geochemical methods;
- suggest how these methods might be used in future site selection, site characterisation and performance assessments (PA) elsewhere in Japan.

It was aimed to disseminate relevant results to the wider scientific public by giving presentations at scientific meetings and publishing papers in the open scientific literature.

1.3 Relevance of the work

Groundwater flow is important because it might transport radionuclides from any future deep underground repository for radioactive wastes (Figure 1). When selecting and characterising future repository sites, it is necessary to identify locations where flow conditions are presently suitable and are expected to remain suitable, for as long the waste remains hazardous. To interpret natural chemical variations, it is also necessary to understand disturbances caused by borehole drilling, testing, sampling, and underground excavations (Figure 2).

Suitable groundwater conditions would cause no unacceptable risks to living organisms. Generally, it is desirable to demonstrate that:

- flow rates will be sufficiently slow;

- flow paths between the repository and the near-surface biosphere will be adequately long;
- flow will be away from potentially vulnerable parts of the biosphere, such as human populations.

Depending upon the particular hydrogeological situation near a potential repository site, it may also be valuable to demonstrate:

- adequate dilution of any radionuclides migrating from a repository.

These objectives can be met most effectively by using geochemical methods **together** with hydrogeological methods (Figure 3). Major advantages of this approach are that:

- Geochemical data can be an independent check on groundwater flow models based on physical hydrogeogeological information.
- Geochemical data can constrain physical hydrogeological models, for example by indicating geologically reasonable boundary conditions.
- Geochemical data often allow groundwater mixing proportions to be calculated more precisely than do calculations based on physical hydrogeological data.
- Geochemical data often allow past states of the groundwater flow system to be interpreted in more detail than do hydrogeological data alone. Thus, geochemical data are essential for palaeohydrogeological studies.

The last point is particularly important because information about past states of a flow system enable:

- realistic scenarios to be constructed for future states of the system;
- the general stability (or instability) of any flow system to be demonstrated;
- demonstration and/or testing of numerical models for the past evolution of the flow system, which can then be used to predict the future evolution of the system.

This combined hyrogeochemical-hydrogeological approach has been used internationally. Many specialist geochemical methods have been developed for this purpose. Spatial and/or temporal variations in groundwater chemistry, mineral chemistry and mineral distributions at a site can be used to develop and/or support general conceptual flow models (e.g. indicate general groundwater sources, flow directions etc). Alternatively, these variations can be used to calibrate numerical flow models. Both conceptual and numerical models are developed iteratively, with data acquisition, during site characterisation. Both types of model are also a basis for PA modelling.

However, in other countries geochemical methods have tended to be developed in groundwater systems that contain saline groundwaters and brines. In these systems mixing is often a more important cause of chemical variations than water/rock interactions (Figure 4). In contrast, in Japan relatively fresh deep groundwater systems are more common. In these systems water/rock interactions are likely to be proportionately more significant controls on chemical variations (Figure 4). This means that many methods employed in other countries need to be tested to establish their applicability in Japan and, where appropriate, the methods need to be adapted.

Prior to the present Fellowship, Japanese research and development for deep geological disposal of radioactive wastes had focused on chemical conditions deep underground. The emphasis had been developing generic methods to determine conditions (e.g. pH and redox conditions) in potential future repository environments. Compared to research in many other countries, there had been less consideration of geochemical methods for understanding past and present groundwater flow. Therefore, there was a need to reassess **how** methods developed in other countries could be applied directly in Japan or adapted for use in Japan. In the present Fellowship, the focus was on assessing whether and how methods used or developed during deep geological disposal-related investigations in the United Kingdom (UK) could be adapted for possible use in Japan.

1.4 Previous experience

The fellow came to Japan from the British Geological Survey (BGS), where he had been employed as a geochemist for 8.5 years. During this time he had worked extensively on groundwater and mineral chemistry. A particular focus of research was the development of geochemical approaches for understanding past and present groundwater flow systems. Particular topics of interest were developing methods and/or approaches to:

- identify groundwater sources;
- constrain groundwater flow directions;
- identify groundwater flow pathways;
- constrain groundwater flow rates, particularly by:
  - ⇒ estimating recharge times for water;
  - ⇒ estimating residence times for water in different rock formations;
  - ⇒ estimating residence times for solutes in different rock formations;
- constrain groundwater mixing proportions;
- constrain/calibrate physical hydrogeological models;
- determine spatial variations in chemical conditions (e.g. oxidation-reduction (redox) states, pH, salinity) along groundwater flow paths;
- determine the stability of/temporal variations in these chemical conditions at any given locality within the flow system.

The work covered mainly radioactive waste-related projects, but also included many other types of project, including water resource investigations and hydrocarbon reservoir evaluations.

Most research was carried out on the characterisation of a potential deep geological repository for intermediate-level and some low-level radioactive wastes at Sellafield in northwest England. Until 1997, this site was being evaluated by United Kingdom Nirex Limited, for which BGS was a major contractor. For two years the fellow managed the geochemical interpretation at this site. He also gained exposure to radioactive waste management projects elsewhere in Europe, largely through involvement in two large projects concerned with palaeohydrogeology, funded by the Commission of the European Communities.

This experience formed the basis for the assessment of geochemical methods for interpreting groundwater flow presented in this report.

2. WORK SCOPE

2.1 General approach

The main approach was to compare methods used internationally with those used in the Tono area, to:

- identify where methods used in the Tono area were more or less advanced than those used internationally;
- suggest how methods used in the Tono area could be improved based on international experience;
- suggest methods that had been used internationally, but not in the Tono area, which could potentially be adapted for use in the Tono area.

A small number of particularly promising methods, which had not been used previously were then tested. This testing was done by targeted studies, mainly as components of three larger studies in the Tono area (see Section 2.2).

An exception was the development and testing of a new method for interpreting groundwater mixing proportions. This work was done as part of an international collaboration project of JNC, that used data from the Hard Rock Laboratory (HRL), which has been constructed by the Svensk Kärnbränslehantering AB (Swedish Nuclear Fuel and Waste Management Company; SKB) at Äspö, Sweden. This was valuable, because sufficient data to develop such a method were not available from the Tono area. This work using the Äspö data was relevant for the planned Mizunami Underground Laboratory (MIU), which will be a broadly similar type of facility to the Äspö HRL.

The applicability of these geochemical methods to investigations of groundwater flow elsewhere in Japan was then evaluated. To do this, information about general characteristics of deep geological environments in Japan, was taken from JNC's Second Progress Report on Research and Development for the Geological Disposal of HLW in Japan.

Finally, general suggestions were made about how geochemical methods for investigating groundwater flow could be applied in site selection, site characterisation and PA. This was based upon experience in the UK.

2.2 Information sources

2.2.1 Information from the published literature

A wide range of published literature concerning sites from around the world was considered during the Fellowship. Most of this literature was related to radioactive waste investigations. However, relevant literature concerning basic methods and approaches, and concerned with groundwater resources and hydrocarbons, was also considered.

2.2.2 Information from the UK

Information about investigations in the UK was taken mainly from documents prepared by United Kingdom Nirex Limited (Nirex). Most of these reports covered the site of Sellafield in northwestern England. Sellafield lies near the coast in an area dominated by a coastal plain, varying between about 20 m and 80 m above sea level. Here, Carboniferous to Triassic sedimentary rocks, capped by Quaternary sedimentary deposits, overstep onto Lower Palaeozoic basement rocks, mainly of the Ordovician Borrowdale Volcanic Group (BVG). The BVG consists of lavas and volcanosedimentary rocks. It was planned to construct the repository within the BVG (within the Potential Repository Zone, PRZ).

This site was investigated predominantly between 1989 and 1997, to assess its suitability for a deep underground radioactive waste repository, planned for intermediate- level, and some low-level, solid wastes. By the end of the investigations 29 deep boreholes (c. 150 m to c. 2 km) had been drilled. These data included hydrogeological, geochemical, petrological and mineralogical data. Chemical compositions for groundwater were obtained at 163 localities in 19 of the boreholes. These groundwaters range from fresh, Na-Ca-HCO_3 waters, to Na-Cl dominated brine with Total Dissolved Solids (TDS) up to around 190,000 mg/l. The fresher waters originated in meteoric recharge in high ground to the east of the site, whereas the brine originated in halite dissolution within evaporite deposits, dominantly in the Triassic rocks to the west of the site. Variations in groundwater salinity across the site mainly reflect mixing between these two water types.

Additional information was also taken from other relevant groundwater investigations in the UK, both connected with deep disposal of radioactive wastes, groundwater resources and hydrocarbon reservoirs.

2.2.3 *Information from Äspö, Sweden*

During international collaborative research conducted by JNC, information was obtained from published reports supplied by SKB, concerning the HRL at Äspö. The HRL was excavated to a depth of 450 m beneath Äspö Island, a low-lying island (< 10 m above sea level) with dimensions of about 1 km x 1 km, that lies in the Baltic Sea, just off the east shore of southern Sweden, approximately 400 km south of Stockholm. The rocks of Äspö island are predominantly fractured granitoids (true granite, granodiorite to diorite), which mostly have ages of approximately 1800 Ma. The groundwater chemistry is very variable, ranging from fresh to saline water with up to around 75000 mg/l TDS. This variability reflects varying inputs from meteoric water, marine water and glacial recharge and deep 'continental shield brines'.

2.2.4 *Information from the Tono area*

Geochemical research by the TGC was divided between several different projects, with several different time scales and various different objectives. However, the technical objective of using geochemistry to understand groundwater flow overlaps these different projects. The Fellowship attempted to draw together relevant information from several of these investigations, irrespective of whether they had been designed specifically to study groundwater flow. Several groups of project were considered:

- research on a reversed fault, the Tsukiyoshi Fault, one of the most prominent structural features in the Tono area;
- natural Analogue Studies (other than the Tsukiyoshi Fault investigation) focused in and around Tono Mine;
- investigations of the flow system around the site of the planned Mizunami Underground Laboratory (MIU);
- investigations of the regional flow system in the Tono area (an area of approximately 30 km x 30 km).

Information was taken from JNC Technical Reports and published documents. Discussions with colleagues in JNC also provided much valuable information.

2.3 Major activities

The Fellowship involved many diverse activities, the chief ones being:

- compilation and summary of relevant literature concerning geochemical methods;
- compilation of groundwater data from the Tono area;
- planning new geochemical investigations in the Tono area;
- logging of rock core;
- interpretation of new hydrogeochemical data from the Tono area, principally halide data;
- preparation of a computer code for interpreting ^{36}Cl data;
- development of a new statistical method for calculating groundwater mixing proportions from groundwater chemical data;
- compilation of thermodynamic data for geochemical modelling;
- geochemical modelling using computer codes PHREEQC and Geochemists Workbench 3.0 (GWB);
- review and correction of documents written by JNC colleagues;
- preparation of publications;
- giving presentations.

3. METHODS AND THEIR APPLICATIONS INTERNATIONALLY

3.1 Purpose of this chapter

This chapter describes briefly the major geochemical approaches that are used internationally to interpret past and present groundwater flow. The information given is based mainly on experience at the Sellafield site in northwest England, though with additional details from other investigations. The main applications of these approaches in radioactive waste management-related investigations are also outlined briefly. The chapter does not give a detailed description of the methods, since details are published in many other freely available documents. Further details of several approaches are also provided in later sections, which are referenced here as appropriate.

The main aim of the chapter is to provide a basis for the discussion of methods and approaches that have been applied in the Tono area. This discussion is presented in Chapter 4.

3.2 General principles

The general approach is to develop models for the spatial distributions of chemically different groundwaters and then to compare these models with the observed distributions of these groundwaters. The models are then modified as appropriate until there is a match between model results and observations (Figure 5).

Figure 5 illustrates the general use of geochemical data when constructing numerical models for groundwater flow. In this case, the aim is for the computer code to reproduce some feature of groundwater chemistry that can be represented numerically, such as solute concentrations.

A similar approach may also be applied when constructing *conceptual* models. That is, basic concepts for groundwater flow patterns must be consistent with general concepts for the distribution and chemical evolution of different groundwaters.

These approaches can also be applied to both present groundwaters and to past groundwaters. For example, mineralogical evidence might suggest that in the past a particular fracture-filling mineral has been precipitated and then later dissolved. This information can be used to deduce a change in the chemistry of formation waters over time. Numerical models describing groundwater flow over time should then match such a change.

An important use of geochemical information is to determine the extent to which a flow system has been stable in the past, either quantitatively or qualitatively (Figure 6). Such determinations can be used as a basis for predicting the future stability of the groundwater flow system (Figure 7).

3.3 Types of data required

All these different applications can use the following kinds of information determined during site investigations:

- chemical and isotopic variations in:
  - ⇒ groundwaters;
  - ⇒ minerals;
  - ⇒ rocks;
- characteristics and distributions of void-filling (pore-space and fractures) minerals;
- characteristics and distributions of secondary (alteration) minerals in both fractures and the rock's matrix.

Groundwater samples may be collected from boreholes or from inflows into underground facilities such as laboratories. Surface waters and meteoric waters are also typically sampled and analysed for comparison.

Minimisation of contamination during sampling from boreholes represents a major challenge. Various approaches have been used internationally:

- sequencing/scheduling of sampling to minimise disturbance to in-situ groundwaters and minimise the chances of causing contamination;
- using appropriate borehole testing methods (e.g. down-hole sampling will minimise the chances of contamination by air);
- using appropriate drilling fluids (e.g. drilling with water dosed with an unreactive tracer will generally allow less-contaminated samples to be obtained than drilling with organic polymer-based drilling mud).

Minimisation of contamination between sampling and analysis can be done by:

- sequencing and scheduling of analysis to minimise post-sampling contamination;
- using appropriate sample preservation methods;
- using appropriate sample storage methods.

Samples for mineralogical and petrographical studies are typically obtained from rock core and from exposures in underground workings. Often exposures in underground workings have undergone oxidation or other alteration related to the construction and operation of the workings. Such effects must be allowed for. Additionally, some detailed information may be lost. For example delicate mineral textures which reveal age relationships can be damaged in mine faces or the disturbed zone surrounding these workings.

Similarly, mineralogical information can be lost by from rock core during drilling (Bath et al. 2000). Generally, triple-barrel coring techniques should be used to preserve the maximum amount of information.

In cases where mineralogical samples are from plastic lithologies, or contain particularly delicate textures, some form of preservation is highly desirable or essential. For example, clay-rich fracture-fills should be kept damp to prevent drying before investigations. Application of investigation methods that avoid drying is also highly desirable.

3.4 Data processing

3.4.1 Removal of the effects of groundwater contamination and disturbance

Before interpreting geochemical data it is essential to evaluate the extent to which it is representative of in-situ conditions. This requires that the sizes of many effects be established, notably:

- physical disturbance of the locations of chemically distinct groundwaters during borehole testing, construction of underground facilities etc;
- reactions (e.g. water/rock reactions, water-water reactions) that may accompany this physical disturbance;
- contamination by drilling fluid;
- reaction with drilling fluids;
- reaction with drilling and sampling equipment;
- contamination by air;
- degassing during depressurisation associated with sampling from depth;
- evaporation during storage;
- contamination or disturbance in the laboratory, during analysis.

The effects of disturbances can be judged by monitoring groundwater chemistry over time and by looking for variations that can be attributed to the effects of disturbance. It may be possible to extrapolate any trends in chemical variation that are observed, to the start of the investigations, thereby allowing for the disturbances.

Integration of numerical groundwater flow models with time-dependent groundwater chemical data, obtained from either tunnels or boreholes is one potentially powerful approach to doing this. This has been one aspect of the investigations being undertaken during Task 5 of the Äspö Groundwater Modelling Task Force, coordinated by SKB in Sweden. This was an international programme of research involving teams from several countries. During the present Fellowship, JNC contributed to this work. The results are presented in Chapter 9.

The quality of the groundwater chemical data is typically evaluated using one or more of the following approaches:

- inter-lab comparisons, in which the same sample is sent for analysis in different laboratories;
- submission of separate sub-samples of the same sample 'blind' (without identification) to the same laboratory;
- submission of standards of known composition to a laboratory 'blind';
- evaluation of the general consistency of the analyses that are obtained, notably:
  - ⇒ determination of charge balance (the total anionic charge should be close to the total cationic charge);
  - ⇒ checking the consistency of alkalinity, total inorganic carbon and pH;

⇒ screening for clearly 'odd' numerical values, such as values that do not plot on a consistent trend with other data, or values that would lie outside normally accepted ranges.

3.4.2 *Data management*

Issues relating to data management are not just applicable to interpreting groundwater flow from geochemical data. However, interpretations of groundwater flow require that the integration of many varied types of data (groundwater chemistry, lithological data, mineralogical data, structural data, hydrogeological information). To do this successfully requires careful management of these varied types of data.

For example, at Sellafield, correlations between calcite crystal shape, groundwater chemistry and hydraulic characteristics were only possible because all data were recorded consistently, with depths reported from the same datum. During the later investigations, this integration was facilitated greatly by the development of a digital database (Nirex Digital Geoscience Database (NGGD); Nirex, 1996) that contained all these types of information. Major advantages of this database were that it:

- contained information about data quality as well as the data themselves;
- enabled integration of these varied datasets;
- ensured that different interpretation teams worked with a consistent set of data of known quality.

An important lesson from the experience at Sellafield is that it is highly desirable to develop data management procedures (e.g. staffing structures, library facilities, mechanisms for data transfer) and structures (e.g. databases) early in a project, before large quantities of data need to be managed.

3.4.3 *Geochemical modelling*

Numerical geochemical modelling codes are an important tool that can be used in the interpretation of groundwater flow systems. They can be used to:

- scope magnitudes of the effects of processes affecting groundwater chemistry along a flow path;
- scope magnitudes of the potential chemical impact of natural perturbations to the groundwater system (e.g. climate change changes to groundwater flow paths etc);
- investigate the potential affects of contamination and/or sampling-related perturbations;
- to help plan investigations that are targeted on parameters that are most likely to be useful.

In the site characterisation at Sellafield, the computer codes EQ3/6 and, to a lesser extent PHREEQC, was used to evaluate mechanisms that could form late fracture-filling calcite. A major aim was to deduce whether it is reasonable to suggest that paragenetically late fracture-filling calcite crystals at the site could record the effects of climate changes related to glaciations. Different scenarios, involving different calcite-forming

mechanisms, flow rates etc were investigated. The observed calcite volumes were calculated to require times within a wide range, depending upon the formation mechanism. However, the majority of times calculated lie in the range 10^1 to 10^4 years. Thus, it is reasonable to suppose that the late calcite formed within the duration of the Quaternary; a longer time scale is not *needed* to explain the quantities of calcite that are observed.

The calculations also provided insights into the relative importance of different methods for precipitating fracture-filling mineral assemblages. An important finding is that the following mechanisms could be significant causes of late calcite precipitation:

- heating calcite-saturated fresh water through a temperature interval similar to that seen presently in the groundwater system;
- mixing between fresh water and saline water brine;
- mixing between fresh water and brine.

Thus, variations in the temperature gradients within the groundwater system and/or decreases in the elevation of the transition between fresh and saline groundwater could both stimulate the production of paragenetically late calcite. The temperature gradients and elevations of the salinity transition could both be partially controlled by climatic processes. For example, variations in these features could reflect fluctuations in the amounts of recharge and changes in the degree to which the area is covered by ice.

The calculations also suggested that the quantities of calcite that can be deposited from a given water volume, could be linked to redox-related processes in the recharge zone. Potentially, the calcium and bicarbonate that are liberated by calcite dissolution in the recharge zone may be re-precipitated as calcite further along the flow path. If pyrite is oxidised during the recharge process then, compared to cases in which no pyrite is present, greater quantities of calcite will be dissolved. Oxidation of pyrite may cause relatively large amounts of paragenetically late calcite to be precipitated further along the flow path.

If pyrite is present in the recharge zone, then variations in oxygen and CO_2 partial pressures, owing to glaciation and deglaciation, will be reflected in marked variations in the amount of calcite that can be dissolved or precipitated by a given volume of water. Conversely, pyrite may be absent from the recharge zone. In this case, variations in the partial pressures of oxygen and CO_2 accompanying glaciation and deglaciation will have a much less marked affect upon the variations in the amounts of calcite that are dissolved or precipitated by a given water volume.

3.5 Interpretation of present groundwater flow

3.5.1 Investigating spatial variations in groundwater chemistry

The interpretation of the kinds of data described above and their wider applications can be illustrated by the experience in the Sellafield area of northwestern England (Figure 8; Section 2.2.2).

During these investigations data were acquired iteratively, so that each new borehole was drilled to address questions posed by earlier boreholes. Specific features of note in Figure 8 are:

- Most of the boreholes were concentrated in the area of the Rock Characterisation Facility (RCF) or PRZ. These were designed specifically to obtain detailed information about the chemical conditions and hydrogeology.
- Apart from 6 boreholes (Boreholes 7A/7B, Borehole 11A, Boreholes 13A/B, and Borehole 14) boreholes at the site scale lay approximately along a northeast-southwest profile. This is roughly parallel to the dominant flow direction, which is from high ground in the east, towards the coast.
- The boreholes that were not drilled along this profile were drilled partly to evaluate any three-dimensional characteristics of variations in groundwater flow and chemistry.
- Boreholes 8A/8B and Boreholes 9A/9B were drilled partly to investigate conditions near the recharge zone.
- Borehole 16 was drilled largely to investigate the nature of the transition between shallower fresh groundwater and deeper saline groundwater, at a locality near the deepest inferred occurrence of this transition.

A key feature of the investigations in the Sellafield area was that there are variations in the level of groundwater salinity across the site (Figures 9 and 10). Two main variations are of interest:

- A transition between shallower Ca-HCO_3 dominated or Ca-Na-HCO_3 dominated fresh groundwater (TDS < 1000 mgl^{-1}), which occurs throughout the site, and deeper Na-Cl dominated saline water (10,000 mgl^{-1} • TDS < 100,000 mgl^{-1}, in the east) or brine (TDS • 100,000 mgl^{-1} in the west).
- A deeper transition between the saline water in the east and the brine in the west, which is steepest in Borehole 10A in the middle of the site.

In the most recent PA, Nirex 97 (Nirex, 1997a), a 3D model for these variations in salinity was constructed (Figure 10) and used as a basis for groundwater flow modelling (Figure 10).

The characteristics of groundwater salinity, other than its level (TDS), also proved valuable for:

- constraining the origins of groundwater salinity;
- suggesting general groundwater flow directions;
- suggesting appropriate boundary conditions;
- constraining mixing proportions between different groundwater masses.

In the Sellafield groundwater system, the ratios Br/Cl proved especially useful. The general principles behind using these solutes for determining the origins and mixing proportions of different groundwater masses are illustrated in Figure 11. Actual Br/Cl ratios for the Sellafield groundwaters are illustrated in Figure 12.

The errors on both the Br and Cl determinations were very high in the fresh groundwater zone, reflecting the nature of the drilling fluid used (generally dosed with LiCl tracer, maintained at a concentration equivalent to about 1000 mgl^{-1} Li). This meant that the

Br/Cl ratios were little use in this zone. However, in the saline water and brine zones, where the groundwaters contained very much more Br and Cl than the drilling fluid, the uncertainties were much less and systematic variations in Br/Cl were found.

The brines in the west have relatively low ratios (c. 1 x 10^{-3} by mass in BH3), compared to those of the saline waters in the east (c. 2 x 10^{-3} by mass in BH2). These variations were interpreted to reflect two main sources of groundwater salinity: halite dissolution in the Permo-Triassic basin fill further to the west; and an unknown source in the crystalline basement to the east. Possibly water/rock interactions in granite basement and/or surrounding Carboniferous rocks may have been important sources of Br in this second case, though this interpretation is tentative. The ratios are all significantly lower than seawater (c. 3.5 x 10^{-3} by mass), precluding the presence of any significant seawater salinity.

The variations in the Br/Cl ratios were useful for estimating mixing proportions between the different groundwaters (Figure 13).

The systematic variations in Cl concentration across the site and its potential for constraining groundwater flow models meant that it was particularly desirable to constrain the residence time of the Cl in the various rock formations. For this reason a study of ^{36}Cl was carried out. This isotope is radioactive with a half-life of 3.01 x 10^{-5} years (Endt and van der Leun, 1973) and is also produced in-situ within rocks. Both these phenomena make the isotope potentially valuable for investigating changes in groundwater flow over Quaternary time scales. Further details of the principles behind the application of this isotope are given in Chapter 7.

The ^{36}Cl study showed that, while variations in Br/Cl ratios could be explained by mixing of different groundwaters across the site, variations in ^{36}Cl/Cl could not be explained entirely by this mechanism (Figure 14). Instead, it appears likely that the groundwater's ^{36}Cl/Cl ratio is partly controlled by in-situ production of ^{36}Cl within the rock. At depth in the east of the site and in the west of the site, the ^{36}Cl/Cl ratios appear to be close to equilibrium with the in-situ production and radioactive decay of ^{36}Cl. This suggests that in these locations the chloride has been resident within the rocks for > c. 1.5 Ma.

Comparisons between theoretical equilibrium ^{36}Cl/Cl and values measured for the groundwater samples provide insights into the spatial scales of mixing. These comparisons also help to trace the movement of chloride between rocks with different production rates (Figure 15). For example in Borehole 2 at Sellafield, the chloride in the groundwater is close to the mean equilibrium value calculated for the rocks of the BVG, which is higher than values calculated for the sedimentary cover rocks in this location (Figure 15). The chloride has therefore most probably resided within the BVG for more than around 1.5 Ma.

Variations in other groundwater constituents, notably ^{34}S/^{32}S, ^{87}Sr/^{86}Sr provided further supporting evidence for the validity of the overall interpretations.

3.5.2 Application of chemical data in flow modelling

In the case of Sellafield the hydrochemical data described in Section 3.5.1 were valuable for constructing a conceptual hydrogeological model for the site (Figure 16). This model was based on both the hydrochemical data and hydrogeological data. A key feature of the model is that general flow patterns interpreted from both types of data are self-consistent.

Many kinds of coupled chemical-hydrogeological model were also constructed. The aim was to reproduce the observed distributions of chemically distinct groundwaters. One such model is illustrated in Figures 17 and 18.

3.5.3 *Statistical processing of hydrochemical data*

The flow models for Sellafield discussed above were based largely on spatial variations in overall groundwater salinity and in key constituents, notably Br, Cl and $^{36}Cl/Cl$. However, often other chemical data can provide important insights into the origins of groundwater salinity, flow directions etc. Interpretation of these variations by constructing simple cross-plots or plots of spatial variations in concentrations is often difficult because many different processes may affect the concentrations of a particular constituent.

Various multivariate statistical techniques can be used to distinguish chemical variations due to these different processes (Figure 19). These methods can help separate, for example, chemical variations due to water/rock interactions, mixing and contamination. The results of multivariate statistical techniques like Principal Component Analysis (PCA) are independent (i.e. uncorrelated) groups of correlated variables. Expert interpretation is needed to assign these groups to actual chemical processes.

During the investigations at Sellafield, all the water chemical data available were subjected to PCA. This identified several different groups of correlated variables. Two of these groups were interpreted to reflect two groundwaters, which mix across the site. For three boreholes, proportions of these waters, termed Water 1 and Water 2, are plotted against depth in Figure 20. It can be seen that there are systematic variations in these proportions, which correspond to the variations in proportions of groundwaters identified previously based on Br/Cl ratios (Figures 12, 13 and 14). It is noteworthy that the shallower saline groundwaters in Borehole 10A are similar to the saline groundwaters further east, whereas the deeper groundwaters in Borehole 10 are similar to the brines further west. An important point is that these differences are distinguished not just on the basis of salinity level, but also on the basis of the ratios of dissolved constituents in the groundwaters.

A different approach for applying multivariate statistics to investigate chemical variations in groundwaters was adopted by SKB, which developed the computer code Multivariate Mixing and Mass balance (M3; Laaksoharju et al. 1999). This code was written to investigate variations in groundwater chemistry at Äspö in southeastern Sweden. The program calculates mixing proportions of extreme groundwater compositions, selected by the user after inspecting a plot of the eigen values of the first two principal components calculated from a set of groundwater data (Figure 21). In the terminology adopted by SKB, these extreme groundwater compositions are referred to as 'reference waters'. However, it is stressed here that these waters are not 'end-members' in the sense of the

term as applied to minerals. This is because even the waters of extreme composition are often mixtures of other groundwaters and hence the 'end-members' are not *limiting* compositions.

By investigating variations in the proportions of these different 'end-members' across Äspö Island, SKB were able to shed considerable light on the processes controlling groundwater mixing. For example, there appears to be a general increase in a basement 'brine' component with respect to depth (Figure 22).

3.6 Interpreting past groundwater flow and predicting future flow

3.6.1 General approaches

A general approach for applying knowledge of past groundwater flow to predict future flow and flow system stability is presented in Figure 23. This approach requires that solutes in the groundwater are interpreted in terms of groundwater residence time and/or that mineralogical evidence is interpreted as a record of past groundwater chemical conditions. Spatial variations in these indicators can together help to build an interpretation of past flow directions, flow rates, chemical conditions and flow system boundary conditions,

3.6.2 Application of groundwater chemistry

The application of groundwater chemistry requires an understanding of relationships between:

- recharge time;
- solute residence time;
- groundwater residence time.

The meaning of these terms is explained in Figures 24, 25, and 26 and general relationships between them are illustrated in Figure 27.

The major groundwater constituents that are used internationally to investigate groundwater residence times are tabulated in Table 1. Typical values of the most commonly used ones are given in Table 2.

Depending upon the nature of the solute and the circumstances in which it occurs, the residence time information that it gives can be:

- quantitative (allow an estimate of absolute residence time to be made);
- limiting (residence time is constrained to be greater than or less than some value);
- qualitative (allows an estimate of relative residence time to be made, e.g. one water has been resident in a rock formation longer than another water, though the absolute residence time is unknown).

Different types of residence time information that can be obtained from three commonly used residence time indicators are illustrated in Figure 28.

3.6.3 *Application of mineral data*

Minerals will typically record information about the chemistry of groundwater from which they precipitated in the following major ways:

- The range of chemical conditions under which a mineral is stable constrains the composition of the water from which it precipitated. For example, the occurrence of pyrite would suggest that conditions were reducing at the time of pyrite formation and place an upper limit on the redox potential of the waters.
- The chemical composition of a mineral may constrain the chemistry of the groundwater. For example, the ratio of Fe and Mn in calcite will be controlled partly by pH and redox conditions.
- Crystal morphology may be controlled by the composition of the groundwater. For example, the shapes of calcite crystals appear to be controlled partially by water chemistry.
- Dissolution features such as etch-pits on crystal surfaces may indicate that in the past chemical conditions fluctuated outside the stability range of the mineral.
- Crystal growth zones, which may have different chemistries, preserve different crystal morphologies, or contain evidence for dissolution features, may provide a record of past changes in conditions.

To relate this kind of information to the groundwater flow system, it is necessary for detailed paragenetic information to be obtained, generally from rock core. The basic approach is to:

- identify the most recent minerals occurring in contact with the present groundwater;
- determine spatial variations in the natures of these minerals, their chemical compositions and their textures;
- compare these mineralogical variations with variations in the present groundwater chemistry;
- compare these mineralogical variations with older mineralogical variations.

During the investigations at Sellafield, a clear correlation was seen between the morphology of paragenetically late calcite crystals and present groundwater chemistry (Figure 29; Milodowski et al. 1998). The lack of calcite showing 'fresh water forms' (c-axis flattened crystals) in the zone now occupied by saline water gave an important constraint on the groundwater flow system. It provided a justification for flow models in which fresh water did not penetrate more deeply than this.

In some places, zoning between 'fresh water forms' and 'saline forms' (c-axis elongate) was found near the present transition between fresh and saline groundwater. This zoning occurred within a depth interval of only a few metres, suggesting that past fluctuations in depth of the transition between the fresh water and saline water were of a similar size.

Variations in the concentrations of Fe and Mn in calcite will result in variations in the luminescence shown by the calcite when viewed under cathode rays. Variations in Fe and

Mn concentrations are also expected to depend on redox and pH conditions (Figure 30). Therefore, zoning revealed by cathodoluminescence could also reflect past variations in redox and pH.

At Sellafield, the paragenetically late calcite also showed variations in zoning revealed by cathodoluminescence (Figure 31). The zoning in the deeper zone presently occupied by saline groundwater and/or brine was generally less variable than that in the fresher water zone. This is consistent with the hypothesis that redox-pH conditions in the deeper groundwater zone were less variable than in the fresh water zone.

3.7 Summary and implications for studies in the Tono area

A basic approach for applying geochemical information when developing concepts for groundwater flow is summarised in Figure 32. A key feature is that the approach is iterative. Concepts derived from existing data guide future data acquisition leading to the refinement of concepts or improvement in confidence of existing concepts.

Important chemical constraints on models for groundwater flow at Sellafield are summarised in Table 3. An important underlying approach was to identify and characterise key chemical features of the groundwater system that coupled flow models could reproduce, or which would constrain the boundary conditions of the flow models.

Broadly similar approaches could be adopted in the Tono area.

4. METHODS AND THEIR APPLICATIONS IN THE TONO AREA

4.1 Purpose of this chapter

This chapter summarises the geochemical approaches for interpreting groundwater flow that have been used at TGC. The chapter compares these approaches to those that were adopted at Sellafield in the U.K.

Based on this comparison, those areas where the Tono programme is equally advanced or more advanced than the Sellafield programme are highlighted. Those approaches used at Sellafield that have not been used at Tono or that were more highly developed at Sellafield, are also listed. The overall purpose is to determine those approaches that were applied at Sellafield that could potentially also be valuable in the Tono area.

The chapter does not aim to present detailed recommendations for how these methods might be applied successfully. To a large extent this must be determined during on-going research in the Tono area.

4.2. The geology and hydrogeology of the Tono area

The location of the Tono area and the main features of its geology are illustrated in Figure 33. The geology of the Shobasama site is illustrated in detail in Figure 34.

The geology of the area has been summarised in several publications, notably in Itoigawa (1974), Yamakawa (1991), Iwatsuki and Yoshida (1999a), Yusa et al. (1993), Hama et al. (2002) and Iwatsuki, et al. (2002). In the area, Pliocene to Pleistocene rocks of the Seto Group (5 to 0.7 Ma) unconformably overlie Miocene sedimentary rocks of the Mizunami Group (27 to 15 Ma). These latter rocks in turn unconformably overlie a basement of Cretaceous Toki Granite (dated at 72.3 Ma; Shibata and Ishihara, 1979).

The flow of groundwater is controlled by topography (Koide et al. 1996). At depths greater than a few hundred metres is thought to be generally from the high ground in the north east of the area, towards the Toki River valley in the south and south-west of the area. Shallower groundwater flow is more variable in direction, being controlled by more local topographical gradients.

Groundwaters have been sampled from all the main rock formations of the area, to a depth of c. 980 m below the surface (about 710 m below sea level; -710 maSL). The chemistry of sampled groundwaters has been determined in several previous studies, notably Iwatsuki et al. (1995), Iwatsuki and Yoshida (1999a,b) and JNC (2000). These studies have revealed that the groundwaters are almost all fresh (TDS << 1000 mg l^{-1}) and have δD and $\delta^{18}O$ values indicating an meteoric origin. The dissolved constituents of the water are dominated by Na^+, Ca^{2+} and HCO_3^{-1} near the surface and by Na and HCO_3^{-1} at greater depth.

4.3. A comparison between the Tono area and the Sellafield area, U.K.

As a basis for evaluating the degree to which methods applied at Sellafield may be applied in the Tono area, it is useful to make a general comparison between the two areas. Information about the Sellafield investigation is summarised in more detail in Bowden et al. (1998) and references therein. The geochemistry of the Sellafield area is described in Nirex (1997b).

Figure 8 and Figure 33 illustrate the general settings of the Sellafield and Tono areas resectively. The hydrogeological settings of the Tono and Sellafield areas are compared in Table 4. There are clear differences between these settings and the scales of the hydrogeological investigations in the two sites, notably:

- The scale of the area covered by the investigations at Sellafield was 4 times the size of the area considered in the Tono investigations.
- At Sellafield, the deeper groundwaters are saline (in the east, near the Potential Repository Zone, up to c. 30,000 mgl^{-1} TDS) or brines (in the west, near the coast, up to 190,000 mgl^{-1} TDS). In contrast, in the Tono area, groundwaters are all dominantly fresh (TDS < 1000 mgl^{-1}) or, to the south of the Toki River, brackish (TDS up to c. 1900 mgl^{-1}).
- In the Sellafield area, groundwater flow is influenced by an interaction between topographical drive from east to west and by basinal processes driving flow from west to east. The former appear to dominate in the eastern part of the site, whereas the latter dominate in the western part of the site. In contrast, topographical head gradients appear to drive groundwater flow throughout the Tono area.
- The sedimentary cover rocks at Sellafield are dominated by aeolian and fluvial quartzo-feldspathic sandstones, whereas the sedimentary cover rocks in the Tono area are dominated by fluvial and marine sandstones, shales and siltstones with a very high volcaniclastic component.
- The basement rocks in the Sellafield area are dominated by fractured volcaniclastic rocks of dominantly intermediate composition, which can be correlated to some degree laterally. In contrast the basement in the Tono area is fractured granite.
- The Sellafield area lies near the coast which in the Quaternary period has changed position owing to past variations in sea-level. In contrast, the Tono area has been far from the coast during this period and unaffected directly by sea level changes.
- In the Quaternary period, climatic effects related to glaciation are particularly important factors that may potentially have changed the hydrogeological system at Sellafield. These effects include the direct effects of glaciation on recharge (which may at various times have been enhanced or diminished) and on topography (caused by glacio-tectonics). Additionally, changing rainfall, vegetation, and sea level are all likely to have exerted an influence. In contrast, the Tono area was not glaciated during the Quaternary and there would have been no glacio-tectonic effects influencing the hydrogeological system there. Here, during this period, variations in rainfall and potentially vegetation are likely to have been the major causes of variations in recharge and consequently groundwater flow.

However, notwithstanding these differences, there are several features that have some similarities between the two sites:

- The area within which the majority of deep boreholes were drilled at Sellafield is comparable in size to the area of the regional hydrogeology investigations in the Tono area.
- At both sites there are basement rocks through which groundwater flow is conducted by fractures.
- Groundwater flow is topographically driven in the eastern part of the Sellafield site and, apparently, throughout the Tono area.
- Both Sellafield and Tono were affected by variations in recharge caused by changes in climate during the Quaternary period. These effects will have caused variations in the isotopic and noble gas compositions of groundwaters at both sites.

4.4. A comparison between data acquisition methodologies in the Tono area and at Sellafield, U.K.

At both Sellafield and Tono there have been investigations of surface waters, shallow groundwaters and deep groundwaters. However, significantly greater amounts of data were produced in the Sellafield programme (c.f. Iwatsuki et al. 2001a and Nirex, 1997b). At Sellafield there was an extensive study of surface water and shallow groundwater, involving compilation of historical data, for example from water supply boreholes, and acquisition of new data. At the time of writing, the surface water and shallow groundwater investigations in the Tono area are not so advanced in so far as they have produced fewer data, though broadly similar approaches to those adopted at Sellafield have been employed at Tono.

At both Tono and Sellafield, geochemical data have been obtained from deep groundwaters. However, again, there are fewer data from the Tono area than there are from the Sellafield area. At the time of writing, chemical data were available from 105 locations from deep groundwaters in the Tono area. In contrast, at Sellafield data were obtained from 163 localities.

At Sellafield there was, as at Tono, a plan to construct an underground laboratory RCF within the footprint of the PRZ. The latter had an area of about 2.5 km^2 while the majority of the deep boreholes were concentrated within a sub-area of this footprint of around 0.7 km^2, an area roughly 6 times larger than the area of the Shobasama MIU site which itself is considerably larger than the New Construction Site (Togari Site).

There were 14 deep boreholes within the RCF area (including two pre-existing boreholes, drilled for mining exploration purposes early in the 20th century). These yielded groundwater samples from 64 intervals during hydraulic testing (there were also samples taken from the two pre-existing boreholes). The deepest of these waters was from a depth of around 1500 m. In contrast, there are only 4 groundwater compositions from the Shobasama site and none from the new construction site (Togari site).

Additionally, in the Sellafield area, data were collected from deeper locations that has been the case in the Tono investigations. Whereas the deepest boreholes in the Tono area are around 1000 m deep, the deepest boreholes at Sellafield were about 2000 m deep. The maximum sample depth in the Tono area was similarly just less than 1000 m, whereas the deepest sample from Sellafield was collected from 1650 m deep.

At Sellafield, the boreholes were drilled with organic polymer-based fluids, except in two boreholes. The polymer used in most cases was xanthan gum. This is an organic polysaccharide manufactured by fermentation of organic matter; it enhances the viscocity of the drilling fluid and drilling fluid losses to the formation. Additionally, NaOH was added to maintain the pH > 9, thereby stabilising the polymer and reducing corrosion. Xanvis additive, which contains less residual sugar than xanthan (about 10%) was used instead of xanthan in two boreholes. In two of the boreholes, fresh water was used as the drilling fluid, though in one of these cases, the fluid needed to be changed to organic polymer-based mud during drilling.

When drilling the first deep Nirex borehole at Sellafield the tracer was nitrate, added as $NaNO_3$ so as to maintain a nitrate concentration of 250-500 mgl^{-1}. However, in this case, the tracer was found to behave non-conservatively in the borehole, limiting its use for evaluating contamination. In most of the subsequently drilled boreholes, the drilling fluids were dosed with LiCl tracer, the concentration of which was maintained to be equivalent to 1000 mgl^{-1} Li. However, in three boreholes, KI was used as the tracer, the concentration of I being nominally 100 mgl^{-1}. In one further borehole, KI and fluorescein (3 ± 0.15 ppm) were used together as the tracer.

Generally, in the Sellafield investigations, groundwater samples were collected from one of several kinds of hydraulic test:

- Environmental Pressure Measurement Tests (EPMs), which were single packer tests spanning 50 m between the packer and the bottom of the borehole. Samples were obtained from a sample chamber attached to the packer assembly. These tests were optimised for obtaining hydraulic data and the groundwater samples collected were usually highly contaminated.
- Swabbing (or flowing EPMs, SEPMs), which were like EPMs except that samples were obtained at the surface by swabbing the test string.
- Full Sector Tests (FSTs), obtained by nitrogen lifting from a large length (or sector) of the borehole.
- Discrete Extraction Tests (DETs) were double packer tests, targeted on zones that were identified as supporting groundwater flow during production testing. The samples were collected at the surface following nitrogen gas-lifting.
- Post- Completion DETs (PCDETs) and Post-Drilling DETs (PDDETs) were similar to DETs, but were performed after borehole completion, soon after drilling (PCDETs) or up to several months after drilling (PDDETs).
- Single Packer Flow Tests (SPFTs) involved a packer being placed above the bottom of the borehole and samples produced using a submersible pump.

Additional types of sample that were obtained were:

- Drill String Samples (DSTs) were collected from the drill string at the surface at the end of a test.
- Down-hole samples were obtained from a Large Volume Sampler (LVS), a wireline tool that collects a fixed 5 l sample. The LVS allows de-gassing within the sampler itself, but gas cannot escape from the sampler.
- Down-hole samples were collected using a Single Phase Reservoir Sampler (SRS), a wireline tool that collects 0.6 l samples at formation pressure, while preventing degassing.

The groundwater samples obtained were all contaminated to a greater or lesser degree. In the cases of samples from the EPMs contamination was generally high and only samples that contained relatively low proportions of tracer were used in the interpretation. Down-hole samples were generally collected late in testing and had relatively low degrees of contamination. Again, this could be monitored by using tracer.

Most of the data used in the interpretation of groundwater chemistry came from the double packer tests. In these cases, several samples were collected during progressive pumping of each test interval. Samples collected later in the pumping were generally less contaminated than samples collected early in a test. By regressing each conservative (non-reactive) determinand of interest (Na, Cl etc) against the tracer concentration, it was possible to extrapolate to zero tracer concentration to obtain an estimate of the in-situ water composition. The precise method for undertaking the regression and the samples to be included varied from test to test. Generally samples known to be problematical were excluded from the regression. The scatter of the data in these regressions gave an estimate of the uncertainties on the estimates of in-situ compositions.

In the cases of non-conservative determinands, such as pH and Eh, this regression approach could not be used. This is because these determinands do not vary linearly as a function of mixing. Instead, in these cases, the general approach was to use the values from the samples with minimal compositions as estimates of in-situ groundwater compositions.

A key feature of the data obtained from the Sellafield area was that they were reported with indicators of data quality, including:

- the minimum concentration of tracer in each sample obtained from each test and used in the regression of conservative constituents;
- a quality score (from 1 to 10, higher numbers representing higher quality), representing relative quality and based on confidence in a number of assumptions about the samples and the correction for drilling fluid contamination that is made;
- quality comments, describing any problems with boreholes drilling, testing, sample collection or sample analysis.

When assigning quality scores to the samples, the validity of the following assumptions was assessed:

- the composition of the drilling fluid is known;
- only one compositionally distinct groundwater occurs in the formation;
- the compositional parameter is expressed as a concentration;
- the sample composition is unmodified by collection or analysis;
- and the analytical results are of known precision.

In contrast, in the Tono area, the general approach has been to drill boreholes with fresh water drilled with a tracer. Mostly, the tracer was uranine or eosin, though amino-G acid or Na-napthionate were also employed in MIU-4. The tracer LiCl was used in borehole MIU-3.

The general approach thoughout has been to pump groundwater samples until there is negligible contamination from the drilling fluid, as indicated by tracer concentrations < 1% of the initial concentration in the drilling fluid. Samples have been obtained either from a Multi-Piezometer (MP) system, from double-packer tests or using JNC's 1000 m groundwater sampler with downhole chemical probe.

The basic approach of pumping until negligible tracer remains has the advantage that in principle, the groundwater samples obtained should be less contaminated than was the case at Sellafield. This is particularly important in the Tono area, where the groundwaters are generally fresh, so that small degrees of drilling fluid contamination could potentially have a relatively large effect on the compositions of the samples. In contrast in the Sellafield area, contamination was less of a problem where saline groundwater groundwater samples or brines were obtained, because there was a large chemical contrast between the drilling fluid and the in-situ groundwater, the groundwater being more concentrated in many constituents. However, in the fresh water zone at Sellafield, estimates of groundwater compositions obtained from the deep boreholes were highly uncertain. At Sellafield, estimates of compositions had uncertainties (derived from the regression statistics) that were typically greater than the estimated concentrations in the groundwater. At Sellafield, this was not such a problem, because the target formation for a laboratory, and ultimately a repository, contained saline water.

However, one area where the drilling fluid used at Sellafield was particularly problematic was in the acquisition and interpretation of C-isotope data for the groundwater samples, notably for ^{14}C. Radiocarbon could not be used to infer recharge times for the deep groundwater samples, owing to carbon contamination from the organic polymer. Furthermore, because breakdown of this polymer in the formation is not a linear process, dependent on degree of mixing, it was not possible to correct for this contamination. Consequently, the main effort in the interpretation of ^{14}C data from Sellafield was to demonstrate that the in-situ groundwater samples in fact contained negligible ^{14}C.

In contrast the samples obtained from the Tono area allow ^{14}C data to be interpreted much more confidently than was the case in the Sellafield area.

One potential disadvantage of the approach adopted in the Tono area is that relatively large quantities of groundwater needed to be pumped to obtain an estimate of in-situ groundwater composition. This large amount of pumping inevitably means that there is a possibility that mixing might occur in the formation between compositionally distinct groundwaters. The fact that large volumes are pumped means that the water composition that is eventually obtained may not be not representative of the sampling interval.

In some of the boreholes (e.g. MIU-3) this problem was compounded by the loss of large volumes of drilling fluid to the rock. Such losses could have been prevented, or at least minimised, had drilling fluid been used.

In the case of borehole MIU-4, this possibility could be evaluated because several samples were analysed from each test interval. In each case the final sample obtained was used to give an estimate of the formation water's composition. However, the variation in water chemistry over time was monitored during the test. Thus, in this respect the approach was intermediate between that adopted in the earlier boreholes and the approach used at Sellafield. In the case of the MIU-4 samples, linear changes in water

chemistry were observed during each test. This provides evidence that the drilling fluid tracer actually behaves conservatively and that there is mixing between only two fluids (drilling fluid and formation water).

One area where the reporting of data is not so advanced in the Tono area as at Sellafield concerns the reporting of quality information. In the Tono investigations, the final compositions obtained during pumping have tended to be reported as representative of the formation waters' compositions. Thus, the general philosophy is to separate the data into 'high-quality data and 'poor-quality data'. Only the former tend to be used in interpretations. However, this view of data quality does not recognise that the quality of data must be judged with respect to the purpose for which the data will be used. For example, at Sellafield, the data from the fresh groundwater zone in the deep boreholes had relative errors that could be in excess of 100%. However, the data were still of adequate quality for demonstrating that fresh water indeed occurred in the sampled locations. In the case of the Tono investigations, it is usually impossible to make such judgements of quality because adequate quality information is not reported with the chemical data.

A related issue is that the Sellafield data were ultimately placed in an integrated computer database, the NDGD (Nirex, 1996), which enabled them to be interpreted readily with other kinds of data, such as geological data, geophysical data etc. Such a database does not yet exist in for the Tono investigations.

The reporting of hydrogeochemical data for the Tono area is not as advanced as the data reporting in the Sellafield investigations. It is recommended that in future data from the Tono area are reported together with quality information, ideally in a computer database that allows these data to be related readily to other types of data.

4.5. Hydrogeochemical data obtained in the Tono area

Table 5 compares the major geochemical approaches that were employed at Sellafield with the approaches that have been used in the Tono area. This table highlights that most techniques used at the former site have been used also in the Tono area. Exceptions at the commencement of the Fellowship were applications:

- $^{87}Sr/^{86}Sr$ in the groundwaters
- $^{34}S/^{32}S$ in the groundwaters
- $^{36}Cl/Cl$ in the groundwaters.

Additionally, while not readily apparent from the table, the application of noble gas data at Tono and Sellafield was slightly different. Studies of He and He isotopes were done at Tono and these were used to calculate model ages for groundwater residence times. At Sellafield, only He concentrations were used in the interpretation. However, in addition to He data, data for other noble gases (Ne, Ar, Kr and Xe, for O_2 + Ar, N_2/Ar ratios and $^{40}Ar/^{36}Ar$ ratios) were also available. These were used to calculate model recharge temperatures for the groundwaters, which could be used in turn to infer the general timing of recharge. Additionally these model recharge temperatures provided a basis for interpreting variations in stable oxygen and hydrogen isotopes in terms of recharge

temperature variations. However, as yet at Tono there has been no use of noble gas data to infer recharge temperatures.

In addition three techniques that have been employed elsewhere, but neither at Sellafield nor at Tono are:

- use of ^{129}I
- use of ^{39}Ar
- use of chlorofluorocarbons

In the Sellafield investigations, none of the isotopes in the first list were measured routinely, but rather during specific studies aimed at evaluating the utility of these isotopes to understand the groundwater system. Variations in $^{87}Sr/^{86}Sr$ were thought to be caused mainly by dissolution of carbonate and sulphate minerals in the sampled rock formations. There was, in fact a reasonably close correlation between variations in the isotopic compositions in the minerals and variations in the coexisting groundwaters. Sulphate minerals are relatively more important in groundwater-conductive features in the western part of the Sellafield site, whereas calcite is relatively more important in the eastern part of the site. Therefore, variations in the Sr isotopes in the groundwaters also varied spatially. The general patterns supported the spatial distributions of different water types deduced from other geochemical evidence.

In the Tono area, analyses of $^{87}Sr/^{86}Sr$ in fracture-filling minerals and whole-rocks in and near the Tsukiyoshi Fault Zone also showed variations from place to place (see Section 5.4.6). Therefore, potentially, there may also be differences in the Sr isotopic compositions of the groundwaters. However, the utility of these data, as at Sellafield, would likely be mainly to help support interpretations made from other data sources. Therefore, while there is merit in investigating their usefulness, studies of these isotopes are not a top priority.

Similarly, at Sellafield, $^{34}S/^{32}S$ data from the groundwaters were useful supporting information used in the refinement of the conceptual model of groundwater flow. In this case, variations in these isotopes reflected the distribution of anhydrite in hydraulically conductive features in the western part of the site and pyrite in features towards the eastern part of the site. They also suggested that some of the sulphur originated in pyrite oxidation in the eastern part of the site and were consistent with this area being nearer to the recharge zone. Similar to $^{87}Sr/^{86}Sr$, analyses of sulphur isotopes in the groundwaters from the Tono area may help to understand the origins of the groundwater solutes, though the information is likely to be mainly useful as supporting data.

In contrast to $^{87}Sr/^{86}Sr$ and $^{34}S/^{32}S$, concentrations of ^{36}Cl vary as a consequence of both the origins of the chloride and the chlorides' residence time in the rock formation. This is because ^{36}Cl is produced in-situ by nuclear decay processes related mainly to U and Th isotope decay, while undergoing radioactive decay with a half-life of 301,000 years (see Section 3.5.1 and Chapter 7). Furthermore, Cl is often relatively unreactive in groundwater systems (in the absence of evaporate minerals such as halite) and where the water contains much more Cl than the rock, water/rock reaction effects can usually be neglected. These factors mean that additional information can potentially be obtained from studies of this isotope that cannot be obtained from the other isotopes. In principle, variations in $^{36}Cl/Cl$ can be interpreted in terms of the timing and directions of

groundwater movement. At Sellafield, the ^{36}Cl data were particularly useful for interpreting the residence times of chloride in the basement and sedimentary cover sequence and helped to infer the movement of chloride between the two in the central part of the site.

In the Tono area, the groundwaters are dominantly fresh, while rocks in the area, especially the granite could potentially contain significant Cl. Therefore, water/rock interactions could possibly cause significant perturbations in $^{36}Cl/Cl$ ratios. This would complicate any interpretations of this isotope in terms of groundwater residence time or flow directions. However, the rocks of the area contain widely varying U and Th concentrations, especially in the vicinity of the Tono uranium deposit. Therefore, in-situ production rates of ^{36}Cl are also expected to vary widely from place to place. This fact may help in finger-printing the origins of the Cl sampled from groundwater,

The second group of constituents could all potentially yield valuable information in the Tono area. The isotope ^{129}I has a half-life of 15.7 million years and is a fission product of uranium-series isotopes. Potentially, studies of this isotope could be particularly valuable in the Tono uranium deposit, where it could potentially shed light on the timing of uranium formation and possible migration. Additionally, as part of the Tono Natural Analogue study, investigations of ^{129}I behaviour could give valuable insights into the behaviour of this isotope in potential future repository environments; ^{129}I is an important constituent of many radioactive wastes.

^{39}Ar, which has a half-life of 269 years could potentially be used to shed light on the timing of groundwater movement within the last 1000 years. However, interpretation of this isotope are complicated by in-situ production by neutron activation of ^{39}K in feldspars and micas, which swamps the atmospheric signature. Additionally, very large groundwater samples must be collected.

Chorofluorocarbons have been increasing in the atmosphere owing to anthropogenic activity, most noticeably since 1945. Therefore, it is possible to identify water recharged within this time-frame and in principle, given knowledge about this atmospheric increase, to calculate actual recharge times within ±4 years.

4.6. Applications of hydrogeochemical data in the Tono area

The main applications of the hydrogeochemical data obtained to date in the Tono area have been to:

- determine in-situ chemical conditions deep underground and the stability of these conditions;
- interpret present groundwater origins and flow directions;
- interpret the timing of groundwater movement (palaeohydrogeology).

A summary of all the types of information that can be used to understand palaeohydrogeology are summarised in Table 6. The parts of the Tono area to which these data apply are summarised in Table 7. Quantitative estimates of the timing of groundwater movement in the Tono area are summarised in Table 8.

There has been little application of geochemical information to constrain directly numerical models for groundwater flow. Recently, Iwatsuki et al. (2001b) reported the use of ^{14}C data for this purpose. However, it would be possible to develop this approach even further by attempting to match variations in groundwater chemistry in coupled flow-transport models. This approach was adopted at Sellafield (Figures 10, 17 and 18). The recent recognition of Na-Cl dominated groundwater in the southern part of the study area at Tono, including brackish water to the south of the Toki River, raises the possibility of constructing groundwater flow models to attempt to match these salinity variations.

The only geochemical indicators of palaeo-recharge conditions to be used in the Tono area so far are stable oxygen and hydrogen isotope variations. It has been noted that deeper waters apparently show a shift towards more negative isotope compositions. This has been interpreted to indicate that the deeper groundwaters were recharged under colder climatic conditions than were the shallower groundwaters. The basic rationale for this interpretation is illustrated in Figure 35.

This interpretation is similar to interpretations at Sellafield and elsewhere, where negative isotopic shifts are used to infer cold-climate recharge groundwaters. However, in the Tono area, the shift is not so marked as at other sites (Table 9; Figure 36). While such an isotopic shift occurs in some localities it is by no means universal and taken together, the data show no systematic variation. Indeed, the scatter in rainwater compositions is actually greater than the variation in groundwater isotopic compositions, while the mean rainwater composition is slightly depleted in heavy isotopes relative to the mean groundwater composition (Figure 36). These observations raise the possibility that any local variations in isotopic compositions could be caused by factors other than climate change. One possibility is that the elevation of recharge has exerted an effect. Altitude-related variations elsewhere have been estimated at 0.15 to 0.5 ‰ per 100 m altitude change for $\delta^{18}O$ and 1.4 to 4 ‰ per 100 m altitude change for δD (Yurtsever and Gat, 1981).

One way to test this hypothesis would be to investigate also the noble gas compositions of the groundwater samples, for comparison with the stable isotopic data. The noble gas compositions enable direct estimates to be made of recharge conditions.

In the Sellafield investigations, integration of groundwater chemical data with mineral data (spatial distributions of different minerals and mineral chemistry) was particularly useful for shedding light on past groundwater movements (see Section 3.6.3). Recent work in the Tono area has demonstrated that this approach also has potential there (Iwatsuki et al. 2002; Figure 37). Here, a range of calcite morphologies from C-axis shortened to C-axis elongate has been identified. Potentially, this calcite could record the flushing of saline groundwater from the Toki Granite. According to this hypothesis, the elongate crystal forms precipitated from saline groundwater, whereas the shortened forms were precipitated from fresher water. One possibility is that the calcite formed during the interval over which marine water was flushed from the Toki Granite. It is plausible that such flushing occurred in view of the fact that some of the marine sedimentary rocks overlying the granite are marine deposits. This marine water may also have penetrated the granite. This hypothesis would also be consistent with the common occurrence of smectite on fracture surfaces in the granite, seawater-granite interactions being capable of causing smectite formation. These hypotheses are, however, presently based on circumstantial evidence and require further testing.

Any precipitation of calcite from saline, possibly marine groundwater could have happened many millions of years ago. However, ^{14}C data suggest that some of calcite has also precipitated within the last 30,000 to 40,000 years (Figure 38). The occurrence of ^{14}C in calcite cannot, however, be used to determine an actual precipitation age, because inevitably the ^{14}C will have been diluted to some extent by ^{13}C and ^{12}C present already in the rocks. Additionally, because it is difficult to separate very small calcite crystals of a particular generation for ^{14}C analysis, it has not been possible to determine the presence or absence of ^{14}C in the various crystal types found in the area (Figure 37). However It is notable that some of the calcite bearing ^{14}C occurs at depths as deep as almost 600 m below sea level, suggesting that calcite precipitation has occurred in the deep groundwater system geologically recently.

4.7 Summary and implications for studies in the Tono area

In summary it can be stated that at their best, the approaches used in the Tono area have yielded high-quality data which, especially for certain determinands such as ^{14}C, allow more confident interpretations of in-situ conditions to be made than was possible in the fresh water zone at Sellafield. However, a disadvantage of the approaches used in the Tono area, as compared to those used at Sellafield, is that potentially large volumes of drilling fluid can easily be lost to the formation and/or relatively large volumes of water must be pumped to obtain uncontaminated samples. Where the impact of this drawback has been tested, in MIU-4, it appears that pumping-induced mixing between compositionally different groundwaters has not occurred. However, this needs to be tested on a borehole-by-borehole basis. It is therefore recommended that the approach adopted in MIU-4, to obtain multiple samples from each test interval and to monitor their compositions as a function of pumping, should be continued in future boreholes.

As at Sellafield, it would be appropriate to conduct small-scale studies of $^{34}S/^{32}S$ and $^{87}Sr/^{86}Sr$ isotopes to investigate their utility in the Tono area, recognising that they are likely to give mainly information to support the overall interpretation of groundwater flow.

In the Tono area, ^{36}Cl data have the potential to yield valuable additional information that cannot be obtained easily from other approaches. Therefore, it is appropriate to give priority to testing the utility of this isotope by means of an initial pilot study. To this end, such a study was done in the Fellowship and is described in Chapter 7.

Studies of ^{129}I, ^{39}Ar and chlorofluorocarbons could also potentially yield valuable information in the Tono investigations. However, these constituents are not normally studied routinely anywhere in the world and considerable effort would need to be expended at Tono to demonstrate their utility.

The controls on the variations of stable oxygen and hydrogen isotopes in the Tono groundwaters are not well understood. Additional work is needed to establish whether these variations do indeed partly represent a palaeoclimatic effect. Studies of noble gas concentrations (Ne, Ar, Kr and Xe, for O_2 + Ar, N_2/Ar ratios and $^{40}Ar/^{36}Ar$ ratios) could be valuable in this regard.

Additional studies of the spatial distributions and chemistry of paragenetically late minerals would help to confirm whether these can be used to obtain palaeohydrogeological information. Recent studies in this regard have been promising.

Further use of geochemistry could be made to constrain models for groundwater flow. So far there has been limited use of geochemical constraints on the timing of groundwater flow to constrain flow models. However, coupled flow-chemical models could also be developed and tested against the known distributions of chemically distinct groundwaters.

Finally, it is recommended that future hydrogeochemical data are reported with additional quality information. Ideally this should be within a digital database that allows ready integration of different data sets and cross-references relevant paper documents.

5. NEW TSUKIYOSHI FAULT STUDIES

5.1 Purpose of this chapter

This chapter outlines new work on fault studies that was initiated or carried out specifically as part of the Fellowship. This work falls into two groups:

- initiation of a new borehole investigation targeted on the Tsukiyoshi Fault in Tono Mine;
- compilation and integrated interpretation of geochemical information relevant to understanding the Tsukiyoshi Fault (whether or not derived from the Tsukiyoshi Fault Project).

During the Fellowship, a project called the 'Tsukiyoshi Fault Project' was also being undertaken by JNC, much of the work being contracted to the BGS. A contribution was made to parts of this project. In particular, progress was reviewed and the work was placed in the context of, and where appropriate integrated with, other JNC studies (for example regional geochemical studies). The major results of the project at the time of writing are given in Milodowski et al. (1999), Gillespie et al. (2000) and Milodowski et al. (2001). It is stressed that at the time of writing, the Tsukiyoshi Fault Project has not been completed. Information from the final year of this project (done in H13) is not included here.

5.2 A borehole (99SI-08) study targeted on the Tsukiyoshi Fault

5.2.1 Introduction to the targeted study

At the start of the work reported in this section, the Tsukiyoshi fault had been examined in detail in seven boreholes (TH1, TH2, TH3, 98SI-03, 98FE-01, TM2 and MIU2) and in two exposures in the walls of the mine tunnels (in the Lower Connecting Drift of N° 2. Shaft and in the north extension of the main drift of Tono Mine). Additionally, the fault had also been examined in lesser detail in rock cores from boreholes TFA1, TF1 and KNA-6. These locations are illustrated in Figure 39.

If the most prominent fault intersections in these boreholes are projected into the same horizontal plane at the level of Tono Mine's main gallery, the trace of the fault appears to be sinuous (Figure 40). While not impossible, this geometry seems less likely than an alternative explanation, that the fault in the vicinity of the N° 2 Shaft has two en-echelon strands. However, prior to the work reported in this chapter, apart from boreholes TFA-1 and 98SI-03, none of the studied boreholes were drilled specifically to intersect the Tsukiyoshi Fault. In the vicinity of the mine, none of the earlier boreholes could be stated definitely to have penetrated the fault zone completely. Therefore, it was impossible to be certain whether the two-strand model for the fault zone near the N° 2 Shaft is a reasonable alternative to the single-strand model.

A further uncertainty, which arose from the unclear spatial relationship between the earlier boreholes and the fault zone, was the uncertain positions of groundwater monitoring intervals relative to the fault's location. These monitoring intervals had been located within boreholes drilled surrounding the N° 2 Shaft and had been used to monitor

groundwater heads during the sinking of this shaft (Yamane et al. 1996; Figure 41). From intersections of the fault in three of the boreholes, TH1, TH2 and TH3, and assuming that the fault is a planar feature, two possible interpretations of the fault's location relative to the groundwater monitoring locations are possible (Figure 41).

A further problem with the previously available core from the fault was that there was significant core loss in the fault zone in the core from several of the boreholes. In such cases, the available core was generally not ideal for the determination of detailed structural, petrological and mineralogical characteristics of the fault zone. Additionally, with the exception of the borehole MIU2, the observations of the fault are all relatively close to the unconformity between the sedimentary sequence and the granite.

In an attempt to reduce these uncertainties it was decided to drill a new borehole, named 99SI-08, within the Tono mine. This borehole is described in the following sections.

5.2.2 *The specific objectives for borehole 99SI-08*

An initial goal of the overall Tsukiyoshi Fault study was to determine the structural, petrological, mineralogical and geochemical characteristics of the fault. Knowledge of this variability could then be used to develop methods for characterising faults of this type. Subsequently, this would contribute to the development of methods for characterising solute transport in fault zones.

To complement the information available from the previously investigated boreholes and exposures of the fault in mine tunnels, it was proposed that borehole 99SI-08 should meet, as far as possible, the following objectives:

- to investigate the Tsukiyoshi Fault at a higher stratigraphical level (within the Akeyo Formation) than had been investigated hitherto;
- to penetrate the full width of the fracture envelope that surrounds the Tsukiyoshi Fault;
- to obtain high quality core from the full length of the borehole;
- to obtain graphical logs by visual logging of the core;
- to identify and suitably preserve samples the core for possible future mineralogical and geochemical studies, should these studies be deemed desirable.

A further objective was to integrate the observations from the core with the observations made in the other boreholes and in the exposures within the Tono mine. By comparing the deformation history in the fault zone within other formations, with the deformation history in the Toki Formation, it might be possible to shed light on the relationship between the fault's movement and structure and the sedimentation history.

When setting the objectives it was recognised that until borehole 99SI-08 was drilled, the detailed geological characteristics of the investigation site would not be known. For example, the Tsukiyoshi Fault may not have been located in the place where it was predicted to be from previously available geological information.

5.2.3 *The drilling location for 99SI-08*

It was considered that the best chances of meeting the above objectives would be offered by an inclined borehole, drilled northwards from the northern end of the No 1 Measurement Drift (Figure 42). This drift extends northwards from the N° 2 shaft at a depth of approximately 40 m.

There are many advantages of drilling a new borehole in this location.

- The intersection of the fault in the Akeyo Formation and possibly the Oidawara Formation could be investigated. The intersection of the fault with these formations had not been investigated previously.
- By comparing the fault zone's deformation history within these formations, with the fault zone's deformation history in the Toki Formation, identified in the other boreholes, it might be possible to investigate the relationship between fault movement and the sedimentation history.
- The results from such a borehole would complement observations made previously in the N°. 2 Measuring Drift, the N° 2 shaft itself and the Lower Connecting Drift. Together, these data would enable the variability of the fault zone along a distance down dip of around 100 m to be investigated.
- A horizontal borehole, TF-1 had already been drilled northwards from the northern end of the N° 1 Measurement Drift (although there is no preserved core from the interval of the Tsukiyoshi Fault). At a later stage it might be possible to conduct cross-hole hydraulic tests between borehole TF-1 and the new borehole, if so desired. Such tests might enable the inferred hydraulic properties, based upon mineralogical and structural observations, to be tested directly. This in turn would be a valuable check on the mineralogical, petrological and structural geological approaches being used to investigate the fault zone.

The recommendation for a drilling location was made according to the following basic principals:

- The borehole should be sited at a location where drilling and any necessary investigations in the borehole are technically feasible.
- The borehole must be drilled at a location in the mine where the Tsukiyoshi fault can be penetrated by a borehole that can be drilled and cored within the available resources.
- It should be sited to avoid interfering with existing experiments.
- It should be sited so as to obtain as much information about the fault as possible, although it is recognised that it is not possible to answer all the outstanding questions using only one borehole.
- It should be sited where it is considered that there is the greatest chance of meeting the objectives described previously.
- It should be sited so as to minimise the chances of duplicating information acquired already.

Besides the recommended location, other locations at which it was technically feasible to drill a borehole were:

- the No. 2 Measurement Drift, driven from the No 2 shaft at a depth of about 90 m;
- the Lower Connecting Drift, driven from the No 2 shaft at a depth of approximately 135 m;
- the NATM drift, near to the existing TFA-1 and 98SI-03 boreholes;
- the lower northern drift that runs parallel to, but deeper than, the uppermost northern drift.

However, all these localities are relatively close to the same stratigraphical level at which the Tsukiyoshi Fault had previously been examined already in the environs of Tono Mine. Thus, a new borehole at one of these localities would not have met the objective of characterising the Tsukiyoshi Fault at a higher stratigraphical level. Additionally, there were other practical difficulties associated with drilling a borehole at the fourth locality. Formerly, the fault was exposed in the walls of the drift here. However, the exposure has since been obscured by the construction of concrete lining to the drift and the installation of new ventilation equipment. This would complicate any drilling.

5.2.4 *Design for borehole 99SI-08*

The design of the borehole is illustrated schematically in Figure 42. The detailed specifications, bearing in mind the available drilling equipment, were as follows:

- Drill inclined at a minimum angle of 55° to the horizontal, northwards from the northern end of the N°. 1 Measurement drift.
- The borehole should be orientated so that a plane through the new borehole and through borehole TF1 is vertical.
- The start of the new borehole should be at the intersection between the floor and the wall of the drift, approximately 1 m below the start of borehole TF1.
- The first 1.5 m of the borehole should be drilled at a diameter of 116 m. A casing of 70 mm internal diameter should then be installed and cemented.
- The remainder of the borehole should be drilled at a diameter of 70 mm and kept as 'open hole'.
- The total maximum planned length of the borehole (assuming an inclination of 55° to the horizontal) is 82 m.
- The minimum planned depth considered to give a reasonable chance of penetrating the fault zone completely, when consideration is given to the intersections of the fault in the other boreholes, is 50 m.
- Core should be recovered with 'core pack' where possible. 'Core pack' is a flexible polythene tube which is inserted into the core barrel. Its purpose is to minimise the fragmentation of the core.
- Following recovery of the core, it should be wrapped in polythene to prevent drying.
- Drilling fluid will be groundwater taken from the Akeyo and Seto formations, dosed with a fluorescein tracer at a concentration of 1 ppm.

The borehole design was constrained by the following considerations:

- There was a need to maximise the probability of penetrating the Tsukiyoshi Fault zone completely.
- It was desirable to intersect the fault zone as nearly as possible at right angles, so as to:
- increase the likelihood that the core would break into disks, along fractures parallel to the main fault, rather than break into irregular rubble, along fractures parallel to the core's axis;
- minimise the thickness of the fault zone intersected by the core, thereby increasing the likelihood that the entire fault zone would be penetrated.
- There was a requirement, imposed by planning permission, for investigations in the mine and its surroundings, not to extend the borehole beyond a vertical line projected through the perimeter of Tono mine.
- The maximum length of borehole that can be drilled within the available resources (equipment, time etc) was around 120 m.
- It was desirable to achieve the objectives while using the minimum amount of resources.

These requirements suggested a minimum inclination of 55° to the horizontal. If the borehole was steepened from this inclination, it was likely that the borehole would intersect the Tsukiyoshi fault more obliquely. In this case, the length of the fault in the borehole core would be increased. Consequently, the borehole length would need to be increased to ensure that the fault zone is penetrated completely, thereby expending more resources. If the borehole inclination was more shallow than 55°, the interval between the top of the fault zone and the projection of the mine's perimeter would be decreased. This will mean less chance that the borehole would penetrate the fault zone completely.

The proposed design meant that the borehole would extend around 30 m below the previously estimated lower extent of the Tsukiyoshi Fault Zone (based upon observations in boreholes TH1, TH2 and TH3). This distance represented a margin by which the predicted fault's location could deviate from the actual location, while still allowing the fault zone to be penetrated.

A further benefit of this borehole design was that the top and bottom of the Akeyo Formation could possibly be penetrated. This could enable an improved constraint to be placed upon the throw of the Tsukiyoshi Fault in the vicinity of the shaft.

5.2.5 *Results from 99SI-08*

Major results from borehole 99SI-08 are summarised in Figure 43. In this locality, the Tsukiyoshi Fault has at least two major strands of deformation (two strands were identified in the borehole). These strands occurred within rocks interpreted to belong to the Akeyo Formation. However, no *major* thicknesses of fault rock were identified, and faulting and fault rock development are represented largely by millimetre-scale granulation seams. These features are most intensely developed between 11.76-26.95 m, where they are interpreted to form a fracture envelope associated with an upper strand of the Tsukiyoshi Fault. An interval of less developed features between 35.30-62.0 m is considered to be a 'weaker' lower fault strand.

Subsequent to initial logging carried out by the Fellow, more detailed structural and petrological investigations were undertaken by Mr A.E. Milodowski and Dr M.R. Gillespie of the BGS. These investigations allowed definition of a sequence of diagenetic and fracturing events as follows:

- alteration of primary glassy and unstable volcanic detritus to ferruginous smectite, and precipitation of framboidal pyrite during early sediment diagenesis.
- main faulting and formation of granulation seams with illitisation of smectite within the granulation seams;
- minor fracture movement and precipitation of traces of REE phosphate (lower fault strand);
- fracture reactivation and formation of zeolite veinlets (lower fault strand);
- fault reactivation with localised hydrofracturing and injection of fluidised quartz-rich sediments (possibly derived from the liquification of adjacent Toki Formation rocks within the overpressured fault zone) into fractures in the Akeyo Formation (upper fault strand only);
- formation of authigenic framboidal pyrite in porous injection sediment, indicating reducing porewater conditions;
- dissolution of pumice and smectite formation, possibly associated with bacterial activity and framboidal pyrite formation. This was possibly concurrent with the formation of pyrite in the injection sediments (see above) but the relationship is unclear;
- precipitation of calcite primarily in open microfissures and occasionally in secondary porosity;
- late stage oxidation of pyrite locally in injection-sediment-filled fractures, and formation of secondary gypsum and iron oxides alteration products.

5.2.6 Conclusions from 99SI-08

The results from borehole 99SI-08 matched the predictions very well (c.f. Figures 42 and 43). An implication of the results is that in the central part of the Tono Mine area (near the N° 2 Shaft) the Tsukiyoshi Fault has an en-echelon structure. Such a structure is not uncommon in fault systems.

A further implication of these results is that the monitoring intervals in the Shaft Sinking Experiment (Yamane et al. 1996, Figure 41), may not have straddled the fault zone completely. Some monitoring intervals were located in the hanging wall of the upper fault strand and others were apparently located in the footwall of the upper fault strand. However, it is not clearly the case that any of the monitoring intervals were located in the footwall of the lower fault strand. Instead it is more likely that the deepest monitoring intervals lay within the fault zone, between the two strands.

The distribution of fracture-filling or lining calcite in the borehole indicates the existence of palaeo-fluid flow channels. It can be seen that these are concentrated near to the lower fault strand, whereas the upper fault strand is characterised by more intense fracturing. Thus, fracture frequency does not correlate with evidence for palaeo-fluid flow. A possible explanation is that the upper fault strand contains abundant granulation seams, which are expected to be low-permeability features that could have restricted fluid flow.

5.3 Compilation of data relevant to understanding the Tsukiyoshi Fault

5.3.1 Types of data compiled

The following types of data have been compiled for the Tsukiyoshi Fault:

- groundwater chemistry for samples collected from the Tsukiyoshi Fault Zone;
- paragenetic information;
- mineral chemistry;
- mineral and whole-rock Sr-isotope data ($^{87}Sr/^{86}Sr$)
- distributions of fault rocks;
- overall widths of identified deformation zones.

These data are given in Appendix 4. Summaries of key information are also given in Tables 10 and 11.

5.3.1 Comparison between geological, mineralogical and hydrogeological data

To examine possible relationships between structural and mineralogical features of the rocks and hydrogeological information, observations made on rock core were compared with hydrogeological data. The locations of fault rocks relative to hydraulic tests are plotted in Appendix 4 while more detailed comparisons between a range of structural and petrological information and hydraulic data are made in Figures 44 and 45.

In borehole TH-1 there is no clear relationship between hydraulic conducitivies and the location of fault rocks. However, in boreholes TH-2 and TH-3, conductivities appear to be higher in the hanging walls, immediately above the upper-most mapped fault rock. In contrast, in MIU-2 and MIU-3, there is an the hydraulic conductivities apparently increase towards the fault's footwall.

In borehole TH-2, there are apparently higher hydraulic conductivities in the hanging wall of the main fault strand. However there is no correlation between hydraulic conductivities and the distribution of palaeo-fluid flow indicators (matrix and fracture calcite; Figure 44). Indeed, the lowest hydraulic conductivities apparently correspond to the most prominent evidence for past fluid flow.

In MIU-3 the highest hydraulic conductivities again occur near to the fault, but this time in the footwall (Figure 45). The highest hydraulic conductivities coincide with open features in the rock core that could potentially conduct flowing groundwater (termed Potentially Flowing Features or PFFs). However, the frequent occurrences of PFFs higher in the core coincide with hydraulic conductivities that are apparently among the lowest in the illustrated borehole interval. There is no systematic relationship between rock alteration and hydraulic conductivities. Instead, the alteration may be related to some degree to degree of fracturing.

Thus, the overall picture that emerges is that there is no clear relationship between palaeo-flow indicators or evidence for open porosity in the rock and present hydraulic conductivities. However, there is a general relationship between the location of the main strand of the fault and presently more conductive rock. Possibly, these observations can be explained by complex inter-relationship between physical deformation and chemical reaction processes within the fault zone. For example, in places the fault zone could be compartmentalised by low-permeability fault rocks, which effectively isolate open fractures (PFFs) between them. In such cases, these PFFs may not correlate with conductive zones. Similarly, evidence for palaeo-fluid flow need not correlate with presently high hydraulic conductivities if the palaeo-flow has reduced the rock's permeability locally, for example by causing the precipitation of porosity-occluding minerals such as calcite. The occurrence of relatively high hydraulic conductivities in the footwall of the main fault strand in some places, but in the hanging wall in other places is not unexpected given that the Tsuikiyoshi Fault Zone contains multiple deformation strands that are expected to interact in complex ways.

Presently, these explanations must be regarded as tentative. To evaluate them in more detail would ideally require a larger dataset of hydraulic conductivities, so that statistically meaningful correlations between features in the rock core and hydraulic test data could be derived. One approach would be to conduct short-interval hydraulic tests at regular intervals throughout the fault zone. This approach was followed in the Sellafield investigations in a borehole drilled along the centre line of a planned shaft (Gutmanis et al. 1998). In this borehole 100 single-packer tests were done at intervals of 1.5 metres throughout the interval of a planned underground laboratory. The resulting dataset enabled correlations to be made between the distributions of features in the rock core, notably PFFs, and variations in hydraulic conductivity.

5.4 Interpretation of geochemical information from the Tsukiyoshi Fault

5.4.1 Evolution of water chemistry

Groundwater chemical data from the Tsukiyoshi Fault Zone are tabulated in Appendix 4. While there is variability in these compositions, there are no clear, systematic variations from place to place in the fault zone, or between groundwater in the fault zone and those from clearly outside this zone. The variability could be explained largely by sampling and analysis-related effects, such as contamination by drilling fluids or exposure to the atmosphere. Groundwater from both the fault zone and from samples outside it are clearly fresh.

5.4.2 Importance of water/rock interactions

Water/rock interactions in the fault zone would influence the chemistry of the groundwaters. These water/rock interactions may in turn control the physical properties of the fault zone, by affecting the chemistry of the waters (notably pH and redox conditions) and hence mineral dissolution and precipitation. There is abundant evidence from the Tsukiyoshi Fault Zone that these processes have operated in the past (Figures 46 and 47).

Potentially, the precipitation of calcite could exert a significant control on groundwater flow by occluding pore spaces. Several processes have been suggested to cause calcite to form during the circulation of fresh groundwaters (Milodowski et al., 1998; Metcalfe et al., 1998a). These mechanisms include:

- increases in temperature along groundwater flow paths, leading to calcite precipitation, owing to the inverse temperature-dependence of calcite solubility;
- mixing between fresh Ca-HCO3 dominated waters and saline Na-Cl dominated waters;
- water/rock interactions involving silicate minerals such as feldspars that increase the pH of infiltrating waters, thereby promoting calcite precipitation.

At the depth of Borehole TFA-1, in the North Extension Drift (NATM) the temperature is insignificantly different from current mean surface temperatures (around 15 °C). Furthermore, these rocks have evidently not been buried by more than about 500 to 600 m more than the present depth of burial within the last 700 ka (Yoshikawa, 1974, quoted in Yusa et al., 1993). Therefore, unless geothermal gradients have been significantly greater than at the present, and the paragenetically most recent calcite formed at a considerable time in the past, the first of these mechanisms is unlikely to be responsible for the calcite precipitation.

The second possibility is also considered unlikely. The only source of saline groundwater that can be stated confidently to have occurred in the Tono area in the past, is the brackish or marine Na-Cl dominated water that covered the area during the deposition of the Akeyo Formation and the Oidawara Formation. However, this water could have been flushed by fresh water prior to the last movement of the Tsukiyoshi Fault, during the erosion that formed the unconformities above the Akeyo Formation and the Oidawara Formation.

Water/rock interactions are considered to be the most probable explanation for any calcite precipitation at the present. Previous studies of other sites (Smellie and Laaksoharju, 1992; Milodowski et al., 1998) suggest that water/rock interactions involving the dissolution of feldspars and the precipitation of clay minerals is a possible cause of increasing groundwater pH along flow-paths. This dissolution leads ultimately to the precipitation of calcite. Such a phenomenon would also be consistent with the observed changes in groundwater pH in the Tono area. Currently, the pH of the flowing groundwaters in the Lower Toki Formation is around 9.2 (data from KNA-6). In contrast, pure water in equilibrium with air has a pH of 5.6 and present surface waters are reported to have a pH of around 6.

5.4.3 Geochemical modelling of porewater chemistry in fault gouge

The analyses of the porewaters from the fault gouge also give insights into the water/rock interactions that occur within the fault zone. Inevitably, the sampling and squeezing procedures perturb the chemistries of the porewaters. However, geochemical modelling, coupled with knowledge of the minerals that occur in the rocks can be used to allow for these effects (Figure 48).

The porewaters all have broadly similar chemical compositions to the flowing groundwaters collected from the Lower Toki Formation and the underlying Tono Granite, from boreholes elsewhere in Tono Mine (c.f. also analyses in (Iwatsuki and Yoshida, 1999a) and (Iwatsuki et al., 1995). The differences are mostly attributable to artefacts of the squeezing process. Notably, compared to the flowing groundwaters, the porewaters have higher SO_4 concentrations and lower Ca concentrations. The porewaters' Na concentrations are towards the high end of the range shown by flowing groundwaters. The value of 63 mg/l reported for the porewater from the sample between 15.04 and 15.30 m is the highest for water from this area. These variations are most easily explained by pyrite oxidation and related reactions during squeezing. This mineral was observed to occur during visual inspections of core samples, although it was below the detection limit of around 5 wt% achieved by XRD analysis.

The porewaters are undersaturated with respect to calcite. This is inconsistent with the observation that fresh (un-corroded) calcite occurs within the fault gouge. The apparent discrepancy is most probably due to a lowering of pH from in-situ values during pyrite oxidation. This interpretation is supported by the fact that SO_4 concentrations and pH are inversely correlated in these porewater samples. However, the Ca concentrations and the inorganic concentrations of the porewaters are lower than the concentrations of these determinands in the flowing waters, which are calcite-saturated. One possible explanation is that the Ca released from the calcite dissolution coupled with pyrite oxidation, exchanged with Na- located on clay minerals. Evidence for such a phenomena has also been observed in other studies (Metcalfe et al., 1998b). However, an additional explanation is required for the relatively low inorganic carbon concentrations in the porewater samples. It is possible that the lowering of pH during sampling and squeezing contributed to a loss of inorganic carbon from the porewater in the form of CO_2.

PHREEQC was used to estimate the pH at which calcite would be saturated, assuming that in the *in-situ* pore-waters, all other chemical parameters besides pH have the same values as those analysed. This approach reveals that for all the waters, calcite would be just saturated if the *in-situ* pH is around 10. This value seems unreasonably high in view of the pH measured for the flowing waters and estimated for in-situ porewaters at other sites (e.g. Bradbury and Baeyens, 1998). A loss of Ca by cation exchange could explain this phenomenon.

The geochemical modelling also constrains the *in-situ* porewater compositions. Smectite is a major phase in the clay fraction of all samples, while chlorite is a significant minor phase. All the porewaters are calculated to be undersaturated with respect to chlorite (14A), but oversaturated with respect to Ca-montmorillonite. However, with an increase in pH, the solubility of chlorite (14A) will decrease (its saturation index will increase), but the solubility of Ca-montmorillonite will increase (its saturation index will decrease). Calculations with PHREEQC revealed that all three porewaters would be very close to saturation with respect to both these minerals when the pH is around 9 (Figure 48). Furthermore, illite was found to be a trace phase in all the clay fractions of most of the samples examined. Unfortunately, for all the porewaters, K was at its detection limit. Therefore, the saturation indices calculated for this mineral using the detection limit are maximum values. Nevertheless, they are all substantially positive, indicating the possibility that in the analysed waters, illite could possibly be oversaturated. However, like the solubility of Ca-montmorillonite, the solubility of illite also increases as pH increases. Using the reported values of the detection limit of K, the waters are calculated

to be at saturation with respect to illite at a pH of around 9, the same as for chlorite (14A) and Ca-montmorillonite. Thus, within the uncertainties in the data, it is conceivable that the porewaters are saturated with respect to chlorite, smectite and illite at a pH of around 9. This value is very similar to the one determined during long-term monitoring of flowing groundwaters from the Lower Toki Formation.

The feldspars albite, anorthite and k-feldspar are all undersaturated (have negative saturation indices) at the analysed pH and at the higher modelled pH. The fact that the saturation indices of K-feldspar are calculated using the detection limits of K (i.e. maximum values) does not alter this conclusion; the actual saturation indices of this mineral must be even lower than those calculated. These results are consistent with the textural evidence for paragenetically plagioclase feldspar dissolution.

In contrast, at the postulated *in-situ* pH of around 9, kaolinite would be oversaturated in all the porewaters (saturation indices between 1.9 and 2.5). Thus, it is possible that kaolinite could be forming in the fault gouge at the present, although its presence has not been confirmed in mineralogical investigations. Potentially, the formation of this mineral could be coupled with the dissolution of the feldspars. Possibly, this phenomenon reflects the inferred infiltration of fresh waters into the fault in the past. The replacement of feldspar by kaolinite and the precipitation of calcite in open porosity would not necessarily imply rapid movement of groundwaters. The calculated saturation indices indicate on-going processes that could be operating extremely slowly. Evidently, the water that infiltrated the Toki Formation c. 15,000 years ago still has not attained equilibrium with the mineral assemblage in the fault rocks.

A possible explanation for the relative immobility of uranium, in spite of the evidence for fluid migration, is that water/rock interactions have buffered the chemistry of the waters in such a way as to prevent uranium being dissolved significantly in circulating waters. It has been suggested that reactions involving organic matter in the Toki Lignite Formation have effectively caused reducing conditions to be maintained (Iwatsuki et al., 1995; Shikazono and Utada, 1997).

5.4.4 *Mineral chemistry*

The available chemical data from the Tsukiyoshi Fault Project are few and give only a general indication of the main mineral types that are present. As yet there has been no systematic study of variations in mineral chemistry within the fault zone, or to establish whether fracture minerals inside and outside the fault zone differ in compositions. Those data that were obtained show no systematic variations between different boreholes or between different rock formations. However, there are local differences, within individual samples and within particular borehole sections.

The best indications to date of local variations in mineral chemistry were found in the fault zone in Borehole 98SI-03. Here there are clear differences in the chemistry of secondary and fracture-filling calcite from green clay-rich fault gouge and calcite from the surrounding mudstone (Figure 49). Local chemical variations in the surrounding rock chemistry, coupled with water/rock interactions could be responsible. However, the data set is too small and there are insufficient supporting data from coexisting minerals to make any detailed interpretations.

5.4.5 *Stable oxygen and hydrogen isotopes*

Porewater data from the Tsukiyoshi Fault gouge in Borehole TFA-1 included stable oxygen and hydrogen isotopic compositions. These data are similar to those of the groundwater sampled from other places around Tono Mine (e.g. Borehole KNA-6).

5.4.6 *Sr isotope data*

The strontium isotope data ($^{87}Sr/^{86}Sr$) from whole-rock samples collected from the sedimentary sequence and the Toki Granite, and from fracture-filling carbonate minerals, are consistent with palaeo-fluid flow upwards in the fault zone.

Whole-rock samples from the sedimentary sequence gave significantly lower $^{87}Sr/^{86}Sr$ ratios than the calcite veins from the same rocks (Figure 50). The ratios given by these veins are, instead, within the range of ratios given by calcite samples from the Toki Granite. The simplest explanation for this similarity between the calcite veins is that those in the sedimentary rocks precipitated from water that ascended from the granite.

It is also noteworthy that, among those calcite samples for which there are both Sr isotope data and stable C-isotope data, those samples from the sedimentary rocks seem to have generally lower $\delta^{13}C_{PDB}$ values (Figure 51). The dataset is still small, so these relationships need to be interpreted cautiously. However, one tentative interpretation is that the calcite in the sediments derived some of its carbon from the organic-rich sedimentary rocks.

5.5 Implications of the Tsukiyoshi Fault study for future fault studies around Tono and elsewhere

The new study has dramatically changed the conceptual model of the Tsukiyoshi Fault. Understanding was greatly improved by detailed mineralogical, petrological data and structural geological data, acquired to complement the data available originally from hydraulic testing and geological studies. The boreholes drilled to investigate the hydraulic properties of the fault, in the absence of this detailed information, did not penetrate the fault zone fully (Figure 41). Consequently, the locations of hydraulic tests relative to the fault zone were often unclear. For example, previously, the hydraulic test at 154.5 maSL in borehole TH-5 was thought to lie in the foot wall of the fault. However, the latest data from boreholes near to TH-5 suggest that this test may lie within the fault zone, albeit on the foot wall side of the main fault strand (though this hypothesis could not be checked because suitable core did not exist from TH-5).

Interpretations of previous data were also complicated by most of the previous boreholes (TM-2, 98FE-01, KNA-6, TH-1, TH-2 and TH-3) intersecting the fault near to the unconformity between the sedimentary rocks and the granite (Figures 39 and 41). In these boreholes, it is difficult to interpret the relative hydraulic significance of stratigraphically controlled lithological changes and fault-related deformation. In contrast, boreholes 99SI-08; TFA-1; 98SI-03 and MIU-2 intersected the fault away from formation

boundaries. Therefore, in these boreholes, structurally controlled porosity variations could be used much more confidently to infer permeability variations.

Some generic lessons for characterising the hydraulic characteristics of faults, based on the Tsukiyoshi Fault study, are illustrated in Figure 52.

Performance Assessments, (PA) for any potential underground radioactive waste repository generally involve risk calculations for a relatively small number of 'scenarios' that represent plausible future states of the repository/geosphere system (Savage, 1995). Scenarios should consider realistic combinations of natural features and processes.

Previously, groundwater flow models used in PA have tended to represent faults as planar, time-invariant features with higher hydraulic conductivities than the surrounding rock mass (e.g. JNC, 2000). The present work highlights that such a representation may be unrealistic.

It is appropriate to take into account the hydraulically effective widths in PA. Ensuring that the planar representation of a fault in a groundwater flow model has the same hydraulic properties as the actual fault zone that it represents can achieve this goal. However, while the present hydraulically significant width of a fault could be established from hydraulic testing, the current study has identified chemical and physical processes that may plausibly change the transmissivity of a fault zone over time. In the Tsukiyoshi Fault's case, the absolute timing of these changes is unknown, but many of the changes must have taken less than 10 Ma. The possibility that they could have occurred over time scales comparable with PA, typically c.1 Ma, cannot be ruled out.

Repository structures should also avoid permeable zones of faults that could act as significant nuclide transfer paths (e.g. JNC, 2000). The present study implies that repository designs should account for possible temporal variations in the widths and locations of these potential pathways.

It is suggested that realistically conservative scenarios should incorporate the highest transmissivities that can be inferred for a fault zone in the past, taking into account structural and mineralogical data. Similarly, this information can be used to deduce maximum distances over which transmissive fracture pathways will extend normal to the fault.

The processes that have affected the Tsukiyoshi Fault after the last fault movement, are most relevant for constructing an initial scenario for any PA (often called a 'base scenario'), since such scenarios are typically representations of the present groundwater system at a site. However, information concerning the properties of the fault during the period when it was active is potentially relevant for constructing other scenarios that take into account the possibility that fault movement might occur in future. Recognition of evidence for changing hydraulic properties connected with both the fault deformation and water/rock interactions following the last fault movement is significant. It appears that a late, relatively small normal reactivation of the Tsukiyoshi Fault may have changed the hydraulic properties of the fault zone significantly. This is important because it implies that a possible changing sense of fault movement may be significant for PA.

5.6 Recommendations for future fault studies

The Borehole 99SI-08 study demonstrated the value of a structured approach to fault investigations. Such an approach has the following main elements:

- model development based on earlier data;
- predictions based on the model;
- design of a borehole to test the predictions;
- comparison between the observations and predictions.

Acquisition of the following types of information would be valuable in future investigations:

- fracture types and distributions;
- types, paragenetic relationships and spatial distributions of porosity-filling minerals, especially fracture-filling minerals;
- types, paragenetic relationships and spatial distributions of secondary minerals, such as replacive minerals in wall-rocks of fractures;
- chemical compositions of porosity-filling and secondary minerals.

Some generic lessons can be drawn for future data acquisition (Figure 52):

- To characterise a fault's hydraulic properties, it is usually desirable that a borehole should intersect the fault away from formation boundaries.
- Continuous fracture logging of rock core during borehole drilling would enable the extent of the damaged zone associated with a fault to be determined.
- It would then be possible to ensure that the borehole penetrates the fault zone fully and any hydraulic tests could be sited appropriately.
- Flexibility in borehole design is required, notably in specifying the length.
- Provision for penetrating a deformation zone at least as wide as the fault's throw is prudent.
- The borehole length needed to penetrate a fault fully could be minimised by drilling at a high angle to the fault.
- To characterise the hydrogeological properties fully, it will be necessary to plan tests within both the hanging wall damaged zone and the foot wall damaged zone.
- The variability of fault-rock frequency, even between boreholes that are closer than 20 m apart means that different water-bearing 'compartments' with dimensions on the scale of metres to tens of metres, may exist within the fault zone. Hydraulic tests would need to be sited carefully with respect to these compartments, if the full range of hydraulic properties is to be characterised adequately.

6. HALIDE STUDIES

6.1 Purpose of this chapter

This chapter describes the available halide (Br, Cl, and F) data from the groundwaters in the Tono area and summarises how they can be used to constrain the origins of groundwater salinity. Recommendations are then made for using such data to constrain flow models for groundwaters in the Tono area.

Dissolved Br and Cl are widely used to constrain the origins of groundwater salinity. To a lesser extent, dissolved F and I have also been used. The stable isotopes ^{35}Cl and ^{37}Cl are also valuable for constraining the origins of dissolved chloride. The radioactive isotopes ^{36}Cl and ^{129}I (to a lesser degree than ^{36}Cl) have been used in recent years to constrain the residence times of dissolved Cl and I respectively, and hence to constrain groundwater residence times (see also Chapter 7).

This chapter concentrates on variations in dissolved Br and Cl, which have been shown to be particularly useful in many studies internationally. However, consideration is also given to variations in F, since the groundwaters in the Tono area contain generally high and variable concentrations of this constituent. Possible applications of iodine data, which might be acquired in the future, are also suggested.

A preliminary study of ^{36}Cl is considered in Chapter 7.

6.2 Principles of halide studies -theory

6.2.1 Chemistry of halides – general

In sedimentary formation waters the abundances of these elements is generally Cl > Br > I > F (Worden, 1996). These reflect the following major controls on the concentration of halides in groundwaters:

- abundance in the earth's crust;
- ability to form soluble minerals;
- affinity for organic matter;
- redox conditions (in the case of iodine).

6.2.2 Chemistry of Br and Cl

During groundwater investigations worldwide, variations in the concentrations of Br and Cl are often used to indicate the origins of groundwater salinity and mixing proportions of different groundwaters (Hanor, 1994; Nirex, 1997b). These variations can often be useful constraints on groundwater flow models (e.g. Nirex, 1997b).

Most previous studies elsewhere in the world have concentrated on Br and Cl in saline waters or brines. There have been relatively few studies of variations in deep fresh groundwaters (Edmunds, 1996). Here, the classification of Carpenter (1978) is used to describe salinity, following the practice of other studies (e.g. Nirex, 1997b). Fresh water

has Total Dissolved Solids (TDS) < 1000 mg/l; brackish water has TDS • 1000 and < 10,000 mg/l; saline water has TDS • 10,000 and < 100,000 mg/l; and brines have TDS • 100,000 mg/l.

Both Br and Cl are usually relatively unreactive in water/rock systems (at least compared to cations like Mg^{2+}, Na^{+}, Ca^{2+} and anions such as HCO_3^- and SO_4^{2-}). Often, the concentrations of Br and Cl in groundwater are higher than concentrations of Br and Cl in the surrounding rock. In these cases, water/rock interactions will have only a small effect on the Br/Cl ratios of the water. Therefore these ratios depend on the origins of the salinity acquired before the water moved into the sampled rock formation. Usually, these ratios are used to distinguish salinity originating in seawater (with Br/Cl mass ratios around 0.0035) from salinity originating in halite dissolution (e.g. groundwaters in northwest England have Br/Cl ratios around 0.0005, caused by halite dissolution; Nirex, 1997b).

If the water is sufficiently dilute and/or there are rocks containing soluble evaporite minerals (notably halite, NaCl), water/rock interactions could have a major effect on the Br/Cl ratios. In these cases, Br/Cl ratios cannot be used to evaluate any origins of salinity outside the sampled rock formation.

Evaporation in surface environments may be another major control on Br/Cl ratios. If this process causes halite to precipitate, the residual water may have even higher Br/Cl ratios than seawater, because Br does not partition into the halite structure very well. Potentially, the resulting saline, high Br/Cl water could descend into underlying rock formations owing to its relatively high density, thereby forming high Br/Cl groundwaters.

Other processes that have been suggested to affect Br/Cl ratios are as follows.

- Evaporation of continental waters will also produce saline water with low Br/Cl mass ratios (e.g. saline lake waters in Australia, produced by evaporation; Vengosh et al., 1990).
- Recrystallisation of halite may cause any small amount of NaBr within the halite structure to partition into the aqueous phase, producing relatively high Br/Cl waters (Stoessell and Carpenter, 1986).
- Water/rock interactions with organic matter could affect Br. In the U.K. Carboniferous Coal Measures typically contain water with relatively high Br/Cl (Edmunds, 1975; Edmunds, 1996).
- Water/rock interactions in certain rocks (notably mafic and ultramafic rocks (Kamineni et al., 1992)), and granite with fresh biotite (Edmunds et al., 1985) may produce water with relatively high Br/Cl ratios. These rocks contain significant Br.
- Input of magmatic fluids to hydrothermal waters has been suggested as a cause of Br/Cl ratios that are lower than seawater (e.g. for hot springs in northern Japan; Uzumasa, 1965).
- Membrane filtration has been suggested as a mechanism by which halogen ratios may be varied. If water is forced through a low-permeability formation such as a mudrock that acts as a membrane, the Br/Cl ratio on the upstream side will theoretically increase. The significance of this process is uncertain however (Hanor, 1994).

- Incorporation of marine aerosols into rainfall will tend to produce rainwater with relatively high Br/Cl ratios (Edmunds, 1996). The relatively elevated Br in the aerosols is thought to come from Br-enriched marine lipids.
- Burning of fossil fuels may release Br to the atmosphere and this Br may find its way into the groundwater system (Edmunds, 1996).
- Addition of salt to roads during the winter and the use of certain fertilisers may also cause the Br/Cl ratios of recharge water to vary locally.

6.2.3 *Chemistry of F*

Relative to bromide and chloride ions, fluoride is a small ion which has a different chemistry to either bromide or chloride. Generally, F reacts much more strongly with non-evaporitic (e.g. non-halite-bearing) rock matrices than the Br, Cl and is affected little by reactions with organic matter, unlike I or Br. The concentrations of F in sedimentary formation waters typically range from < 1 ppm to around 30 ppm, though almost 70% of 166 analyses reported by Worden (1996) have values in the range 1 – 10 ppm. The highest F concentrations are found with the highest Cl concentrations in such waters, indicating that the same processes may control both (Worden, 1996). However, this is only apparent for the waters with higher Cl concentrations than c. 20,000 ppm. At lower Cl concentrations there is no correlation.

Common minerals that may retain fluorine are:

- fluorite;
- amphibole;
- phlogopite;
- apatite;
- biotite.

All may contain up to % levels of F.

Most data suggest that deep groundwaters have fluoride concentrations governed by equilibrium with respect to fluorite (e.g. Edmunds et al., 1987; Hitchon, 1995). However, Hitchon (1995) noted that the concentration of F was sometimes in excess of the levels consistent with fluorite equilibration. He speculated that the excess fluoride may have been liberated to the water during the alteration of adjacent shales, or alternatively of nearby bentonite. He concluded that Mg-F complexes were significant in the more saline waters. Thus, diagenetic alteration of mudrocks containing Mg-bearing pore-waters, such as connate seawater, might potentially produce formation waters that carry relatively high concentrations of F.

High-temperature water/rock interactions, involving rocks containing fluorine-bearing minerals, may release fluoride to the water. Interactions between saline groundwaters and granitic rocks at temperatures between 80°C and 250°C were shown experimentally, to produce significant increases in F concentrations in the waters (Savage et al., 1990). However, the solution merely approached saturation with respect to fluorite over time, and very high concentrations of fluoride were not attained during these experiments. The

starting fresh groundwater had 0.8 mgl^{-1} of fluoride, and even after 98 days at 250°C, the fluid had only 13.5 mgl^{-1} of fluoride.

These levels of fluoride are not significantly higher than concentrations reported in deep groundwaters (e.g. values reported in: Gascoyne et al., 1987; Frape and Fritz, 1987; Edmunds et al., 1987; Hitchon, 1995). There have been many studies of fluoride in shallow, fresh groundwaters used for drinking water supplies, because fluoride concentrations in excess of 1.5 mgl^{-1} are deemed to be harmful. However, relatively few fluoride concentrations have been reported for deep, saline groundwaters and brines. Brines in the crystalline rocks of the Canadian Shield generally contain < 1 mgl^{-1} to a few mgl^{-1} fluoride, but may contain up to c. 27 mgl^{-1} (Gascoyne et al., 1987; Frape and Fritz, 1987). Brackish and saline waters in Wheal Jane mine, near the Carnmenellis Granite of southwest England, generally contain < 8.5 mgl^{-1} fluoride, although one anomalous brackish, acid-sulphate water yielded 44 mgl^{-1} of fluoride (Edmunds et al., 1987). This acid sulphate sample also yielded high levels of aluminium (25 mgl^{-1}), leading Edmunds et al. to postulate that Al-F complexing occurred, leading to high levels of dissolved fluoride.

6.2.4 *Chemistry of I*

Iodine exists in two principle redox states in natural waters: I(I) (as I^-) and I(III) (as IO_3^-). However, the latter is only present in certain near-surface, highly oxidising environments and is not found in deep groundwaters.

By far the major control on I in deep groundwaters is the affinity of this element for organic compounds and it cycling by biological processes compounds (e.g. Fuge and Johnson, 1986). Therefore, the presence of organic matter in a water/rock or water/sediment system may perturb the abundance of I and its ratio to the other halogens.

Iodine tends to be much more enriched in recent marine sediments than in recent non-marine sediments (Falck and Hooker, 1991; Fuge and Johnson, 1986; Mackenzie et al., 1990). Recent marine muds contain from c. 30 ppm to c. 200 ppm I, whereas lake sediments contain only 5 or 6 ppm I (Fuge and Johnson, 1986). However, the halogen contents of sediments must be interpreted with caution, because variable organic inputs and organic matter diagenesis can result in highly variable Br, I and Cl concentrations and associated ratios.

6.3 Halide data from groundwaters in the Tono area

6.3.1 *Br and Cl data*

Data for Tono groundwaters are summarised in Tables 12 and 13 and illustrated in Figures 53 and 54.

The halide Cl was analysed routinely during the investigations at Tono. For natural waters (in groundwater, surface water and rainwater; excluding drilling fluids) 273 Cl concentrations have been reported at the time of writing. Of these concentrations, 8 are quoted as less than a detection limit of 1 mgl^{-1}.

Only 31 Br concentrations are reported for natural waters from the Tono area. There are also Cl data for the same water samples. Thus, compared to many other similar studies elsewhere, there are relatively few groundwater samples from the Tono area that have both Br and Cl data. Additionally, most waters with Br and Cl data come from boreholes close to the Toki River. For both these reasons it is difficult to judge the significance and magnitude of spatial variations in chemistry.

Some water samples came from the Toki Granite (e.g. samples from DH-4 and DH-12), but it is suspected that most water samples come from the sedimentary cover sequence, principally the Mizunami Group, since uranium exploration boreholes were sampled. However, water flow from the uranium exploration boreholes was probably mostly artesian. Therefore, it is not certain which rock formation was sampled and there is a possibility that water from different rock formations mixed in the boreholes. The deeper uranium exploration boreholes are thought to intersect the granite. Therefore, possibly there is also a component of water from the granite.

Most of the samples with Br and Cl data come from these uranium exploration boreholes. These are relatively old boreholes, within which there was probably mixing before sampling. Furthermore, some samples were collected and analysed more than 12 years ago, before the research programme had progressed to its present level of sophistication. In particular fewer records are available with which data quality can be evaluated, than is the case for the more recent boreholes. Therefore, compared to more recent boreholes, for which there are few Br data, the quality is not so easily determined.

Most samples contain very little Br (sub-ppm levels) and the more dilute samples contain only ppm levels of Cl (Figure 53). These samples are likely to have relatively large errors on the Br/Cl ratios. However, these errors are difficult to quantify. Unfortunately, for many samples, the analytical techniques used to obtain the data are not known and the analytical precisions, which would provide an estimate of the minimum uncertainties, are not available for any samples. However, for all samples for which analytical techniques were recorded, Br and Cl were analysed by ion chromatography. Experience in other studies elsewhere suggests that in samples where both Br and Cl are well above their detection limits, the 2σ relative precision on the analyses of both Br and Cl would be around ±10%. In the Tono waters the Cl concentrations should all be above the detection limit usually obtained by ion chromatography. However, many of the Br analyses are very close to the detection limit in these waters. Therefore, the precision on the Br analyses could possibly be much higher. For these reasons 2σ precision of ±10% probably represents the **minimum** uncertainty. However, at these uncertainty levels, the corresponding uncertainty in Br/Cl ratios would be consistent with all except the most dilute samples having ratios significantly less than seawater. The fact that several samples of varying chloride contents gave lower Br/Cl ratios than seawater is perhaps the best indication that this conclusion is correct (Figure 54).

Assuming that the data represent in-situ water compositions, several variations can also be seen in the chemical data. Deep groundwater from the area near to the Toki River, for example from borehole DH-12 and uranium exploration boreholes, has significantly different chemistry and salinity from the deep groundwater further to the north of the Toki River. In the north, the groundwater is all fresh, Ca-Na-HCO_3 or Ca-HCO_3 dominated and has Cl concentrations of only a few ppm. In contrast, ground water to the

south of the Toki River, though still fresh (except for one brackish water with c. 1550 mg/l Total Dissolved Solids), is more saline, has an Na-Cl dominated chemistry and contains up to several hundred ppm Cl (Figures 53 and 54).

6.3.2 F data

Like Cl, F has been analysed routinely during the investigations around Tono water and rainwater. Of these, 247 are above detection limit, while 38 are quoted to be below detection limit. The surface water samples have F that is mostly below detection limit. Where a value is quoted, the detection limit is mostly < 0.02 to < 0.1 mg/l, depending on the sample. Analyses of F corresponding to samples for which there are also Br and Cl data are reported in Table 13. Variations in F concentrations are compared to variations in Cl concentrations in Figure 55, while Figures 56 and 57 summarise the variations in F with respect to lithology and depth respectively.

From these plots several important features can be observed:

- Many of the groundwater samples are relatively high in F contents, often above World Health Organisation (WHO) guideline limits.
- There is no correlation between F and Cl concentrations;
- In groundwater from any given rock type there is a wide scatter in the F-concentrations;
- Surface waters and groundwaters from the Seto Group, Oidawara Formation and Akeyo Formation have generally lower F concentrations than groundwater samples from the Toki Lignite or Toki Granite formations;
- Groundwater samples from the Toki Lignite and Toki Granite have generally similar mean and ranges of F concentrations.
- The highest F concentrations were found in the uranium exploration boreholes.
- In borehole DH-7, in the Toki Granite, there is an increase in the F-content of groundwaters with respect to depth, but in other boreholes there is a less clear relationship between F concentration and depth.
- Excluding the samples from boreholes DH-12 and MIU-4, the data from the Toki Granite show a general increase in F concentration with respect to depth. The samples from boreholes DH-12 and MIU-4 had higher F concentrations than can be explained by a depth-related trend interpolated among samples from the other boreholes.

6.3.3 I data

At the time of writing, no I data have been reported for the waters of the Tono area.

6.4 Preliminary interpretation of halogen data in the Tono area

6.4.1 *Br and Cl data*

Some alternative possible explanations for the chemical **variations** in Br and Cl among the different waters are:

- Possibly, the water south of the river was originally similar to the more northerly water, but has been chemically modified by more extensive water/rock interactions than has the water further to the north. Note that this does not mean that waters from the north and south of the river are necessarily genetically related to one another. It is possible that the water near to the river is part of a different flow system compared to the water further north. Perhaps, the water to the south of the river originated in a recharge area further to the south.
- The Cl-rich water south of the river contains a component of 'fossil' seawater. Possibly, in this case, the water has not been flushed by more recent fresh recharge water as extensively as the bicarbonate water further to the north. Some of the sedimentary rocks in the Tono area are marine in origin and therefore marine water was present in the area in the past.
- The Cl-rich water to the south of the river contains a component of Cl originally of magmatic origin. This is a similar explanation to the one suggested for relatively low Br/Cl ratios in waters from hot springs in Aomori Prefecture and Hokkaido (ratios reported for these waters are 1 x 10-3 to 4 x 10-3, but mostly lower than the sea water ratio; Uzumasa, 1965). The fact that the sample with the highest Cl content from the Tono area came from Takasago Onsen may be significant.

There is no evidence for other major sources of Cl-salinity in the area.

The variations in the Br/Cl ratios among the groundwaters could be explained by mixing between different groundwaters. When a low-Cl water with a high Br/Cl ratio mixes with a significantly more Cl-rich water with a much lower Br/Cl ratio, the Br/Cl ratio of the mixture will approach that of the more saline water after only a small degree of mixing. It can be seen that mixing between the most dilute and most saline samples from the Tono could theoretically explain much of the variability in the halide contents (Figure 54). However, the consistency of the theoretical mixing line and the data is **insufficient to prove** that this mixing has actually occurred. In particular more information about the errors on the data is needed before any firm conclusions can be made.

Any of the above explanations could be **consistent** with the groundwater to the south of the river being relatively close to a discharge zone, compared to the groundwater from north of the river. This case is consistent with relatively long travel pathways and hence relatively extensive water/rock interactions and/or relatively little flushing by fresh recharge water. On the other hand, the water to the north of the river could be relatively close to a recharge zone, where there has been relatively little time for water/rock interactions to have a large effect and/or flushing has been relatively extensive. **Again it is emphasised that the recharge zone in the north and the discharge zone in the south are not necessarily part of the same flow system.**

The waters that have Br/Cl mass ratios similar to, or higher than, that of seawater are generally the freshest ones. The relatively high uncertainties that are expected for these ratios make their significance difficult to assess. By comparison with other studies

elsewhere (e.g. Edmunds, 1996), it is conceivable that these ratios reflect recharge values. However, in the absence of data for recharge waters, this hypothesis is speculative.

The ratios lower than the seawater value come from the more saline (though still fresh, except for one brackish case) Na-Cl dominated waters to the south of the Toki River. **Provided the estimated uncertainties on the ratios are realistic**, the Na-Cl dominated salinity of these samples cannot be explained just by simple dilution of seawater. This view is also supported by ratios of other constituents, notably Na/Cl and Na/Ca, which are all significantly different from seawater.

This conclusion does not rule out the possibility that the salinity here could be **partly** from seawater. However, in this case, some other sources of salinity are also required. For example, if seawater was diluted by fresh meteoric water, to produce water of approximately the observed salinity and then water/rock interactions added a small amount of Cl to the water, it might be possible to produce the observed composition. To determine whether or not this mechanism could have occurred it would be valuable to obtain Br and Cl data for the rocks and minerals that could have been in contact with the groundwater. Low-temperature water/rock interaction experiments might also help to evaluate whether or not this water/rock interaction process is a feasible explanation. At the present time, there are no Br or Cl data for minerals and no Br analyses of whole-rock samples. Furthermore, Cl data appear to exist for only 6 rock samples (Yoshida et al., 1994a). Nevertheless, the analyses for the sedimentary rocks of the area ranged between 38 and 526 ppm, whereas a single analysis of the Toki Granite gave 22 ppm Cl. This range of values is comparable to the range of Cl concentrations in the more saline relatively low Br/Cl groundwater samples. Thus, it is **reasonable** to suppose at this stage that a significant proportion of the dissolved chloride in the groundwater **could** have been obtained during water/rock interactions. However, the effect of these water/rock interactions on Br concentrations and on Br/Cl ratios cannot be judged.

One possible objection to this hypothesis is that water/rock interactions, besides those involving halite, often tend to increase the Br/Cl ratios, rather than lower them. For example, alteration of biotite in granite has been suggested as a cause of high Br/Cl water in granitic rock in England (e.g. Edmunds et al., 1985). By comparison with experience in U.K. coalfields, organic matter, for example in the Lower Toki Formation, could also possibly produce relatively high Br/Cl ratios. If either of these processes affected seawater, it might be expected that higher Br/Cl ratios than seawater would be seen, rather than the lower ratios that in fact occur. Once again, Br and Cl data for rocks and minerals coupled with low-temperature laboratory experiments could help to determine the feasibility of these processes.

Therefore, the first hypothesis above, namely that the majority of the salinity, even in the more saline waters originates in water/rock interactions, cannot be excluded.

The third hypothesis is entirely speculative at the present stage. Uzumasa (1965) appears to have suggested that Cl from a magmatic source could explain the relatively low Br/Cl ratios in onsen waters, simply because of the proximity of many hot springs to volcanic activity. However, it is stressed that the first and third hypotheses are not exclusive. Any chloride presently in minerals in the rock is likely to be dominantly from initial magmatic source.

To make a rigorous interpretation of the data, possible palaeo-environmental variations also need to be considered. Variations in seawater composition over time are probably insignificant, since Br and Cl ratios vary very little in modern marine water. Additionally, both have relatively long residence times in the oceans (residence time is in the order of 100,000,000 years for both; Stumm and Morgan, 1981). This means that changes to the overall contents of Br and Cl in the oceans will be very slow. However, in contrast, there could potentially be a significant variation in the compositions of meteoric water input. Generally, Br/Cl ratios tend to increase from coasts, inland (Edmunds, 1996). Thus, the location of the coastline, which depends on sea level and hence climate, could influence the Br and Cl content of meteoric recharge water. The nature of vegetation in an area can also affect the ratio Br/Cl in recharge waters, through combination of Br with organic matter. Vegetation is also climatically controlled.

6.4.2 *Fluorine data*

The lack of a correlation between Cl and F concentrations (Figure 55) suggests that different processes control the abundances of these elements in the groundwaters of the Tono area. Once possible explanation is that mixing between different groundwaters is a more important control on variations in Cl concentrations than are water/rock interactions, whereas the reverse is true for F.

If water/rock interactions control F concentrations, possible candidates for the source of the F are fluorite, apatite and biotite. All of these minerals occur in the Toki Granite, while altered biotite occurs in the sedimentary rocks (e.g. McKervey et al. 2001).

There are, unfortunately, no chemical data for apatite and only limited chemical data for biotite that can be used to evaluate the plausibility of these as sources of the fluoride. McKervey et al. (2001) report that altered biotite from the Lower Toki Formation in borehole 98SI-03 had up to 0.76 wt % F, while altered biotite in the Toki Granite had up to 0.42 wt% F. It is anticipated that fresh biotite would contain higher levels of F than these. Thus, it is plausible that biotite alteration could explain the relatively high F concentrations in the groundwaters.

Simple calculations with Geochemist's Workbench (GWB) in conjunction with JNC's thermodynamic database thermotgrp.dat suggest that the range of concentrations of F in the groundwaters could potentially be explained by equilibration with respect to fluorite (Figure 58). However, the thermodynamic data for fluorite are somewhat uncertain. For example, the data in the database thermo.dat, supplied with GWB imply that, at the temperatures of groundwaters in the Tono areas, concentrations of F controlled by equilibrium with fluorite would be significantly lower than the maximum concentrations encountered in the Tono area.

In summary, there is some doubt about the exact mineral that could control the variations in F concentrations encountered in the Tono area, but it is plausible that water/rock interactions are a major control on these variations.

The spatial variations in the concentrations of the F in groundwaters can be accommodated by this model. If the concentrations are indeed controlled by water/rock interactions it would be expected that longer residence times and/or reactions at higher

temperatures would result in higher F concentrations in the groundwaters. Thus, water/rock interactions could explain the observed general increase in F concentration with respect to depth. The departures from this trend seen in MIU-4 and borehole DH-12 could potentially be explained by local variations in the rates of circulation of groundwater and/or by these boreholes lying relatively large distances from the recharge locations. Again, it is emphasised that this model does not necessarily imply that the groundwater in DH-12, to the south of the Toki River, are genetically related to the groundwaters in the other boreholes, to the north of the Toki River.

6.5 Summary conclusions from halide data in the Tono area

- The relatively more saline (but still fresh) groundwater to the south of the Toki River has generally lower Br/Cl ratios than seawater.
- Assuming that these ratios are truly those of in-situ water, seawater alone cannot be the source of the salinity. Dilution of seawater by fresh water would not produce all the observed Br/Cl ratios in the more saline groundwater.
- If seawater was the source of some of the Br and Cl, then, in addition to dilution by fresh water, Br has since been removed and/or Cl has been added to the water.
- Water/rock interactions, involving phyllosilicate minerals like biotite could potentially affect the Br and Cl concentrations in the water.
- Whatever the sources of the Br and Cl, the variations in Br/Cl ratios could theoretically be explained largely by mixing between different water types, though more data are needed to confirm or refute this hypothesis.

6.6 Potential future applications of halide data in the Tono area and elsewhere

6.6.1 Potential applications in the Tono area

Variations in the concentrations and ratios of the halides in the groundwaters of the Tono area could potentially be used to constrain/improve confidence in concepts of groundwater flow. In particular, if more data were available for the variations in salinity and Br/Cl ratios in the vicinity of the Toki River, the nature of the transition between HCO_3 dominated groundwater to the north of the river and Cl dominated water to the south could be established. The degree to which this transition is sharp or gradational would have important implications for the southern boundary of the groundwater flow models that have been constructed to the north of the river. Additionally, variations in the Br/Cl ratios could be an important check on the mixing proportions between different groundwater types that are calculated by groundwater flow models.

If the variations in F concentration can indeed be related to groundwater residence times, they could be a qualitative check on relative groundwater residence times inferred from groundwater flow models.

6.6.2 Potential applications elsewhere

While halide chemistry is commonly used to interpret the origins of groundwater salinity and the mixing proportions of different groundwaters, there have been few applications of these constituents for these purposes in deep, fresh groundwater systems. If the investigations at Tono could demonstrate the utility of these constituents in such groundwater systems, it would also serve to demonstrate their potential value in fresh groundwater systems elsewhere in Japan.

6.7 Recommendations for future halide studies

- Data for the Cl and Br content of the rocks and minerals of the area would help to interpret the Br/Cl ratios. Similarly, low-temperature water/rock interaction experiments could produce useful information.
- Data for the F contents of the rocks and minerals of the area would help to determine the reasons for the variations in F concentrations found in the groundwaters.
- It is recommended that Br data, in addition to Cl and F data, should continue to be obtained routinely during future sampling.
- It would also be valuable to analyse Br in rainwater in addition to Cl, to give an indication of inputs of Br and Cl to the groundwater system.
- Isotopic data for Cl, notably $^{37}Cl/^{35}Cl$ ratios and $^{36}Cl/Cl$ could help to shed further light on the origin of the chloride salinity (see Chapter 7 for details of a preliminary $^{36}Cl/Cl$ study in the Tono area).
- Analyses should in future be reported with an indication of the analytical method and with the analytical precisions and other quality information.

7. ^{36}Cl STUDIES IN THE TONO AREA

7.1 Purpose of this chapter

This chapter describes small-scale studies of the radioactive isotope ^{36}Cl in groundwater from the Tono area. A preliminary interpretation of the data is also given.

The chapter develops interpretations that were based on the investigations of Br, Cl and F presented in Chapter 6.

7.2 Principles of using ^{36}Cl -theory

Applications of ^{36}Cl analyses in hydrogeology are covered by an increasingly large literature (e.g. Phillips et al., 1986; Andrews et al. 1986; Andrews et al. 1989; Andrews et al., 1994). This section summarises only the main principles of using ^{36}Cl that are relevant to investigations in the Tono area. These principles are illustrated in Figures 59, 60 and 61.

The abundance of ^{36}Cl is usually expressed as the ratio of ^{36}Cl atoms to atoms of stable chlorine atoms. This ratio changes in a groundwater system over time due mainly to:

- variations in the recharge ratio;
- mixing of different waters;
- production of ^{36}Cl *in situ* within the rock mass;
- radioactive decay of ^{36}Cl;
- water/rock interactions, in cases where the rock contains much more chloride per unit mass than does the water and/or the chloride resides in relatively reactive mineral phases, such as biotite or halite;
- physical fractionation processes.

Physical fractionation processes are generally considered to be unimportant compared to the other processes.

The variations in ^{36}Cl/Cl have two main purposes when applied to deep groundwaters:

- Where there are large variations in the *in-situ* ^{36}Cl production rates in different rock formations within an area, the measured ^{36}Cl/Cl ratios may be useful tracers for the origins and flow directions of the waters.
- The ^{36}Cl/Cl ratios may enable the residence time of chloride within a particular rock formation to be constrained, either by allowing an absolute time to be calculated or by placing a limit on the residence time.

This second application depends on the fact that, with increasing residence time in a rock, the ^{36}Cl/Cl ratio of dissolved chloride will change from its initial value upon entry to the rock, towards an equilibrium value at which the ^{36}Cl production rate is balanced by the ^{36}Cl decay rate.

At depths greater than a few metres (typically around 20 m), the main source of *in-situ* ^{36}Cl production in the water is usually the neutron activation of stable ^{35}Cl. In this case,

the *in-situ* neutron flux results from radioactive decay processes in the rock. The change in the $^{36}Cl/Cl$ of the dissolved chloride due to this process is termed 'ingrowth'. In addition to 'ingrown' ^{36}Cl will be ^{36}Cl produced in the rock matrix, and released subsequently by water/rock interactions. This is likely to be important when the waters are relatively fresh and/or the rock contains relatively abundant Cl-bearing minerals (e.g. micas in acid igneous rocks and halite in evaporites). In cases where such water/rock interactions have occurred significantly, it will usually be impossible to use the ^{36}Cl data to estimate a meaningful residence time for the water, though it may be possible place limits on this residence time.

Uncertainty in the chloride concentration of the rock is an important contributor to uncertainty in the equilibrium $^{36}Cl/Cl$ ratio in the water is very low. Under these circumstances, ^{36}Cl production by neutron activation of ^{35}Cl may be comparable to ^{36}Cl production by alpha-neutron reactions involving ^{39}K in the rock matrix. In this case $^{36}Cl/Cl$ ratios will not be independent of the chloride concentration and uncertainty in chloride concentration will cause uncertainty in the $^{36}Cl/Cl$ ratio. In contrast, at higher concentrations of chloride, the dominant source of ^{36}Cl is neutron activation of ^{35}Cl. In this case, the rate of ^{36}Cl production is proportional to the amount of chloride present and the equilibrium $^{36}Cl/Cl$ ratio approaches a constant value as chloride concentration increases.

To evaluate the relative importance of mixing and *in-situ* production of ^{36}Cl, *in-situ* equilibrium $^{36}Cl/Cl$ ratios must be estimated, using knowledge of *in-situ* neutron-producing reactions. In the work reported here, chemical analyses of the rocks were used, in conjunction with equations and approaches described in (Andrews et al., 1986) and (Andrews et al., 1989). The rate of neutron production by fission of uranium and thorium and (α,n) reactions involving light elements such as O, F, Na, Mg, Al, Si and K is first calculated, using:

$$N_P = {}^{238}N\lambda_{SF}\nu + a[U] + b[Th] \qquad \text{Equation 7.1}$$

where: N_P is the neutron production rate in neutrons $a^{-1}\,g^{-1}$ of rock; ^{238}N is the number of ^{238}U atoms g^{-1} of rock; λ_{SF} is the decay constant for ^{238}U ($8.5 \times 10^{-17}\ a^{-1}$); ν is the average number of neutrons emitted per spontaneous fission of ^{238}U; [U] and [Th] are, respectively, concentrations of uranium and thorium in the rock, in ppm; and

$$a = \frac{\sum_{1}^{x} S_x F_x Y_x^U}{\sum_{1}^{x} S_x F_x} \qquad b = \frac{\sum_{1}^{x} S_x F_x Y_x^{Th}}{\sum_{1}^{x} S_x F_x} \qquad \text{Equation 7.2.}$$

where: S_x is the mass stopping power in MeV $g^{-1}cm^{-2}$; F_x is the fractional abundance of element x by mass; and $Y^u{}_x$ and $Y^{Th}{}_x$ are the neutron yields per ppm of U and Th respectively, when in equilibrium with their daughters.

The neutron flux is then calculated by allowing for the absorption of neutrons, principally by Cl, K, Ca, Ti, Cr, Fe, Mn, Co, Ni, Sm and Gd, using:

$$\sigma_{matrix} = \sum_{1}^{x} \sigma_x N_x \qquad \text{Equation 7.3.}$$

where: σ_{matrix} is the absorption cross section of the rock matrix in moles barns g^{-1} (a barn is 10^{-24} cm^2); σ_x is the neutron absorption cross section of element x; and N_x is the mole fraction of element x.

and

$$\phi = \frac{N_p}{\sigma_{matrix}} \quad \text{for time} > 10^{-3}\ s \qquad \text{Equation 7.4.}$$

where: ϕ is the neutron flux in neutrons $cm^{-2}s^{-1}$.

The equilibrium $^{36}Cl/Cl$ ratio is then given by:

$$\frac{^{36}Cl}{Cl} = \frac{\phi\sigma_{Cl}}{\lambda_{Cl}} \times \left(\frac{^{35}Cl}{Cl}\right) \qquad \text{Equation 7.5.}$$

where: ^{36}Cl is the number of atoms of chlorine-36; ^{35}Cl is the number of atoms of chlorine-35; Cl is the number of atoms of stable chlorine; σ_{Cl} is the neutron capture cross section of chlorine (33.6 barns); and λ_{Cl} is the decay constant of ^{36}Cl (7.3×10^{-14} s^{-1}).

In principle, the approach has the advantage that it considers the contribution of all the chemical constituents responsible for generating a neutron flux. In practice, the available whole-rock analyses do not include data for some relevant elements. Furthermore, in the cases of Ti, Mn, C, Cl, Cr, Co, Ni, Sm, Gd, and N, mass stopping powers and/or neutron yields produced by alpha particle irradiation are unknown. This means that any neutron production by (α,n) reactions involving these elements must be neglected in the calculations.

For rock constituents that had not been analysed, published mean values could be used with introduction of only small errors. Natural variations in concentrations of these elements within any particular rock type would cause only small variations in calculated $^{36}Cl/Cl$.

The lack of mass stopping powers and/or neutron yields for certain elements apparently does not cause a large error for silicate rocks ((Andrews et al., 1989). However, this could be a problem when applying the approach to other sites where there are none-silicate lithologies. Additionally, the lack of these stopping powers could limit estimations of *in-situ* production within carbonate-dominated fracture-filling minerals.

A disadvantage of this approach is that distances between whole-rock samples are often relatively large (within each borehole typically on a scale of metres to tens of metres e.g. borehole MIU-4). Consequently it is difficult to assess the variability of *in-situ* production that might occur.

It is possible to estimate the timing of chloride movement by assuming there was only one source of Cl and by applying the equation:

$$t = \frac{-1}{\lambda_{^{36}Cl}} \ln\left(\frac{R - R_{se}}{R_0 - R_{se}}\right)$$ Equation 7.6.

where: t = time in years
λ_{36Cl} = decay constant of ^{36}Cl ($2.30 \times 10^{-6}\ a^{-1}$)
R = measured $^{36}Cl/Cl$ ratio;
R_0 = initial ratio on entry to the rock formation;
R_{se} = secular equilibrium ratio that would be produced by *in-situ* neutron flux.

7.3 36Clip – A computer program to calculate equilibrium $^{36}Cl/Cl$ ratios

In order to calculate equilibrium $^{36}Cl/Cl$ ratios in the rocks of the Tono area, a computer program, 36Clip, (^{36}Cl *in-situ* production) was written in Microsoft Visual Basic for Applications™, within Microsoft Excel 98™ for Apple Macintosh computers.

Whole-rock analyses are input. If required by the user, the program can insert compositions for determinands that have not been analysed, from published mean rock analyses. The user then chooses whether the composition of the chloride in the rock or ingrown in the water is required. Upon running, equilibrium $^{36}Cl/Cl$ ratios are calculated for the rock type. A listing of the code is presented in Appendix 3.

The program uses the equations and approaches described in (Andrews et al., 1986) and (Andrews et al., 1989). These make several approximations and the results are necessarily approximate. Notably, it is assumed that all the neutrons produced in the rock are thermalised by multiple scattering events and that all the neutrons are eventually absorbed in the rock matrix. In reality, some of the neutrons will be epithermal and will not be capable of producing ^{36}Cl. Therefore, calculated neutron fluxes, and hence $^{36}Cl/Cl$, are likely to over-estimate real *in-situ* values.

However, in studies of the Stripa Granite, in Sweden, these approaches gave estimated neutron fluxes that were within 20% of measured values (Andrews et al., 1989; Andrews et al., 1986). This is small compared to variations in $^{36}Cl/Cl$ that typically occur in rocks and groundwaters at any particular site. These variations can be up to several orders of magnitude. Therefore, the approach is useful for investigating general variations in equilibrium $^{36}Cl/Cl$ ratios groundwater compositions.

Estimates of equilibrium $^{36}Cl/Cl$ ratios in various lithologies from the Tono area are given in Table 14.

7.4 Studies of ^{36}Cl in groundwaters the Tono area

7.4.1 Investigations in Tono Mine

7.4.1.1 Description of study

To evaluate the feasibility of obtaining ^{36}Cl data from the very fresh groundwaters in the Tono area, a preliminary study was undertaken in Tono mine.

Samples of groundwater were collected by Mr K. Hama from the upper part of the Toki Granite and the sedimentary rocks in the lowermost part of the overlying Toki Formation. The samples were obtained from packed-off sections of borehole KNA-6 (Figures 39 and 62), which is described in (Ota and Hanamuro, 1996). This borehole was chosen because it was accessible and there was already a large amount of supporting information concerning the rocks penetrated by the borehole and the chemistry of the groundwaters there.

Three samples were collected, two separate samples from the same packed-off interval in the Toki granite, and one from a packed-off interval in the overlying Lower Toki Formation (Figure 62; Table 15).

The samples were sent for analysis to the Purdue Rare Isotope Measurement Laboratory (PRIME lab) at the University of Purdue in Indiana, U.S.A. This laboratory is a recognised leader in the analysis of cosmogenic isotopes such as ^{36}Cl. The analyses were performed by Accelerator Mass Spectrometry (AMS) (described in (Elmore and others., 1993) and in the web page http://primelab.physics.purdue.edu/). This method uses a particle accelerator in conjunction with ion sources, large magnets, and detectors, to separate out interferences and count single atoms in the presence of $1x10^{15}$ (a thousand million million) stable atoms.

The single sample from the lowermost Toki Formation was split into two parts at PRIME Lab and each part was then analysed in the same way.

The groundwater analyses were compared with theoretical equilibrium values. Where possible, these latter values were calculated using rock compositions for samples from borehole KNA-6, compiled in (Ota and Hanamuro, 1996) and for two samples from the Lower Toki Formation, from borehole 98FE-01 and the lower part of No. 2 Shaft. These latter two analyses were taken from compilations by the British Geological Survey (BGS; Excel file 06546v2.xls, supplied by A.E. Milodowski on 5th April, 2000) and (PNC, 1994) respectively. The rock compositions used are summarised in Table 16.

The data in these various sources taken individually were insufficient to allow equilibrium $^{36}Cl/Cl$ values to be calculated. Therefore, where appropriate, reasonable values for certain chemical components were taken from compositions reported for rocks from elsewhere in the Tono area. These values were taken from a combination of (Iwatsuki et al., 2000c), (PNC, 1994) and the BGS compilation (BGS; Excel file 06546v2.xls, supplied by A.E. Milodowski on 5th April, 2000). Additionally, values for certain trace elements were not available in any of these compilations. In these cases, the models used values for the Stripa Granite, Sweden, taken from (Andrews et al., 1989), or else mean shale or granite compositions reported in (Smith, 1989).

The theoretical equilibrium values were calculated using the code 36Clip (Section 7.3 and Appendix 3).

7.4.1.2 ^{36}Cl results and discussion

The groundwater analyses from borehole KNA-6 are summarised in Tables 17 and 18. Initial estimates of equilibrium values, calculated using data available on 1st August 2001 are given in Table 19. The measured and equilibrium values are also compared in Figure 62.

The study showed that it is possible to obtain ^{36}Cl data from groundwaters sampled from the Tono area. The study suggested that it would be worthwhile to proceed with further studies of ^{36}Cl, in particular in Borehole MIU4.

The results reveal the following:

- The water from near the base of the lower Toki Formation yielded $^{36}Cl/Cl$ ratios that are slightly higher than the waters from the upper part of the Toki Granite.
- The duplicate analysis of the same sample from near the base of the Toki Formation gave results that are 19×10^{-15} different from one another, considerably greater than the 2 σ error.
- The $^{36}Cl/Cl$ ratios measured for the waters lie within the range of the theoretical equilibrium values for the granite in KNA-6.
- The $^{36}Cl/Cl$ ratios measured for the waters are all lower than the equilibrium values for the basal Toki Formation sedimentary rocks.
- The highest equilibrium $^{36}Cl/Cl$ ratios for the water are those calculated for ingrowth when ^{36}Cl production by potassium alpha-neutron reactions are included in the calculation.

The experimental blanks were low relative to the measured values and the analysts considered that the results are reliable. However, mean $^{36}Cl/Cl$ ratios for the two splits from the same Lower Toki Formation sample, TL/G-1 and TL/G-2, differ by 19×10^{-15}. The reasons for this difference are unclear, but may be due to instrumental fluctuations. This follows from the fact that the three analytical cycles for TL/G-1 gave very consistent results, while two of the three analytical cycles for TL/G-2 were also consistent. The three $^{36}Cl/Cl$ ratios for this latter split are 143.2×10^{-15}, 137.3×10^{-15} and 114.8×10^{-15}. Thus, the average is reduced significantly by the third value, which appears anomalously low, compared to the other two. The analysis of the blank corresponding to this low analysis is also lower than the other blank analyses, consistent with the variation reflecting analytical fluctuations. If only the first two values are considered, together with the reported errors, the results from the two splits of the sample from the Toki Formation are within 1 σ of one another.

A contributor to uncertainties in the theoretical equilibrium $^{36}Cl/Cl$ ratios is the incomplete nature of the rock chemical data. In addition to the elements that have been analysed routinely during the investigations of the Tono area, the estimated values for the following elements were also used in the calculations of equilibrium $^{36}Cl/Cl$ ratios:

Cl, F, Cr, Co, Ni, Sm, Gd, Be, N, Li, B, Th

The degree to which the calculated equilibrium $^{36}Cl/Cl$ ratios are accurate will depend upon how closely the concentrations estimated for these elements approximate their actual concentrations.

Of these elements, uncertainties in Cl and Th concentrations are the most important contributors to uncertainties in equilibrium $^{36}Cl/Cl$ values. In addition, H_2O and CO_2 data may also be necessary, particularly in relatively hydrous lithologies, because they may be significant contributors to the oxygen content of the rock, which is in turn a control on the neutron flux. A 10% change in the oxygen content alone would affect the $^{36}Cl/Cl$ ratio by only around 20×10^{-15}. This is smaller than the equilibrium values to be expected in most of the rocks around Borehole KNA-6, except in the extreme case where the granite has concentrations of U and Th near to the lowest values observed in this area. Uncertainties in the other constituents combined will probably contribute to uncertainties of only a few percent in the equilibrium $^{36}Cl/Cl$ ratio. As an illustration, changing values of all the other trace elements (F, Cr, Co, Ni, Sm, Gd, Be, N, Li, B) between those for a typical shale and those for a typical granite would affect the equilibrium values calculated by up to around 30×10^{-15}.

The chloride concentration at which uncertainty in chloride concentration in the rock becomes important depends upon the relative abundance of potassium and chloride and hence upon lithology. In the present scoping study, only one analysis of chloride in the Toki Granite was identified. This analysis is 22 ppm, towards the low end of the range for granites (PNC, 1994). For chloride concentrations greater than this, the resulting uncertainty in $^{36}Cl/Cl$ ratio would probably be less than about 5%.

The concentrations of chloride in the groundwater samples from borehole KNA-6 were not determined during the present study. However, previously, groundwaters from the same sampling intervals have been studied extensively (PNC, 1994). These studies showed that the dissolved Cl concentrations are around 1 ppm. Therefore, this value was used in the scoping calculations. However, for the reasons explained above, at such low Cl contents, there will be relatively large uncertainties on calculated equilibrium $^{36}Cl/Cl$ ratios in the groundwaters. This can be appreciated by comparing the equilibrium ratios calculated for ingrowth in the water, when ^{36}Cl production from potassium alpha-neutron reactions is both included and excluded. It can be seen that the largest $^{36}Cl/Cl$ ratios are calculated when these alpha-neutron reactions are included. As an illustration of the significance of uncertainties in chloride concentration, a doubling of the chloride concentration to 2 ppm, would decrease the equilibrium $^{36}Cl/Cl$ ratio calculated for ingrowth by several tens of percent (the actual amount will depend on the potassium content of the rock).

In summary, uncertainties in chloride concentrations could potentially be contributors to uncertainties in $^{36}Cl/Cl$ in both rocks and waters. However, for the *rocks* of the Tono area, these uncertainties are expected to be only a few percent. In contrast, uncertainties in the *waters'* chloride concentrations would be much greater contributors to uncertainties in $^{36}Cl/Cl$. Uncertainties in the other constituents of rocks for which estimates had to be made are much less significant for the present scoping calculations.

A potentially large, but unquantified uncertainty, is the variability in rock compositions in the Tono area. This variability leads to a large variability in the equilibrium $^{36}Cl/Cl$

ratios calculated for the rocks. The extent to which this variability would affect the $^{36}Cl/Cl$ ratios of groundwater chloride depends upon how variable the rock chemistry is along groundwater flow paths and upon which parts of the rock mass are actually accessible for water-rock interactions. Evaluation of these factors was outside the scope of this study.

The $^{36}Cl/Cl$ ratios yielded by the water from the Lower Toki Formation, are similar to the ratios given by the waters from the Toki Granite, when account is taken of the measurement uncertainties and uncertainties in *in-situ* values. However, the chloride in the waters from the Toki Formation is clearly not equilibrated with the *in-situ* production of ^{36}Cl in any of the rocks considered. The simplest explanation for this similarity is that the water sampled from the Lower Toki Formation originated in the upper part of the granite. This is not surprising given the close proximity of the sampling section to the unconformity.

If variations in measured $^{36}Cl/Cl$ in the water reflect ingrowth, water/rock interactions, or both, they will to some extent depend upon variations in rock compositions. During this study a relatively small number of rock samples were considered. However, it is apparent that within this small group, there was considerable variability in the calculated equilibrium $^{36}Cl/Cl$ ratios. This means that is not possible to state with certainty whether or not the $^{36}Cl/Cl$ measured for the water reflects equilibrium with the average rock encountered by the water along its flow path. In order to do this, further information is required regarding the variability of rock compositions and the relationships of this variability to the groundwater flow paths.

7.4.2 *Investigations in MIU-4 and DH-12 boreholes*

7.4.2.1 Description of study

Following the ^{36}Cl study in KNA-6, which demonstrated the feasibility of obtaining ^{36}Cl data from the groundwaters of the Tono area, data were acquired by Mr K. Hama from a small number of samples from:

- the Shoba River in the Shobasama MIU site (one sample);
- between 71 m and 275 m below ground level in the Toki Granite in borehole MIU-4 within the Shobasama MIU site (3 samples);
- between 157 m and 472 m below ground level in the Toki Granite in borehole DH-12, just south of the Toki River (3 samples).

These sampling localities are illustrated in Figures 33 and 34.

The samples were selected to give some idea of the likely values of $^{36}Cl/Cl$ in:

- fresh recharge water;
- HCO_3-dominated fresh groundwater from the Toki Granite to the north of the Toki River;
- Cl-dominated slightly more saline groundwater from the Toki Granite to the south of the Toki River.

7.4.2.2 ^{36}Cl results and discussion

The data from this second study phase are tabulated with the earlier data in Table 20 and illustrated in Figure 63.

The main features of these data are:

- The surface water has significantly higher $^{36}Cl/Cl$ than any of the groundwaters.
- The three samples from MIU-4 gave similar $^{36}Cl/Cl$ and the three samples from DH-12 also gave $^{36}Cl/Cl$ that are similar to one another.
- The HCO_3-dominated fresh groundwater from MIU-4 has similar $^{36}Cl/Cl$ ratios to the HCO_3-dominated fresh groundwater from borehole KNA-6 in Tono Mine.
- The lowest $^{36}Cl/Cl$ ratio is given by the most saline, Cl-dominated samples from borehole DH-12.

The relatively high $^{36}Cl/Cl$ of the surface water compared to the deep groundwater is to be expected.

The chloride and $^{36}Cl/Cl$ contents of the recharge water are uncertain. Here, it is assumed that the Shobagawa River water is similar to the ancient meteoric waters that recharged to form the present deep groundwater samples. Furthermore, the chloride content was not reported for the same sample as the one for which ^{36}Cl data were obtained. This means that mixing curves, between the Shobasama River water and the more chloride-rich deep groundwaters from DH-12 (Figure 63) are uncertain. If the chloride concentration of the Shobagawa River water was only 0.25 mgl^{-1}, then the variations in $^{36}Cl/Cl$ ratios and chloride concentrations could all be explained by mixing between this river water and the most saline DH-12 sample. In contrast, if a chloride concentration of 1 mgl^{-1} is assumed for the Shobagawa River water, then the MIU-4 and KNA-6 results would not lie on this mixing curve. The relationship between $^{36}Cl/Cl$ ratios in the deep groundwater and the original recharge water could be established more confidently if data were available for samples from different places along the same groundwater flow path.

At the time of writing, complete chemical analyses for rocks MIU-4 and DH-12 are not available. Furthermore, there are no spectral gamma wireline logs, from which whole-rock and thorium and uranium contents could be estimated. This makes it impossible to estimate theoretical *in-situ* equilibrium $^{36}Cl/Cl$ ratios from data taken from these boreholes. However, values can be estimated from uranium and thorium analyses taken from other boreholes, together with other supporting information:

- Mean values of SiO_2, TiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, MgO, CaO, Na_2O, and K_2O for the Toki Granite in DH-13.
- The mean Loss on Ignition (LOI) for rocks in this borehole was assumed to be due entirely to H_2O.
- Concentrations of the trace elements Cl, F, Cr, Co, Ni, Sm, Gd, Be, N, Li and B were for an average granite composition.
- Uranium and Thorium values were taken from analyses from MIU-3.

Calculations were done with 36Clip and the results are given in Table 21..

This approach suggested that mean $^{36}Cl/Cl$ is c. 45 x 10^{-15}. This is very close to the values actually reported for the samples from borehole DH-12, but only around 30% of the values from KNA-6 and MIU-4.

MIU-3 is very close to MIU-4. Therefore, it is possible that the whole-rock compositions in MIU-4 are similar to those in MIU-3. In this case an implication is that the $^{36}Cl/Cl$ in the groundwater from MIU-4 is far from equilibrium with the ^{36}Cl produced *in situ* and has resided within the Toki Granite for << 1.5 Ma.

If the granite in DH-12 is also chemically similar to that in MIU-3, then a tentative conclusion is that the chloride in the DH-12 samples could be equilibrated with the *in-situ* neutron flux in the granite. This implies that the chloride in the DH-12 groundwaters have resided in the granite for > c. 1.5 Ma.

However, these assumptions about the general similarity of the granite in boreholes MIU-3, MIU-4 and DH-12 may be invalid. Comparison between the data from KNA-6 and those from MIU-3 suggest that the Toki Granite is variable in composition. The mean equilibrium $^{36}Cl/Cl$ value calculated from the MIU-3 data is lower than the local KNA-6 value. The $^{36}Cl/Cl$ in the water from KNA-6 (which is similar to the values given by MIU-4 groundwaters) could be at local equilibrium with the in-situ production in this borehole, when allowance is made for the local chemical variability in the granite (Section 7.4.1.2).

7.5 Preliminary interpretation of ^{36}Cl in the Tono area

7.5.1 General conclusions

In general ^{36}Cl data are most valuable when:

- there are large contrasts in the *in-situ* production rates in different rocks along a flow path;
- water/rock interactions are a relatively small contributor to the chloride content of the water;
- there are large contrasts between the ^{36}Cl concentration in recharge water and equilibrium values.

The scoping calculations reported here illustrate that in the Tono area, the first of these criteria is met and that there are probably large contrasts in the *in-situ* production rates within different rocks. The largest contrast is likely to be between the sedimentary cover sequence and the granite. However, the variability of the *in-situ* production rates in the granite is uncertain. While it is clear that there are significant variations, the spatial scales over which these variations occur are not well known.

However, it is also clear that water/rock interactions could contribute a significant amount of the chloride dissolved in the Tono groundwaters and that therefore the second requirement is probably not met. This will limit the value of the ^{36}Cl data for constraining actual residence times since, as discussed previously, the $^{36}Cl/Cl$ measured in the rocks

will reflect the time for which the Cl has been resident in the rock, not the residence time of the water within the rock. However, it may still be possible to use the $^{36}Cl/Cl$ data to calculate limiting residence times of the water, where there are large contrasts between the values measured in the water and theoretical *in-situ* equilibrium values. The calculation made above illustrates this approach.

If there are large differences between the recharge $^{36}Cl/Cl$ ratios and the theoretical equilibrium $^{36}Cl/Cl$ ratios then potentially, it would be possible to use the ^{36}Cl data to indicate general directions of groundwater flow and possibly as a qualitative indicator of the extent of water/rock interactions. Preliminary data from the MIU-4 borehole in the Shobasama MIU site suggest that there could indeed be large differences between the $^{36}Cl/Cl$ ratios in the recharge and in the deep granite.

7.5.2 Conclusions from the study of groundwater in borehole KNA-6

The uncertainties in the measured and calculated equilibrium values mean that it is impossible to interpret the ^{36}Cl data from KNA-6 confidently in terms of absolute chloride residence times. Additionally, the variability in the equilibrium $^{36}Cl/Cl$ ratios in the granite is too great to state definitely whether the chloride in the water has actually reached equilibrium with the mean ^{36}Cl production in the granite. In other words, it is possible that the chloride in the samples from the granite has resided within the Toki Granite for more than around 1.5 million years (i.e. sufficiently long to be in equilibrium with the mean *in-situ* production in the granite). However, this possibility cannot be proved with the data from KNA-6 alone.

Even if the *chloride* has indeed been resident in the granite for longer than around 1.5 million years, the *water* has not necessarily been resident within the granite for such a long time. This follows from the possibility that water/rock interactions could have contributed the majority of the dissolved chloride.

In contrast to the waters from the granite, the water from the sedimentary section in KNA-6 gave much lower $^{36}Cl/Cl$ ratios than the theoretical equilibrium $^{36}Cl/Cl$ ratios calculated for *in-situ* production in these rocks (^{36}Cl production neglecting potassium alpha-neutron reactions). Assuming that the sedimentary rock compositions are typical, and that the average ^{36}Cl production rate in these rocks really is higher than in the granite, these differences imply that the chloride has not been resident in the sedimentary rocks for very long in geological terms. This interpretation is reasonable in view of the distribution of the Tono uranium deposit in the sedimentary rocks.

As an *illustration* of the approach to using ^{36}Cl for residence time studies, a maximum time before the present for movement of *water* from the granite to the sedimentary rocks can be estimated assuming that:

- the chloride dissolved in the water sampled from the sedimentary rock originated in the granite;
- there has been no significant contribution of chloride to the water from water/rock interactions in the sedimentary rocks;
- the composition of the rock from 30.8 m depth in borehole KNA-6 is typical of rock compositions in this part of the Toki Formation.

- the apparent difference in mean compositions between the water sampled from the granite and the water sampled from the Lower Toki Formation is real and not simply due to experimental factors.

These assumptions result in calculated times in the order of 10000 years. It should be borne in mind that this number is highly dependent on the assumptions and is very uncertain. However, many inaccuracies in these assumptions would tend to imply shorter residence times.

These inferred short residence times of water and chloride in the Lower Toki Formation are unsurprising owing to the close proximity of the sedimentary rocks and the granite. The possibility that water flowed from the granite into the packed-off sedimentary section during borehole testing and monitoring cannot be ruled out with the available data and indeed would be consistent with the observed head gradient in borehole KNA-6 (Ota and Hanamuro, 1996).

Interpretations of the $^{36}Cl/Cl$ ratios in the waters in KNA-6 are limited by uncertainties in the spatial variability of rock compositions. These uncertainties are due to the limited rock data that it was possible to consider in this small scoping study and to the lack of appropriate analytical data for the rocks. The degree to which data obtained from the waters in the granite are useful will depend largely on the spatial scales over which *in-situ* production rates are variable and on the magnitudes of these variations. A further factor affecting the usefulness of the data will be the extent to which *in-situ* equilibrium values are different from recharge values.

7.5.3 Conclusions from the study of ^{36}Cl in surface water, DH-12 and MIU-4

The data from the Shobasama River and the DH-12 and MIU-4 boreholes show:

- There are significant differences between the $^{36}Cl/Cl$ ratios of surface water and deep groundwater.
- There are significant variations in the $^{36}Cl/Cl$ ratios of different groundwaters at the site scale.

Chloride in DH-12 groundwaters has possibly resided in the granite for > 1.5 Ma. There are two possible explanations for this relatively long residence time.

- The DH-12 groundwaters possibly contain a component of very old chloride-bearing water, which has also been resident in the granite for > 1.5 Ma.
- The chloride in groundwater in DH-12 has been supplied locally from the granite during water/rock interactions.

Four main explanations can be advanced for the variations in groundwater $^{36}Cl/Cl$ composition at the site scale.

- The variations could be caused by mixing between different groundwaters containing chloride from different sources. As an illustration, if the most saline DH-12 groundwater were to mix with the Shobasama River water, then a mixture with a

similar chloride concentration and $^{36}Cl/Cl$ ratio to the MIU-4 water would contain < c. 1% of the DH-12 water.

- The variations in $^{36}Cl/Cl$ in the groundwater could have been caused entirely by radioactive decay of ^{36}Cl, following recharge. As an illustration, around 600,000 years would be required for radioactive decay to produce waters with similar $^{36}Cl/Cl$ ratios to the MIU-4 groundwaters, from water with the same $^{36}Cl/Cl$ ratio as the Shobasama River. Ratios of $^{36}Cl/Cl$ similar to those in the DH-12 groundwaters would require > c. 1.5 Ma to be produced from ratios similar to those in the MIU-4 groundwaters > c. 1.5 Ma.
- Variations in $^{36}Cl/Cl$ could be due to variable water/rock interactions across the site. In this case, more of the chloride in the more saline groundwater from DH-12 has been produced by water/rock interactions than is the case further north, in the MIU-4 borehole for example.
- The variable $^{36}Cl/Cl$ ratios could be explained by the Toki Granite having a variable composition. An implication of this explanation would be that the Toki Granite in the vicinity of DH-12 is less radiogenic (has lower U and/or Th) than the granite further north in MIU-4.

A combination of these processes could also explain the variability in the $^{36}Cl/Cl$ ratios across the site. However, coupled with the higher chloride in the DH-12 groundwater compared to the MIU-4 groundwater, a general implication is that the chloride in the DH-12 groundwater had a relatively long residence time. Section 7.7 suggests some approaches that might enable the validity of these different explanations to be supported or refuted.

7.6 Integrated conclusions, from the studies of halide concentrations and ^{36}Cl

A general conceptual model for variations in groundwater chemistry within the Tono area, which fits in with both the halide concentration data and the ^{36}Cl data is illustrated in Figure 64. However, there are several possible alternative variations that can be envisaged which also fit the observed data. In particular, the nature of the transition between the HCO_3- dominated groundwater to the north and the Cl-dominated water to the south of the Toki River is uncertain (Figure 65). If this boundary could be characterised in more detail and with more certainty during future investigations, it could be used to help demonstrate confidence in models for groundwater flow. One possibility would be to employ a basic approach similar to that employed at Sellafield , illustrated in Figures 17 and 18 and described in Sections 3.5.2 and 4.6.

7.7 Potential future applications of ^{36}Cl in the Tono area and elsewhere

7.7.1 Potential applications in the Tono area

In the Tono area, ^{36}Cl data could potentially be used for one or more of the following:

- identify the spatial limit of recent recharge water (as a complement to tritium data);

- trace the movement of water (i.e. indicate general flow directions) between the sedimentary cover sequence and the granite basement, provided that any water/rock interactions are slow compared to the rates of water movement;
- trace the movement of water (i.e. indicate general flow directions) in the granite, provided that the ^{36}Cl production rate varies over sufficiently large spatial scales and that any water/rock interactions are slow compared to the rates of water movement;
- place limits on the residence time of chloride in the various rock formations of the area.

The actual spatial scales of relevance will depend on the rate of groundwater movement relative to the rate of water/rock interactions. For a given flow rate, the faster the water/rock interactions, the smaller will be the spatial scale over which *in-situ* production rates may vary if ^{36}Cl data are to be useful. However, presently, there are insufficient data with which to judge this variability in the granite. If there are contrasts between theoretical *in-situ* equilibrium $^{36}Cl/Cl$ ratios, and ratios measured for the dissolved chloride, it would be possible to place limits on the residence times of the chloride within the different rocks and hence potentially upon the rates of groundwater flow.

7.8 Recommendations for future ^{36}Cl studies

7.8.1 Obtain rock analyses of additional trace elements (other than Cl)

It is recommended that, in addition to the chemical constituents that have been analysed routinely in the rocks of the Tono area, data for the following constituents are also obtained to support future studies of ^{36}Cl (in approximate decreasing order of importance):

U, Th
CO_2, H_2O
F, Cr, Co, Ni, Sm, Gd, Be, N, Li, B

It is planned to analyse all these constituents in the rocks of MIU-4, except for N, which is unlikely to cause significant uncertainties in the equilibrium $^{36}Cl/Cl$ ratios that are calculated.

7.8.2 Obtain rock analyses of chlorine

Water/rock interactions could affect the chloride content of the groundwater by a relatively large amount. This effect is due to the groundwater being very fresh. To judge the importance of such water/rock interactions it is recommended to obtain chlorine data for representative samples of the main rock types.

7.8.3 Acquire and use spectral gamma wireline data

It is recommended that in future borehole drilling, spectral gamma wireline logs are run. These allow variations in the concentrations of U and Th to be estimated at high

resolution (scale of centimetres) continuously down a borehole. The estimates of U and Th can then be used to estimate variations in ^{36}Cl production.

The U and Th concentrations in the rock, estimated from the logs are used with the following equations from (Lehmann and Loosli, 1991):

$$\phi = (\alpha \times [U] + \beta \times [Th]) \times 10^{-5} \qquad \text{Equation 7.6.}$$

and

$$\frac{^{36}Cl}{Cl} = \phi \times 4.55 \times 10^{-10} \qquad \text{Equation 7.7.}$$

where: α and β are constants that depend on the rock type. Values for typical rock types are quoted in (Lehmann and Loosli, 1991). The values given by these authors for sedimentary rocks are $\alpha = 0.56$ and $\beta = 0.16$; for granite they are $\alpha = 0.86$ and $\beta = 0.3$.

A complementary approach is to use the whole-rock data from rock core to derive site-specific values of α and β.

7.8.4 *Continue to obtain ^{36}Cl data for recharge waters*

It is also recommended that ^{36}Cl data are acquired for recharge waters, for comparison with the deep groundwaters and that data are acquired from all the main lithologies along the groundwater flow paths that are inferred from the hydraulic models.

8. EXCHANGEABLE CATION STUDIES

8.1 Purpose of this chapter

This chapter presents the results of a pilot study of exchangeable cations in the major rock units of the Tono area. A preliminary interpretation of these results is given.

8.2 Principles of exchangeable cation studies -theory

Clay minerals such as smectite will tend to exchange certain cations with any coexisting groundwater. The compositions of proportions of these exchangeable cations will be determined both by the selectivity of the ion for the exchange site (e.g. divalent ions will tend to displace monovalent ions) and by the composition of the groundwater. In fresh groundwaters, Ca^{2+} tends to dominate over Na^{+}. Owing to this composition, combined with the higher selectivity of Ca^{2+} for exchange sites, the exchangeable cations in clay minerals coexisting with fresh groundwater tend to become dominated by Ca. In contrast, seawater contains a much higher concentration of Na^{+} than Ca^{2+}, which acts to overcome the tendency for Ca^{2+} to displace Na^{+} on the exchange sites of clay minerals. Consequently, clay minerals that are in contact with seawater tend to have exchangeable cation populations that are dominated by Na^{+}.

8.3 Studies of exchangeable cations in the Tono area

In the Tono area, part of the Mizunami Group is of marine origin. Consequently, seawater must in the past have occupied the pore space in these rocks and possibly also saturated the underlying Toki Granite. There is little evidence that any of this marine salinity remains in the area since, except to the south of the Toki River, the groundwaters of the area are all Na-HCO_3 or Ca-Na-HCO_3 dominated. However, potentially, porewater in lower-permeability rocks and/or exchangeable cation populations for these rocks could preserve evidence for the past existence of marine salinity. The occurrence of Na-exchanged clay minerals would be consistent with the past occurrence of marine salinity. Possibly, variations in exchangeable cation populations could give a general indication of patterns of past flushing of groundwater salinity in the area.

Additionally, it has been suggested that in the Tono area, cation exchange is a major cause of the variation from shallower Ca-Na-HCO_3- dominated groundwater to deeper, Na-HCO_3-dominated water. However, there were no cation exchange data with which to judge independently the likely significance of this effect.

For both these reasons, it was decided to conduct a small-scale study of exchangeable cation populations in the rocks of the Tono area. Samples were taken from each major rock unit, from within the Tsukiyoshi Fault Zone and remote from the Tsukiyoshi Fault zone. Samples were all hand-picked from rock core, using hammer and chisel where necessary. Lithologies of low-permeability were sampled since these should preserve evidence for the 'oldest' waters. Other samples were taken from the wall-rocks of open fractures since these should reflect the chemistry of the most recent waters passing through the fractures.

It is noted that, with the exception of samples from borehole 99SI-08, none of the samples had been preserved specifically for the purpose of obtaining exchangeable cation data. While efforts were made to disregard samples that had obviously undergone post-drilling oxidation, the possibility that exchange has occurred cannot be ruled out. Additionally, except for the samples from 99SI-08, all the samples were dry and in most cases came from core that had been stored for a considerable time, up to several years.

The samples analysed from 99SI-08 had all been double-wrapped in polythene at the drilling site in Tono Mine, within a few hours to several days after sampling. At the time of wrapping there had been no sign of the core undergoing oxidation, nor had there been any opportunity for the core to dry significantly. At the time when these samples were sub-sampled for exchangeable cation analysis, they were in good condition and had undergone no apparent degradation during storage.

In all cases, there is potential for drilling fluid to have interacted with the samples to some degree. This is least likely to have occurred in the case of the more argillaceous lithologies from 99SI-08 and in the cases of rock matrix that was freshly exposed during sub-sampling of the core from other boreholes for the purposes of the present study.

Some samples were analysed either by the British Geological Survey (BGS) or by a Japanese contractor (detailed in Appendix 4). Details of sample analysis methods used at BGS are given in Milodowski et al. (2001) and a Japanese contractor's report (Iwatsuki pers comm 3/9/01).

The results obtained from this study are summarised in Table 22 while the actual data are presented in Appendix 4.

8.4 Preliminary interpretation of exchangeable cation data in the Tono area

There are a wide range of cation exchange capacities reported for the samples. Those from the Akeyo Formation in borehole 99SI-08 have capacities in the range 23.9 to 71.3 meq/100g. In contrast, the samples from the Toki Granite in the other boreholes yielded markedly lower values. These range from 0.6 to 3.1 meq/100g for fresh granite. The fracture surfaces analysed and the altered granite gave a wide range of exchange capacities, from values similar to the fresh granite, up to 20.8 meq/100g. However, compared to the granite matrix, the fracture surfaces and fracture-filling minerals had generally higher exchange capacities.

These results are consistent with knowledge about the mineralogy of the samples. The sedimentary rocks are rich in smectite while fracture surfaces in the Toki Granite may also be lined by smectite (Milodowski et al. 2001). While the results need more rigorous evaluation, it does seem that there could be significant cation exchange capacity in the fractures of the granite and that consequently it is reasonable to hypothesise that cation exchange could be an important control on the chemistry of the fresh, bicarbonate-dominated groundwater in the area.

By comparing the exchangeable cation populations with published data for samples equilibrated with fresh water or seawater (Table 22) it is apparent that none of the samples from Tono have a seawater chemical signature. This is particularly interesting in

the case of the samples from the Akeyo Formation, which is a marine deposit. One possibility is that the exchangeable cation populations have been affected by drilling fluid circulation, thereby removing any residual marine signature. However, assuming that this has not occurred significantly in the case of the Akeyo Formation samples, an implication is that the original marine porewater has been flushed from this formation. Furthermore, sufficient flushing occurred to displace the Na-dominated exchangeable cation populations that originally occupied the cation exchange sites. The samples from 99SI-08 were both the best preserved samples and showed no signs of obvious matrix or fracture porosity in hand specimen. Thus, these samples are possibly the least likely to have been affected by sampling and storage.

In contrast, the fractured granite samples must have interacted to some degree with the drilling fluid and it is possible that this interaction affected the exchangeable cation populations. This possibility could be tested experimentally, by first placing some granite samples under Na-Cl dominated water, so that they become Na-exchanged and then exposing them to similar water to that used in the drilling fluid.

The exchangeable cation populations appear to show little variability between the different rock types considered. All the clays are dominantly Ca-exchanged. There may, however, be a systematic difference between the exchangeable Mg contents of the sedimentary rocks and those of the Toki Granite in boreholes other than MIU-3. Compared to the samples from borehole 99SI-08 and MIU-3, the granite in these other boreholes seem to have higher average Mg contents and slightly lower average Ca contents. The significance of these findings requires further evaluation and in particular it is important to asses the degree to which interaction with drilling fluid may have perturbed the exchangeable cation populations.

8.5 Conclusions from exchangeable cation data and recommendations

In summary, the exchangeable cation data allow a judgement to be made as to the plausibility of cation exchange controlling groundwater chemistry, as has been suggested to occur previously. It appears from the data that this is a reasonable hypothesis to make, though the implications need to be evaluated more rigorously than has been possible here. One approach would be to carry out mass balance calculations to evaluate how much of the present fresh groundwater could be chemically conditioned by the present cation exchange capacity of the rock.

There is no evidence for the preservation of a marine signature in the exchangeable cation populations. An implication is that there has been complete flushing of the original marine porewater present in the Akeyo formation.

The samples from the Akeyo formation are the least likely to have interacted with drilling fluid so as to alter their exchangeable cation populations. The fractured granite samples, on the other hand, must have interacted with drilling fluid to some extent.

It is recommended that in future more careful sampling is done to obtain samples specifically for exchangeable cation analysis. This would involve preservation of samples immediately after sampling. The possibility that interaction with drilling fluid has

affected the exchangeable cation populations should be examined. Two approaches to doing this are:

- determination of the extent of drilling fluid tracer penetration into the core (in the cases of non-fractured samples);
- sample-water interaction experiments to evaluate the possibility that exchangeable cation populations might be affected by the drilling fluid.

9. A NEW METHOD FOR INTERPRETING SALINITY ORIGINS AND MIXING

9.1 Purpose of this chapter

This chapter summarises a new method for interpreting the origins of groundwater salinity and the proportions of chemically different waters that have mixed to form any water that is sampled. The potential applications of this method in the Tono area in particular and in Japan in general are then outlined.

9.2 Need for a method

The value of multivariate statistics for interpreting groundwater chemistry has been demonstrated by investigations in Europe. Notably, this processing helps to:

- identify different components of groundwater salinity, which can be related to the origins of different groundwaters;
- constrain the mixing proportions of different groundwaters in a site, which can be a constraint on models for groundwater flow.
- correct for contamination during groundwater sampling.

Such processing could also be valuable in Japan. However, the investigations in Europe, notably at Sellafield in England and at Äspö in Sweden, have concentrated on sites dominated by saline groundwaters and brines. The approaches need to be adapted for application in fresher groundwater systems, common in Japan generally and in the Tono area in particular. For this reason, it was desirable to refine the approaches to make them more generally applicable to groundwater systems of various kinds.

The most integrated computer program available specifically for statistical processing of groundwater data is the M3 code, which was developed by SKB at Äspö, Sweden. However, there are limitations to applying this code generally. In particular, the reliance of the method on the first two principal components may not be appropriate in fresh groundwater systems. In such cases the first two principle components are more likely to reflect factors other than groundwater mixing. For example, water/rock interactions are likely to be a more significant cause of chemical variation in fresh groundwater systems than in saline groundwater systems. In such cases, it will be necessary to consider other principal components besides the two most important one, in order to deduce information about groundwater mixing.

By not considering principal components other than the first two, M3 potentially disregards important information that might be used to evaluate more precisely the validity of the underlying assumptions, such as the assumption that all end-members are present in all waters.

While sensitivity calculations were conducted by SKB and its contractors to evaluate underlying uncertainties in the M3 method (Laaksoharju, 2000), the results of these calculations have not been reported in detail. Therefore, the precise significance of these uncertainties for JNC's modelling approach is not clear.

Even though the end-members used in the M3 modelling were chosen with reference to a hydrogeochemical model for the site, there is still considerable subjectivity in their selection. The chosen end-members, while having extreme compositions near the limits the range of sampled waters compositions, are themselves mixtures of other waters. Additionally, some chemically similar waters have probably been introduced into the groundwater system at Äspö several times during the site's history. For example, sub-glacial water has presumably been recharged several times during the repeated glaciation of the site within the Quaternary period.

9.3 Approach to revised modelling

During the Fellowship, an opportunity arose to develop a refined statistical approach to investigating groundwater mixing, during Task 5 of the Äspö Groundwater Modelling Task Force. The Japan Nuclear Cycle Development Institute (JNC) is a member of this Task Force, which is coordinated by SKB. There is a large amount of groundwater chemical data from Äspö. There are also many supporting geological data. The groundwater chemistry data from Äspö were therefore used to develop a revised statistical method. By adopting this approach it was also possible to compare the results of the new approach against those of the M3 approach.

It was decided to carry out revised modelling, using a chemometric algorithm (Cave and Wragg, 1997; Cave and Harmon, 1997) which makes no initial assumptions about the nature of the end-members present, and which considered all the contributions to chemical variability in the groundwaters (Figures 66 and 67).

In the basic approach matrix **A** is the supplied groundwater data matrix and matrices **B** and **C** need to be found. The process for finding matrices **B** and **C** was carried out in a four stage process:

- Principal Component Analysis (PCA) and Eigenvalue Analysis were initially used in a similar fashion to the M3 method.
- The varimax rotated loadings matrix from the PCA of matrix A, containing the initial groundwater compositions, were used to produce a first approximation of matrix B, which contains the mixing proportions.
- The 'pseudoinverse' method for non-square matrices was then applied to matrices A and B, to produce a first approximation of matrix C, which contains chemical components that contribute to the chemical variability in the groundwaters, some of which should correspond approximately to end-members.
- Matrices B and C were refined iteratively using the 'pseudoinverse' method until both matrices contained estimates of mixing proportions and chemical component compositions that are consistent with the groundwater compositions in the original matrix A.

It is important to note that the chemical components obtained from the new modelling are not principal components, but are derived from the principal components. Neither are the chemical components 'end-members' in the sense of the M3 end-members. However, it is

expected that there should be some similarities between compositions of the new chemical components and the M3 components.

To compare the results of the new modelling and the results of the M3 end-member modelling, the new mixing proportions were also expressed in terms of proportions of the original M3 end-members. This was done by a least squares approach, using the proportions of the new chemical components in each of the original M3 end-members and in each of the other waters as follows.

Several alternative cases were evaluated during the new modelling (Table 23). Some of these cases used exactly the same data as was used to produce the M3 model results in Data Delivery 9. This approach was to allow comparison of the results between the two methods. Other cases used a sub-set of this data, to explore the significance of departures from this approach.

9.4 Key assumptions and uncertainties in the revised modelling

Unlike the original M3 modelling, the new model makes no prior assumptions about the numbers or compositions of chemical components (analogous to end-members in the M3 modelling). However, other assumptions are made, notably:

- the compositions of at least some of the chemical components derived statistically will approximate to real groundwater compositions;
- the assumption that δ–values for ^{18}O and D are additive over the range considered is valid;
- that all the chemical variability in the groundwaters is expressed by the chemical constituents (Na, Ca, Cl etc) used in the modelling, which form a subset of the actual constituents.

These last two assumptions were also made in the M3 modelling.

9.5 Results of the new modelling

The compositions of the chemical components obtained from each model are compared with the compositions of the groundwater end-members used in the M3 modelling (Table 24). It is important to note that the chemical components are not placed in order of significance for the overall chemical variations; they are not principal components, though they are derived from principal components. Additionally, chemical components designated by the same number, but produced by different models are not necessarily equivalent.

None of the models produced components with the same compositions as the 'end-members' used in M3. This result is expected since:

- The new approach makes no a priori assumptions about the compositions of waters that mix to form the sampled waters.
- The new approach aims to identify chemical components of the groundwaters, which reflect underlying *processes* rather than actual groundwaters.

- Even if some of the components do represent possible natural waters, it is not unexpected that they differ from the M3 end-members. These latter are simply waters of extreme composition chosen by the user of M3; some of these M3 end-members are themselves mixtures of other waters. It is these 'other waters' that could potentially be identified by the new approach.

Several underlying features are common to the results of all models:

- There are usually three or four chemical components that are close to charge balance. Potentially, these could represent the compositions of actual waters.
- The charge-balanced chemical components in any model are generally broadly similar to the charge-balanced chemical components produced by the other models (though as noted previously, the numbers used to designate a particular chemical component may change from model to model).
- There are always components that do not charge balance. These chemical components cannot represent actual waters, but instead possibly represent other processes such as water/rock interactions.
- In all the models, there is at least one component that contains HCO_3 and little else. It is possible that this component reflects microbial activity, notably the oxidation of organic matter. Microbial processes were also suggested to be important, based on the M3 modelling (Laaksoharju et al. 1999).

By comparison between the results of different models, several general conclusions can be drawn:

- Model 1 showed that a single consistent model for the solutes in the water could not be produced without the inclusion of stable oxygen and hydrogen isotope data and tritium data. When these data were not included, the waters had to be divided into three groups to ensure a self-consistent result.
- The inclusion or omission of tritium from the model does make a significant difference to the compositions of all the chemical components, except the most saline component (comparison of Models 2 (v3) and Model 3).
- Addition of a small number of waters of extreme composition to a data set could have a small but significant effect on the compositions (and hence proportions) of the chemical components (comparison of Model 2 and Model 2(v5)).

The relatively large effect of tritium on the results is important, because this isotope is radioactive with a half-life of only 12.43 years. Therefore, considerable decay of tritium must have occurred during the investigations at Äspö, which have lasted more than 10 years. Variations in the reported tritium values will generally not reflect only groundwater mixing. Thus, tritium cannot be considered a conservative tracer for groundwater flow. The fact that the inclusion or omission of tritium significantly affects most of the chemical components in the present model means that errors due to its radioactive decay cannot be allowed for just by neglecting a single component. Thus, it would strictly be more appropriate to exclude tritium from consideration altogether.

Notwithstanding this potential drawback, the results of Model 2 (which includes tritium) were used with the groundwater flow model to predict the compositions of inflows to the tunnel. The reason for using these results was that Model 2 employed the same data as the original M3 modelling (which included tritium). Thus, the predictions based on the

revised statistical modelling could be compared more easily with the original M3 modelling results.

In Model 2, all the chemical variability could be attributed to 7 principal components (Figure 68). This suggested that 7 chemical components could be used to model the groundwater chemistry. When the 7 original principal components were adjusted by iteration, the resulting fit between the reconstructed compositions of the waters (i.e. calculated from matrices B and C above) and the actual compositions was very good for all components except for stable oxygen and hydrogen isotopes (Figure 69). This approach demonstrates a high degree of internal consistency in the model. However, the model did not give a good fit for light (relatively heavy-isotope-depleted) water compositions (Note that the isotopic compositions were converted to positive values for the PCA). One possible explanation is that the waters may not all be mixtures of the same end-members. However, additional processing would be required to evaluate this more fully.

The main features of the chemical components that were calculated by Model 2 are:

- The components in Model 2 do bear some similarity to real waters or to water/rock interactions/contamination effects:
- Chemical component 1 is broadly similar to the brine end-member identified by Laaksoharju et al.;
- Chemical component 2 is broadly similar to the seawater and/or Litorina sea water identified previously by Laaksoharju et al. (1999);
- Chemical component 3 is broadly similar to a glacial reference water reported previously by Laaksoharju et al. (1999);
- Chemical components 5 and 6 could potentially represent water/rock interactions and/or microbially mediated reactions;
- Chemical component 7 has some similarities to a sediment pore water identified by Laaksoharju et al. (1999) previously.

In support of the hypothesis that microbial action might explain component 5 is the fact that this component tends to be more abundant in waters from boreholes that monitored conditions in a zone over which redox conditions changed, than in other boreholes. In the redox-monitoring boreholes the mean is 1.2445×10^{-2}, std dev 0.0049, whereas in the other boreholes the mean is 3.9475×10^{-3}, std dev 0.0056. Microbial processes have been well-documented previously from the 'redox zone'.

Component 4, produced by Model 2, is the most difficult to ascribe to a real process. This is because it is not charge-balanced and appears to contain very high concentrations of K and Mg (much higher concentrations than are in fact observed in any actual water). Possibly, component 4 could represent a water/rock interaction, such as cation exchange of Ca and Na for Mg and K. In fact, component 4 composes a maximum of only 1.77% of any actual water (and usually much lower than this). Since water/rock interactions of this kind would be expected to have a relatively small effect on the overall compositions of the predominantly saline waters, this small value is consistent with component 4 representing water/rock interactions.

The general similarity of some of the chemical components and some of the M3 end-members can be appreciated by comparing the results from the two sets of modelling.

There are generally similar patterns in the depth dependence of the new chemical components and the M3 end-members.

9.6 Comparison between results of M3 and new modelling

The results of the new Model 2 are plotted versus depth in Figure 70. For comparison, the same results are expressed as proportions of the original M3 end-members plotted versus depth in Figure 71. The Model 2 results expressed in this way are also compared with the proportions of the same end-members, as calculated in the original M3 modelling and reported by SKB in Data Delivery 19 (Figures 72). It is apparent that:

- There is generally a positive correlation between proportions of end-members calculated by Model 2 and the proportions calculated by M3.
- There is a particularly good positive correlation between the proportions of brine calculated from Model 2 and the proportions of brine calculated by M3.
- Compared to the M3 modelling, the new modelling calculated generally higher proportions of Baltic sea water at shallower depths (above around 400 m) and generally lower proportions of meteoric water at greater depths (between around 400 m and 1000 m). However, the general depth distribution is similar.
- The maximum proportion of the Baltic seawater end-member calculated from Model 2 is around 0.8, whereas the maximum proportion calculated by M3 is close to 1.

However, in contrast to the M3 modelling, the new modelling predicts ***negative*** proportions of meteoric water for samples of intermediate salinity (Figures 71, 72 and 73). These are clearly unrealistic and initially seem inconsistent with the M3 results. However, a detailed comparison reveals a high degree of underlying consistency, notably:

- The negative proportions given by the new model are almost all given by samples for which M3 also calculated a large deviation between theoretical Cl concentrations (assuming all samples are mixtures of all end-members) and actual Cl concentrations (Figure 74).
- The proportions of end-members given by the new calculations can also be used to calculate 'deviations' between theoretical and actual concentrations of determinands. There is a positive correlation between Cl deviations obtained from the new results and Cl deviations calculated from the M3 results (Figure 75).
- The Cl deviations, as a percentage of the total, are largest for waters of low salinity in both the latest modelling and the original modelling.

The reasons why the new model results and the original M3 modelling is consistent are:

- The M3 approach uses calculated mixing proportions and end-member compositions to derive theoretical water compositions, for comparison with actual water compositions. The M3 modelling ***assumes*** that all waters contain all end-members. For some waters, this assumption results in calculated Cl concentrations that are lower than the actual concentrations . Since Cl is relatively unreactive in groundwaters, the most logical explanation is that in these, the estimates of meteoric water concentration, based on the assumption of conservative mixing, are too high.
- In contrast, the new modelling adopted the opposite approach. The actual compositions of the waters and the end-members to calculate the mixing proportions.

Therefore, the calculation of negative proportions of meteoric water effectively amount to the same thing as the negative deviations for Cl calculated by M3.

A plausible explanation for these discrepancies is that the actual waters are not actually all mixtures of all end-members. This possibility can be appreciated from considering Figures 76 and 77. The first of these figures illustrates the possibility that variations in the stable isotopic compositions of a significant number of the samples could be explained simply by mixing between meteoric water and Baltic seawater. Similarly, other mixing lines between two or three components could be plotted that would explain much of the variability without the other two or three components being needed. The stable isotope compositions that are reconstructed from the Model 2 results illustrate that two separate mixing trends could explain the variability in the oxygen isotope compositions.

The possibility that all end-members may not occur in all water samples was also pointed out by Laaksoharju (2000). However, based on the M3 modelling, it was considered that the uncertainty due to this phenomenon could be encompassed by a ±10% error on the proportion of each component.

The new modelling produced negative proportions of meteoric water as low as around –0.35. An implication is that the uncertainty for individual components could be much greater than the ±10% suggested by Laaksoharju (2000).

9.7 Conclusions from applying the new method at Äspö

- The new approach should be more generally applicable than the M3 approach, since it takes into account all the chemical variability in the groundwaters.
- The new method allows chemical variability that is due to mixing to be distinguished from components of chemical variability that are due to water/rock interaction. Chemical components that are not attributable to water/rock interactions or other effects can be considered 'conservative' tracers for groundwater flow.
- An internally consistent model of all the solute data cannot be obtained if stable oxygen and hydrogen isotope data are not used.
- When stable oxygen and hydrogen isotopic data are included in the model, the internal consistency of the model for solutes is very good. However, the model is not consistent for waters that are relatively depleted in the heavy isotopes. Though the reasons for this could not be evaluated fully, it may be due to the waters not all being mixtures of the same end-members.
- It is possible to express the results of the new method in terms of real groundwaters if so desired, allowing mixing relationships among real groundwaters to be distinguished. In the present study this was done for the original M3 end-members.
- Inclusion or exclusion of groundwater constituents and/or additional waters of extreme composition has a significant effect on the outcome of the method.
- Seven principal components are needed to explain all the chemical variability in the data, when the same data as those used by M3 are employed.
- The M3 results and the new modelling are broadly consistent.
- The proportions of brine in any water are most likely to be reliable.
- It is probable that not all the M3 end-members are actually present in all the Äspö groundwaters. In particular, meteoric water is probably not present in many groundwaters from intermediate depths.

- Better consistency and more precise mixing proportions could probably be obtained by splitting the data set into several parts and applying the model to each part. In general, an iterative procedure would be needed, involving repeated splitting of the data set and modelling of each part, until the most consistent set of results are obtained. This procedure was outside the scope of the present project.

9.8 Using the new method to constrain disturbed groundwater flow

The mixing proportions calculated using the new approach were used to calibrate predictions of the chemistry of in-flows into the tunnel of the Äspö HRL. Figures 78, 79 and 79 illustrate the basic approach. The predictions were made by Golder Associates, using a discrete feature network/channel network approach (DFN/CN). In this approach, both major deterministic fracture zones and background fracturing were modelled explicitly as two-dimensional discrete features using FracMan/FracWorks codes developed by this company. Flow and transport were modelled by transforming the fracture network to a topologically equivalent pipe network using the codes FracMan/PAWorks, also developed by Golder Associates.

The detailed approaches adopted and results of this modelling are described in the report (Dershowitz et al. (2000). Only a summary of the approach is given here. Basically, the work involved:

- using hydrogeological models to predict the movement of the chemically distinct groundwaters described in Section 9.8, into the Äspö tunnel;
- using this information, predict the variations in chemistry of the water in these inflows over time;
- comparing the prediction with the actual observed variations in the chemistry of inflowing groundwaters over time;
- if there were differences between the predictions and the observations, modify the hydrogeological model to improve the fit between the observations and the predictions.

Thus, this approach used the disturbance of the groundwater system caused by the construction of the Äspö tunnel, to calibrate the hydraulic models. As pumping connected with tunnel construction continued, groundwaters from increasing distances from the tunnel contributed to the inflows (Figure 78). Owing to the chemically heterogeneous characteristics of the undisturbed groundwater system, this meant that there are also variations in the chemistry of the inflowing groundwaters over time (Figure 79). The modelling:

- identified the pathways followed by groundwater as it flows from its initial position prior to the construction of the HRL, into the tunnel that provides access to the HRL;
- calculated travel times taken by the waters to flow from their initial positions into the tunnel;
- calculated the proportions of the water originating in different rock volumes characterised by groundwaters of different composition.

The proportions of the various groundwater end-members entering the tunnel at each inflow point were calculated as a function of time. The aim was to compare these

calculated proportions with the proportions of the different end-members that are actually present within the groundwater inflows to the tunnel. The integration of the fracture network modelling and the statistical modelling is illustrated in Figure 80.

Therefore, there were two main applications of hydrochemical data in the modelling approach that is adopted by JNC:

- hydrochemical data for the distributions of groundwaters prior to and during the construction of the tunnel that are used to predict the compositions of groundwater inflows into the tunnel;
- hydrochemical data for the groundwater inflows into the tunnel are used for comparison with the predicted compositions.

The general procedure for integration of hydrological and hydrochemical information in the Äspö Task 5 modelling was staged. The stages could be summarised as:

- develop a regional model of the site including only the large scale features;
- develop a conceptual model for the background fractures, including the orientation, size, intensity, and transmissivity of the non-regional features;
- develop boundary conditions for the modelled region;
- create a finite element model including the major features, background features, and boundary conditions and calibrate it to the measured head distribution by varying the fracture properties and boundary conditions;
- use this calibrated model to predict chemistry distributions and calibrate this model to the measured chemistry and head distribution by varying the fracture properties and boundary conditions.

The model that achieved the best results used a model for the initial spatial distribution of groundwater chemistry derived by projecting water compositions from the actual sampling points into major conductive fracture zones contributing to the inflows. A pathways algorithm was run using the hydrogeologically calibrated fracture model and boundary conditions. Fits between the measured and modelled chemistry were very good (Figure 81). Differences between the modeled and observed chemical compositions were related primarily to travel velocities, not spatial locations. The results indicate that for a large modelled region the initial geochemical spatial variation used in the model is very important. The travel velocities were then calibrated by varying the storativities of specific large scale features, further improving the fits.

The head and geochemical data provided differing constraints on the model. The former are essential and should be used to calibrate the model before the geochemical data are used. The reasons for using the head data first are that this information is less ambiguous. The time dependent head information is dominated by local connectivity and transmissivities as the tunnel section is being constructed, and by the regional connectivity and boundary conditions later on. Therefore, if the original fracture model accurately reflects the major connectivity, missing connectivity and boundary conditions can be calibrated reasonably successfully.

In contrast, the geochemical data provided the only real constraint (or validation) on the source locations of waters predicted by a model. This 'geochemical' calibration provides

information, like the head data, on whether a major hydraulic connection is missing. However, like the head calibration, it relies on having a good underlying discrete fracture network model that already replicates most of the major hydraulic structures. The significance of this requirement can be appreciated from Figure 82.

Additionally, geochemical data can be used to calibrate transport apertures and storage affects. These effects are difficult to calibrate using solely time dependent heads measures at tunnel sections.

9.9 Potential future applications of statistics at Tono and more widely in Japan

The approach adopted at Äspö is particularly relevant for constraining models for disturbed groundwater flow at the scale of an underground laboratory. Potentially the method could be used to constrain models for disturbed flow around a future deep geological repository for radioactive wastes.

Though some statistical modelling has been done in the Tono area previously it was not exactly the same as the statistical modelling done in Task 5. Specifically, the modelling at Tono has used hierarchical cluster analysis (HCA). Additionally, since this earlier modelling was done, more data have become available. These new data show that:

- some trace elements not considered by the previous modelling at Tono (e.g. Br) do seem to show systematic variations across the area.
- more saline (brackish) water occurs to the south of the Toki River.

Therefore, the new statistical approach does have some potential to be valuable for distinguishing different water types even in areas like Tono.

However, the approach could be useful more widely in Japan for several reasons:

- Over a wide area of Japan there could well be chemical differences between fresh waters of different origins (notably water recharged in a cold-climate and modern meteoric water). The Task 5 work showed that the method can distinguish between modern meteoric water and glacial recharge water. Parts of Hokkaido have been glaciated and it can be speculated that there may be a component of glacial recharge water in groundwaters in some parts of this prefecture. Possibly such waters could be widely distributed there.
- The possibility that groundwater salinity with many origins could be widespread at depth in Japan, cannot be ruled out. Such varied water may possibly be encountered during future investigations. Elsewhere in the world it is striking that saline waters and brines are very widely distributed at depth, even when there are no obvious salinity sources like evaporites (e.g. shield brines). At present, there are very few data with which to evaluate this possibility in Japan. Even in the Tono area, where there has been a relatively large amount of drilling, the deepest samples are only from c. 1000 m. It is quite possible that more saline waters than have been encountered so far are present at greater depths.
- Statistical data could be used to correct deep groundwater analyses for contamination.

In the third case, the basic idea is that drilling fluid is effectively an 'end-member' and is represented by a principal component correlated with drilling fluid tracer. The remaining principal components represent the natural groundwater. This could be valuable wherever drilling is undertaken.

If the geochemical data are to be integrated with models for groundwater flow, site characterisation must produce information about the following aspects of geology and hydrogeology:

- location and size of all major features;
- orientation, size and intensity of background fracturing;
- topography, location of streams, etc., to provide boundary conditions;
- aperture information;
- hydrogeological properties of the major features;
- hydrogeological properties of the background fracturing;
- time-dependent heads (both raw data and density-corrected data);
- measurements distributed both in main fracture zones and in the background network, to allow verification of the relative permeabilities of the Discrete Fracture Network.

Geology only provides the orientation and size information, intensity and transmissivity should be derived from hydraulic testing.

Additionally, the following geochemical information is required:

- time dependent geochemistry both within the major features and the background fracturing;
- interpretation to provide geochemical overview of the site (*in-situ* controls on the chemistry variations (e.g. saline – freshwater interface, long term chemical reactions, age of waters, etc.)).
- variations in groundwater chemistry due to perturbations connected with borehole drilling and/or underground tunnel construction.

The groundwater chemical data and hydrochemical data from Äspö would probably enable a method to be developed that could be applied to the MIU, provided that there are sufficiently large chemical contrasts in the groundwaters from different places in the MIU.

At Äspö there are large chemical variations in the groundwaters from different places. In principal, this makes the application of the method relatively straightforward at this site. In contrast, if the groundwaters in the MIU site are similar to those that have been sampled elsewhere in the Tono area and MIU areas, they will be all be fresh. Therefore, the chemical constituents that might form the basis of the technique are more limited than in the case of Äspö. An appraisal of the existing data from the area near to the MIU site and in the Tono mine area suggests that variations in the following determinands are most likely to be useful:

- Tritium
- $^{18}O/^{16}O$, D/H
- ^{14}C
- Br, F, Cl

- ^{36}Cl

Tritium will be of little value unless excavations and associated chemical studies are done over a time scale much shorter than 12.43 years, the half-life of tritium.

However, if ^{14}C is to be used, the data will need to be corrected for water/rock interactions, such as calcite precipitation or dissolution, that may occur in response to groundwater mixing caused by the perturbations related to activities such as borehole drilling, hydraulic testing and ultimately MIU construction.

Potentially, other constituents may also be useful. For example, F shows proportionately large variations in concentration in the groundwaters. ^{36}Cl has also been shown to vary significantly. Variations in this isotope due to radioactive decay would be insignificant during any underground investigations, because its half-life of 301,000 years is sufficiently long.

If the method is to be applied successfully in the MIU area, it is essential for information necessary to evaluate the quality of spatial and analytical data obtained from the MIU investigations to be documented thoroughly and transparently.

It is also essential that any numerical manipulations of the data are documented thoroughly and transparently.

9.10 Recommendations for future statistical studies and calibration of flow models

It is suggested that in future investigations in the Tono site, statistical processing of the groundwater chemical data are used to:

- investigate the relative importance of mixing between different groundwater types and water/rock interactions as controls on deep groundwater chemistry;
- correct groundwater analyses for contamination effects, by removing the principal component (or components) that are correlated with variations in drilling fluid tracer (this would be most useful in cases where it is impossible to sufficiently cleanup the samples during pumping).

Future applications of geochemistry to improve hydrogeological models, for example in the MIU site, should use give careful consideration to the:

- quality of the actual hydrochemical data;
- reporting of relevant quality information with the actual data.

It is also recommended that trace element data (Br, F etc) are also collected routinely in the future investigations. These data could enable different components of groundwater salinity to be identified more readily than at the present.

The main uncertainty in the hydrochemical data in long-term programmes like that being undertaken in the Äspö Hard Rock Laboratory arises from the disturbance to the hydrochemical system by borehole drilling and testing. On the other hand, such extended programmes of drilling are usually inevitable prior to and during the construction of any

underground laboratory. Consequently, disturbance to the groundwater system is also inevitable. However, in any future investigation, the effects of this disturbance could be allowed for in any modelling by:

- optimising drilling and testing methods (i.e. as far as possible, similar techniques should be employed throughout the programme of investigation);
- minimising the volumes of fluid pumped during the drilling programme;
- determining the groundwater chemistry using specialist boreholes designed to acquire hydrochemical data, prior to any extensive hydraulic testing or tracer tests.
- applying the approach being adopted by JNC in the present study iteratively, at various stages of the investigations, so as to build up a cumulative picture of the disturbance to the groundwater system.

At each stage of the investigations in the MIU it is advisable to undertake a modelling exercise that calibrates hydraulic models against groundwater chemistry as far as possible. This approach should enable the effects of progressive disturbances to groundwater masses by on-going investigations to be evaluated.

Statistical processing of the groundwater data could be an important tool in applying the technique.

10. RELEVANCE TO SITE SELECTION, SITE CHARACTERISATION AND PA

10.1 Introduction

The purpose of this Chapter is to provide a brief summary of how the work presented in the previous chapters could be relevant to site selection, site characterisation and PA connected with radioactive waste management by deep geological disposal in general. The topics covered are each very broad and a major study would be needed to cover each one in detail. Therefore, this chapter aims only to highlight some key topics, and does not claim to present a comprehensive evaluation of site selection and characterisation and PA.

10.2 Relevance to site selection

The past applications of geochemistry in site selection internationally have been reviewed in Savage et al. (2000). They note that in most programmes internationally, geochemistry has been used only indirectly to support site selection, if at all. More usually, although it is recognised that geochemical factors are important for controlling nuclide retardation and waste canister degradation, it is considered that suitable conditions would occur widely. Hence, it is generally believed that geochemical conditions need not be considered explicitly in site selection (e.g. SKB, 1991). There are, nevertheless, exceptional cases where geochemistry has been considered to be important, as in France where Toulhoat et al. (1993) considered that systems with deep CO_2 input, resulting in carbon dioxide rich groundwaters, should be eliminated when selecting candidate sites for future repositories.

Elsewhere, the main geoscientific factors considered in site selection have fallen into two main groups:

- geological factors;
- hydrogeological factors.

More specifically, these factors have included:

- topography;
- distances between probable groundwater recharge and discharge zones;
- rock mass characteristics – a ***general*** understanding of fracture zone distributions, crush zone distributions etc, rock permeabilities, sorption capacities, thermal capacities, mineral solubilities and geotechnical properties;
- depth, thickness and areal extent of possible target rock formation;
- uplift and subsidence;
- erosion;
- seismic and tectonic activity.

Similar factors to these were considered in the U.K. during site selection in the 1980's, which distinguished four basic kinds of environment that might be suitable for hosting a repository (Figure 83).

In the above list, geochemistry is considered under rock properties, but the geochemistry of groundwater and its application for understanding past and present groundwater flow or capability to influence engineered barriers or nuclide migration, are not featured. Similarly, gas and hydrocarbon geochemistry are not evaluated.

It can be argued that ruling out a site based on these geological and hydrogeological factors might to some extent automatically rule out sites with unsuitable geochemical conditions. However, this would not invariably be the case since groundwaters, gases and petroleum are to some degree mobile and need not reflect the present physical environment in which they occur. Furthermore, geochemical information may help to support selection based on the other criteria. Most geochemical information will necessarily be obtained following initial site selection, during site characterisation. However, readily available information such as 'historical' data on groundwater quality, or data easily acquired from the surface, such as river water chemistry, may help to understand the general patterns of groundwater flow.

Bearing issues such as these in mind, a conclusion of Savage et al. (2000) was that it would be beneficial in future to give more prominence to geochemical information in site selection. They noted that '...a better understanding of site properties that are most important in controlling the long-term geochemical evolution of the site over a range of possible scenarios would enable the potential sites to be ranked in terms of their suitability to host a repository'.

An additional factor that will possibly be important in Japan is the 'characterisability' of a site. It is likely that the ease with it is perceived possible to characterise a site so as to determine its suitability, will be one factor that will determine the relative ranking of potential candidate sites.

Given these points it is likely that the main generic contribution of the Tono site selection will be the provision of basic information on the approaches that can be applied to characterise potential future sites elsewhere. While the most obvious relevance of the Tono investigations is to possible future sites in crystalline rock, many of the basic methods will also be applicable to some degree to other rock types.

10.3 Relevance to site characterisation

Geochemical investigations invariably have a high profile in site characterisation. There are generally three main uses:

- demonstration of suitable chemical conditions to ensure the stability and proper functioning of engineered barrier systems and to retard radionuclide migration through the natural geosphere barrier;
- provide a constraint on groundwater flow models that is independent of hydrogeological data;
- enable the past evolution of a site to be characterised to provide a basis for predicting the site's future evolution (palaeohydrogeological studies).

The investigations at Tono are particularly relevant for:

- demonstrating that appropriate site characterisation techniques exist in Japan;
- developing palaeohydrogeological approaches applicable to an environment where plate tectonic processes, in addition to climatic change, have probably influenced the hydrogeological system;
- developing characterisation methodologies that can be applied in fresh groundwater environments;
- developing data management protocols and software (e.g. digital databases);
- developing quality management protocols.

The development of methods that can be applied in fresh groundwater environments is significant in Japan because on-shore deep groundwater systems are apparently dominated by fresh groundwater (Figure 84). Saline groundwaters are most likely to be encountered should a future repository be sited near the coast (Figure 84). In this case, it is possible that the location and nature of the transition between fresh groundwater towards the on-shore area and saline water towards the offshore area could be an important feature to characterise. The following aspects of the work described in this report could be particularly relevant to such characterisation:

- investigations of halide chemistry;
- investigations of ^{36}Cl;
- investigations of mineralogical evidence for past movements of saline/fresh groundwater;
- statistical methods for interpreting the origins and mixing proportions of groundwaters.

The Tsukiyoshi Fault studies in the Tono area could also be an important basis for developing generic characterisation methods for faults that could be encountered in possible repository environments elsewhere. Very large faults, which may or may not be active, could be avoided in an initial site characterisation excercise (JNC, 2000), whereas any detrimental effects of very small fractures could be avoided by careful waste canister emplacement. Faults of intermediate scale, which would probably occur in or near a future repository could affect the layout of any repository (Figure 85). A fault like the Tsukiyoshi Fault could be classified as such a 'layout-determining fault'. Thus, the investigation methodologies that are being developed by TGC could be applicable to characterising such faults.

Particularly relevant aspects of faults to be characterised are illustrated in Figure 86. One of the findings of the Tsukiyhoshi Fault project is that there is apparently a coupling between chemical processes and physical deformation processes that influence these features.

10.4 Relevance to performance assessment (PA)

Performance Assessment has generally used geochemical information in two main ways:

- to support conceptual model development;
- to support scenario development.

There is also increasing recognition that palaeohydreogeology, based to a large extent on geochemical information, could be used more prominently in PA. This application is the subject of a recently commenced research project 'Palaeohydrogeological Data Analysis and Model Testing' (PADAMOT), which is being supported by the European Commission under the Fifth Framework Programme.

Numerical information from palaeohydrogeological studies have not generally been used directly in PA, but rather the interpretations derived from these data have provided a support for the PA. This was the case in the Nirex 97 safety assessment (Nirex, 1997a; Table 25; Figure 87). One area where geochemical site-data have been used to parameterise the PA models is the initialisation of nuclide transport calculations in Nirex 97 (Figure 87). In this case, the transport model used a 3-dimensional model of the distribution of groundwater salinity (Figure 10).

In the case of the Tono investigations, on-going work is producing an improved understanding of the features events and processes (FEPs) which are relevant to one particular Japanese environment, namely an uplifting basement in which there is fresh, topographically-driven groundwater flow. The extent to which this is directly applicable to any future PA at an actual site elsewhere will depend upon the nature of the site(s) that is (are) selected and how closely they resemble the Tono area. However, if there is a fresh groundwater flow system in the vicinity of such a site, it is likely that to some extent the experience gained at Tono will be relevant. For example, calculation of dilution factors as deeper groundwater that has passed through a repository mixes with shallower, more rapidly-moving groundwater could be relevant for safety assessment (Figure 88). In such a case it is desirable to be able to characterise the chemistry of the fresh groundwater system, to provide the data necessary for calculating such dilution factors.

The knowledge obtained at Tono could be useful in any future generic scenario development exercises. However, possibly the two main applications of the studies are:

- the potential opportunity it gives for site characterisation and PA workers to gain experience of working with one another;
- the opportunity to evaluate how palaeohydrogeological information could be applied in PA in Japan.

In the cases of this second application, the studies at Tono have the potential to yield information that cannot be obtained from other studies internationally. In Europe the main focus of palaeohydrogeology is to understand the impact of climate change and related effects such as sea level variation on groundwater flow. Research under the on-going European PADAMOT project is focusing on this issue. However, in Japan, in addition to climate change, plate tectonic effects will also have influenced past groundwater flow. Methods are needed to characterise these effects and to distinguish them from climatic effects. The Tono investigations have an opportunity to address this issue and to evaluate the implications for PA.

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Figure 1. Schematic illustration of the importance of groundwater flow.

What is:

- ➔ Travel time repository ➡ near-surface?
- ➔ Direction of flow?
- ➔ Chemical evolution along flow path?
- ➔ How will these features change?

} **Must Answer For PA**

Figure 2. Schematic illustration of two situations in which geochemical information can be used to develop groundwater flow models.

Figure 3. Schematic illustration of the importance of chemical gradients in groundwater for recording past states of the flow system. In A. the chemical gradient in the groundwaters is similar to that in B. However, the head gradient in A. is significantly steeper than in B.

From present hydraulic data alone, system stability poorly known

Up to c. 1Ma most relevant

Head and chemical gradients change at different rates

But .

Present chemical gradients may record past states of flow system

Figure 4. Schematic illustration showing how mixing between different groundwaters and variations in water/rock interactions are both related to groundwater flow. The overall variation in groundwater chemistry from place to place depends on both mixing and water/rock interactions.

Figure 5. Schematic illustration of a basic approach to constraining groundwater flow models using geochemical information. The flow-model conditions (e.g. boundary conditions) are changed until the modelled distribution of chemically different groundwaters matches the observed distributions.

Figure 6. Schematic illustration of a basic approach to evaluating the stability of the present groundwater flow system.

Figure 7. Schematic illustration of how knowledge of the past stability of the groundwater flow system can be used to evaluate future stability.

Figure 8. Sketch maps showing the Sellafield area, and the boreholes drilled while investigating the potential site for a deep underground repository for intermediate- level and some low- level radioactive wastes.

Figure 9. Variations in the concentration of chloride in groundwater from three boreholes at Sellafield, north-west England.

Figure 10. A 3D model for groundwater salinity variations (represented by chloride contours) across the Sellafield area, north-west England. This model was used in flow modelling during the Nirex 97 Safety Assessment.

Figure 11. Schematic illustration showing one situation where Br/Cl ratios can be used to determine mixing proportions between waters from different sources. The mixing proportions can be used to calibrate a coupled flow-chemical model.

Figure 12. Variations in the ratio Br/Cl (by mass) in groundwater from three boreholes at Sellafield, north-west England. The ornament on the stratigraphical columns is the same as in Figure 9.

Water chemistry suggests origins, hence flow directions and flow model boundary conditions

Figure 13. Illustration of how variations in Br/Cl ratios in groundwater samples from Sellafield, north-west England constrain the mixing proportions of groundwaters from different places across the site.

But...

- ➔ Proportions model-dependent
- ➔ Insensitive to mixing for higher proportions of more saline water

[1]In this model variations in Br/Cl ratio are assumed to be due entirely to mixing between deep Borehole 3 water and deep Borehole 2 water

Figure 14. Illustration of $^{36}Cl/Cl$ variations in groundwaters from Sellafield, north-western England. Values of $^{36}Cl/Cl$ and Br/Cl ratios are correlated (A.) suggesting that variations in $^{36}Cl/Cl$ reflect mixing between high and low Br/Cl waters. However, although variations in Br/Cl can be explained by mixing (B.) variations in $^{36}Cl/Cl$ cannot be explained by mixing alone (C.). In-situ ^{36}Cl production probably explains the variations.

Figure 15. Comparison between $^{36}Cl/Cl$ ratios in groundwaters (hydraulic tests) and equilibrium ratios calculated from wireline data (grey dots), for borehole 2 at Sellafield, U.K. The water data are close to mean equilibrium rock values, but these equilibrium values are more variable than groundwater ratios.

Figure 16. Simplified cross-section through the Sellafield area, showing the main features of a conceptual hydrogeological model based on ***both*** hydrogeological data and hydrogeochemical data.

Figure 17. Simplified north-east/south-west cross-section through Sellafield, with the boundary conditions use in one coupled flow-density model. Many kinds of model were run and this is just one example.

Figure 18. The same cross-section as that illustrated in Figure 17, with chloride contours, representing salinity, predicted by one coupled flow-chemistry model produced using the code SUTRA.

Figure 19. Schematic illustration of the use of PCA to separate chemical variations between groundwater samples that are due to mixing, from chemical variations due to other effects like water/rock interactions or contamination by drilling fluid.

Figure 20. Plots showing how multivariate statistics were used at Sellafield to constrain mixing proportions between two different groundwaters across the Sellafield site. The approach differed from using Br/Cl ratios, because it took into account variations in all dissolved solutes.

Figure 21. Schematic illustration of the basis of the computer code 'Multivariate Mixing and Mass Balance' (M3). A. Plot of the two most important principal components identified by PCA. Actual waters are enclosed by a polygon. The apices indicate the reference waters that are assumed to mix to form the actual waters. The proportions of the reference waters are calculated geometrically. B. The proportions calculated in A. are used to calculate theoretical concentrations of solutes in each water. These theoretical proportions are compared with actual concentrations. In the case of potentially reactive constituents, differences between the two sets of values are considered to be due to water/rock interactions,. Deviations in constituents expected to be non-reactive, like chloride, suggest it is incorrect to assume mixing between the chosen reference waters.

Figure 22. Variations in the proportions of 'end-members ' in groundwaters from Äspö, Sweden, as defined by SKB. The proportions of these end-members were calculated using the computer code M3 and the groundwater chemical data in Data Delivery 19.

Figure 23. Flow chart illustrating a general approach for using hydrogeochemical evidence for past groundwater flow to predict future groundwater flow

Figure 24. Possible alternative definitions of recharge time. Usually, in the literature, recharge time means T1 or T2. However, to be rigorous, it is necessary to state what is being recharged.

Solute Residence Time

Figure 25. Concentrations of two solutes along a groundwater flow path, illustrated schematically. Each solute has a different residence time within the groundwater at any point. Radiocarbon (^{14}C) enters the water at recharge. The concentration of ^{14}C then decreases, but its residence time increases. Sodium (Na) enters the fresh water by water/rock interactions and by mixing with seawater. Thus, the residence time of the Na in the water also increases along the flow path, but initially it is less than that of ^{14}C. At the mixing zone, the concentration of ^{14}C rapidly decreases to zero, but the concentration of Na increases. Downstream, the concept of residence time is meaningless for ^{14}C, while the residence time of Na is depends on both water/rock interactions and also on the seawater/fresh water mixing proportions.

Figure 26. Possible alternative definitions of groundwater residence time. The groundwater residence time can mean the residence time in any of the reservoirs indicated.

Relationship between solute residence time and groundwater residence time

Figure 27. Schematic diagram illustrating the relationship between residence time of a solute in groundwater, the residence time of the solute in a rock formation and the residence time of the groundwater in the rock formation. It is necessary to specify a reservoir when estimating a solute's residence time (τ) (after Metcalfe et al. 1998a).

Figure 28. Comparison between types of 'dating' in groundwater sampled along Z-Z. A. Tritium occurs only near-surface and **limits** recharge to the last 30 to 40 years. B. Above the lower granite ^{14}C constrains recharge times **quantitatively**, but is absent from the deeper granite. C. A near-surface man-made (e.g. bomb testing) $^{36}Cl/Cl$ peak **limits** the Cl residence time to 30 to 40 years. Deeper, $^{36}Cl/Cl$ is greater than equilibrium, **limiting** residence time to < c.1.5 Ma. Here $^{36}Cl/Cl$ varies little because the residence time is short (< c. 30,000 years, from ^{14}C) compared to ^{36}Cl's half-life. In the upper granite, groundwater flow is slower and $^{36}Cl/Cl$ decreases towards equilibrium as depth increases. Here a **quantiative** Cl residence time can be estimated. Deeper, $^{36}Cl/Cl$ is equilibrated with *in-situ* ^{36}Cl production, **limiting** the residence time to > c. 1.5 Ma.

Figure 29. Figure showing how the morphology (crystal shape) of paragenetically late (recent) fracture calcite at Sellafield, north-western England correlates with the salinity of co-existing groundwater. No 'fresh-water' calcite occurs in the zone presently filled by saline water. This suggests that fresh water has never penetrated much more deeply than its present limit.

Figure 30. Pourbaix diagrams constructed using Geochemist's Workbench (GWB) version 3 and the GWB thermodynamic database Thermo.dat. The proportion of Fe and Mn that is combined in carbonate minerals is expected to vary according to the oxidation state and pH of the water and to affect the cathodoluminescence shown by the minerals. Possibly, this can be used as a palaeo-redox indicator.

Plot made for the following conditions:
$Log\{Fe^{2+}\} = -6.45$ $Log\{SO_4^{2-}\} = -6.28$
$Log\{HCO_3^-\} = -2.83$ $Log\{Siderite\} = -2.24$

Plot made for the following conditions:
$Log\{Mn^{2+}\} = -5.74$ $Log\{SO_4^{2-}\} = -6.28$
$Log\{HCO_3^-\} = -2.83$ $Log\{Rhodochrosite\} = -1.74$

Figure 31. Illustrations of fracture-filling calcite crystals sampled from Sellafield, north-western England. The samples are showing cathodoluminescence. Each image is approximately 2mm along the longest axis. Images supplied by A.E. Milodowski, BGS.

Calcite from fresh water zone

Calcite with bright and dark zones over-grows calcitethat is bright. Implies that later in the history of calcite growth, redox conditions were more variable than early in crystal growth.

Calcite from saline water zone

Entire crystal bright - implies less variable Eh and pH conditions over the time for which the calcite was precipitated.

Figure 32. A simplified scheme illustrating important elements in a prediction exercise/data acquisition cycle, based largely on an approach adopted at Sellafield, UK (Nirex, 1998).

Figure 33. Simplified geological map of the Tono area showing the main study localities.

Figure 34. Simplified geological model for the Shobasama site, showing the locations of deep boreholes and the general location of the Tsukiyoshi Fault

7 deep boreholes,
4 water samples

Much fewer than Sellafield lab site:

14 boreholes,
63 water samples

Figure 35. Schematic illustration of relationship between climate change and the stable isotopic compositions of rainfall.

Figure 36. Variations in stable oxygen and hydrogen isotopes in groundwaters of the Tono area.

Figure 37. A comparison between the morphologies (crystal shapes) of late fracture-filling calcite crystals from Sellafield, north-western England and the morphologies of late fracture-filling calcite crystals from the Toki Granite.

Sellafield Fracture Calcite

Calcite forms identified at Tono (from Iwatsuki et al. 2002)

Freshwater form

2 mm

Elemental rhombohedral calcite, DH-6/-6 m S.L.

Saline water form

Elongate rhombohedral calcite, DH-9/-295 m S.L.

Further work needed but possibly calcite a palaeosalinity indicator in the Tono area

Figure 38. Distributions of fracture-filling calcite which contains detectable ^{14}C, sampled from the Toki Granite in regional (DH) boreholes. An implication is that a component of the groundwater at depths of several hundred metres was recharged within the last 50,000 years. Adapted from Iwatsuki et. al. (2002).

Figure 39. Simplified illustrations of Tono Mine and its surroundings, showing the locations at which the Tsukiyoshi Fault was studied. The trace of The fault illustrated in the inset diagram is based on earlier studies.

Figure 40. Diagram showing a model for the geometry of the Tsukiyoshi Fault in Tono Mine, *assuming* that it is a single planar feature. This feature is constructed through the intersections of the fault in the various boreholes examined.

Figure 41. Some results reported for the shaft sinking experiment, conducted during the sinking of No. 2 Shaft in Tono Mine. Heads were monitored in boreholes near the shaft, during shaft sinking. The boreholes were sited around the shaft and monitoring intervals were thought to lie on opposite sides of the Tsukiyoshi Fault. The location of the fault plane illustrated in the diagram is based on the data available at the time of shaft sinking.

Responses differ on opposite sides of the fault - suggest barrier

Figure 42. Diagram showing the plan for Borehole 99SI-08, designed specifically to intersect the Tsukiyoshi Fault near to the N°2 Shaft. The location of the Tsukyoshi Fault, predicted before borehole drilling, is shown.

Figure 43. Summary log of borehole 99SI-08, taken from Milodowski et al. (2001). The diagram contains information obtained by the fellow, during logging immediately after borehole drilling, and more detailed information obtained obtained later during logging by A.E. Milodowski and M.R. Gillespie of BGS.

G Intraformational conglomerate

F Carbonaceous, tuffaceous massive sandstone

E Carbonaceous, tuffaceous medium sandstone and siltstone

D Cycles of course, medium, fine sandstone, siltstone and claystone

C Intraformational conglomerate

B Cycles of pebbly siltsones, pebbly sandstones and mudstones

A Clast- and matrix-supported conglomerates with granite clasts fine upwards through sandstones, to siltstones

Figure 44. Combination of fracture data and hydraulic conductivity data obtained by JNC with alteration and Potential Flowing Feature data obtained by BGS, for Borehole TH-2.

Figure 45. Combination of fracture data and hydraulic conductivity data obtained by JNC with alteration and Potential Flowing Feature data obtained by BGS, for Borehole MIU-3.

Figure 46. Photomicrographs of samples from the Tsukiyoshi Fault zone in Borehole 98SI-03, in the Lower Toki Formation. The textures are evidence for past groundwater flow in the fault zone.

Calcite replaces clay matrix of sandstone

'Fibrous' calcite vein in clay fault gouge

- Largely post fault-movement effects

Calcite replaces clay fault gouge

Plagioclase dissolution fracture surface in mudstone

Figure 47. Photomicrographs of samples from the Tsukiyoshi Fault zone in Borehole MIU-2, in the Toki Granite. The textures are evidence for past groundwater flow in the fault zone.

Calcic plagioclase dissolution - porosity generation (blue dye)

Calcic plagioclase altered to smectite- porosity lining

- Largely post fault-movement effects

Figure 48. Example output from a geochemical model calculated using the computer code PHREEQC, designed to investigate the change in chemistry of pore water from fault gouge during squeezing. The pore water was sampled from gouge in the Tsukiyoshi Fault, intersected by borehole TFA-1.

Figure 49. Variations in calcite chemistry from the Tsukiyoshi Fault in Borehole 98SI-03.

Figure 50. Summary of Sr isotope data obtained for calcite samples and whole-rocks during the Tsukiyoshi Fault Project. The data were obtained by BGS.

Figure 51. Plot showing stable carbon isotope and strontium isotope data from carbonate minerals sampled from the Tono area.

Figure 52a. Some general lessons from the Tsukiyoshi Fault studies for future borehole design to characterise a fault zone.

- ➔ Drill with core preservation
- ➔ Log core during drilling
- ➔ Drill at high angle to fault
- ➔ Avoid hitting fault near formation boundaries

Here 2. better than 1.

Possible siting of hydraulic tests to characterise the fault

Figure 52b. Some general lessons from the Tsukiyoshi Fault studies for future characterisation of a fault zone.

- Site tests in this zone, based on petrographic data
- Evaluate temporal changes Due to WRI

Figure 53. Plot of Br against Cl for all groundwaters from the Tono area that have both Br and Cl data.

Figure 54. Variation in Br/Cl (mass) with respect to chloride concentration for groundwater samples from the Tono area (black diamonds). Only samples with Br concentrations above detection limit are plotted.

Figure 55. Plot of F against Cl for all groundwaters from the Tono area that have Br, Cl and F data.

Figure 56. Ranges and means of F concentrations in groundwaters from the major rock units of the Tono area.

Figure 57. Plot of fluoride concentration versus elevation above sea level for ground water from the Toki Granite.

Figure 58. Fluoride concentrations versus temperature for a fresh water based on the composition of soil water MC-21, calculated using the computer code Geochemist's Workbench (GWB) and various thermodynamic databases and reacting mineral assemblages.

Figure 59. General principles for using ^{36}Cl to understand Cl residence time and groundwater flow. In rainfall $^{36}Cl/Cl$ is relatively large, due to high atmospheric production rates. ^{36}Cl is also produced in-situ, but at different rates in Rocks 1 and 2. With increasing residence time in Rock 1, $^{36}Cl/Cl$ decreases from rainfall values to in-situ equilibrium in Rock 1. The Cl entering Rock 2 approaches a different value as residence time increases.

If know:
- → in-situ production rate
- → $^{36}Cl/Cl$ in inflowing water
- → $^{36}Cl/Cl$ in water now

} → Calculate residence time of Cl in rock
→ Constrain Cl source

Figure 60. Cartoon showing major processes affecting ^{36}Cl/Cl in groundwater. All Cl is assumed to be from rainfall. In the atmosphere cosmic rays form ^{36}Cl from ^{40}Ar and ^{36}Ar. The Cl then enters groundwater from rainfall. Human inputs (e.g. bomb testing) within the last c. 40 years, cause a near-surface peak in ^{36}Cl/Cl. At greater depth ^{36}Cl/Cl decreases towards equilibrium with ^{36}Cl production from tthe neutron flux in the sedimentary rock (equilibrium can be reached only if flow is slow enough). After water enters the granite, ^{36}Cl/Cl increases towards a higher equilibrium value caused by a higher neutron flux.

Figure 61. Schematic illustration of ^{36}Cl in-situ production within a rock.

Figure 62. Illustration of the sampling localities and the ^{36}Cl data obtained during a feasibility study to assess the possibility of obtaining and using ^{36}Cl data in the Tono area.

Figure 63. Summary of ^{36}Cl data from groundwaters of the Tono area.

Figure 64. A cartoon showing a simplified north-south cross-section across the Tono area, which fits the observed variations in halides (Br, Cl) and the variations in ^{36}Cl.

Figure 65. Cartoons showing a simplified north-south cross-section across the Tono area and alternative conceptual models for the variations in groundwater flow and chemistry.

Main Features

- Fresh water flows from the north and near the Toki River meets fresh water flowing from the south.
- Flow directed partly by limit of a different, denser, more saline Na-Cl water at depth.
- Expect traces of slightly more saline water in the relatively fresh waters near the Toki River.

Main Features

- Fresh water flows from the north and near the Toki River meets slightly more saline Na-Cl water flowing from the south, which follows deeper and hence longer flow paths.
- Na-Cl salinity partly from water/rock interactions
- Expect traces of slightly more saline water in the groundwater to the south of the Toki River.

Flow out of plane of paper

Flow direction - thickness proportional to flow rate;
length proportional to component out of plane of paper
(shorter arrows along a flow path indicate higher proportion out of plane of paper.

Figure 65. Continued.

Main Features

- Fresh water flows from the north and north of the Toki River meets slightly more saline Na-Cl water flowing from the south.
- Na-Cl salinity partly from water/rock interactions
- Expect traces of slightly more saline water in the groundwater to the north and south of the Toki River.

Main Features

- Fresh water flows from the north and south of the Toki River meets slightly more saline Na-Cl water flowing from the south.
- Na-Cl salinity partly from water/rock interactions
- Expect traces of slightly more saline water in the groundwater to the south of the Toki River.

Flow out of plane of paper

Flow direction - thickness proportional to flow rate; length proportional to component out of plane of paper (shorter arrows along a flow path indicate higher proportion out of plane of paper.

Figure 66. Relationships between the matrices used in the revised modelling.

Figure 67. Summary of the procedure adopted in JNC's revised statistical modelling.

Figure 68. Plot showing eigen values, reflecting the contribution of each principal component to the overall chemical variance, for groundwater samples in Data Delivery 19 for Äspö, supplied by SKB.

Figure 69. For groundwaters from Äspö, comparison between concentrations of each major solute, calculated from the compositions and proportions of statistically-derived components in each water, as calculated by JNC's new method, Model 2, and the actual concentrations of these solutes in each water.

Figure 69. Continued.

Figure 70. Plot showing variations in the proportions of chemical components of Äspö groundwaters versus depth, calculated from Model 2.

Figure 71. Variations in the proportions end-members used in M3 modelling, calculated from the results of Model 2.

Figure 72. Comparison between proportions of 'end-members' calculated by M3 and reported in Data Delivery 19, and proportions of the same 'end-members' calculated using JNC's revised Model 2.

Figure 73. Comparison, for each sample, between proportions of the meteoric 'end-member', defined previously by SKB, but calculated in JNC's Model 2, and the actual chloride concentration.

Figure 74. Comparison between the proportions of the meteoric water 'end-member' defined previously by SKB, but calculated from JNC's Model 2 and the deviation between actual and theoretical chloride concentrations, as calculated by M3 and supplied in Data Delivery 19.

Figure 75. A comparison between deviations in chloride concentration (calculated - actual), calculated from JNC's Model 2 and from the proportions supplied by SKB in Data Delivery 19, having been calculated by the computer code M3.

Figure 76. Comparison between the stable isotopic compositions of groundwater samples, and the isotopic compositions of 'end-members' identified previously by SKB.

Figure 77. Comparison between the stable isotopic compositions of groundwater samples, reconstructed from the compositions and proportions of chemical components calculated by the new statistical method, Model 2, and the isotopic compositions of 'end-members' identified previously by SKB.

Figure 78. Sketch diagram showing the how the chemistry of groundwater flowing into a tunnel in the Äspö HRL depends upon both the initial spatial distribution of chemically distinct groundwaters and on the flow paths between the inflow point and these different groundwaters.

Figure 79. Schematic illustration of JNC's modelling approach. Compositions of groundwaters inflowing to the tunnel are not calculated directly. Instead, proportions of waters originating in different portions of the rock mass are calculated. Knowledge of these waters' compositions is then used to calculate inflowing groundwater compositions. Uncertainties in the initial waters' locations or compositions will cause uncertainties in calculated inflow compositions.

Figure 80. Diagram illustrating the role of statistical processing in JNC's new approach for integrating geochemistry and physical hydrogeology. The statistical processing is used to identify chemical components that vary as a result of mixing.

[1]Done by Bill Dershowitz and Dawn Shuttle of Golder Associates
[2]Done by Mark Cave of the British Geological Survey

- ➔ Compare observed and predicted inflow chemistry
- ➔ Adjust flow model until consistent
- ➔ Method can suggest new fracture pathways for flow

Figure 81. An example of chemical predictions and corresponding observations for one monitoring point, SA1229A, in the Äspö tunnel. A. The groundwater chemistry is expressed in terms of the 7 geochemical components obtained from the new chemometric statistical approach. B. The same results as in A,. but expressed in terms of the four 'end-members' defined by SKB and calculated from the abundances of the 7 components illustrated in A.

Figure 82. Schematic illustration of the possible effects of a fracture zone on the accuracy of predictions of groundwater inflow compositions. The behaviour of the fracture zone may control the chemistry of the inflows (cf A. and B.). However, the chemical data used to predict these inflows may reflect borehole drilling and pumping, rather than the natural distributions of the groundwaters (C. and D.).

Figure 83. **General** environments considered for deep disposal of radioactive waste in the U.K. (after Nirex 1987)

Figure 84. A schematic illustration showing possible situations in which geochemical constraints on groundwater flow systems may be useful in Japan.

Figure 85. Schematic illustration showing how faults and fractures are significant for siting and design of a repository for radioactive wastes (based on concepts discussed in Birgersson et al. 1992; NAGRA, 1994; McEwen, 1995; Nirex 1995, 1997). Precise distances between structures and the repository would be specific to the site, disposal concept and detailed repository design. These distances would need to be defined on a case-by-case basis.

Figure 86. Schematic illustration of a fault, summarising some general reasons for studying faults in connection with deep geological disposal.

Figure 87. The place of geochemical constraints on groundwater flow in Performance Assessment: an example from Nirex 97 (Nirex, 1997a).

KEY MESSAGE: Geochemistry valuable even if not a direct numerical input to PA model

Figure 88. **One example** of a possible application of methods being developed in the fresh groundwater system of the Tono area.

Table 1. Summary of the major approaches used to estimate solute residence times.

Determinands	Time Scales	'Age'Type **(Typical)**	**Main** principle*
CFC	10^1 yrs	Quantitative	Human input
^3H ^{85}Kr Agrichemicals	10^1 yrs	Limiting	
Ar, Kr, Xe $^{18}O/^{16}O$ and $^2H/^1H$	10^4 yrs	Relative	Variation in natural recharge condition
^{39}Ar ^{14}C ^{81}Kr	10^2 yrs 10^4 yrs 10^5 yrs	Quantitative	Decay from recharge
^{36}Cl U-series nuclides ^{129}I	10^5 yrs 10^6 yrs 10^7 yrs	Quantitative	In-situ production and decay
^{21}Ne ^{40}Ar ^4He	10^6 yrs	Quantitative	In-situ accumulation
Other solutes	Undefined	Relative	Spatial variations constrain hydrogeological models

*Other principles are also important

Table 2. Typical values of constituents of groundwater that are used most commonly to estimate groundwater residence times.

Groundwater	^{3}H T.U.	$^{18}O/^{16}O$ ‰SMOW	^{14}C pmC	$^{36}Cl/Cl$ $x10^{-15}$	^{4}He cm^3/cm^3	NGRT[1] ^{o}C
	Commonly Used					
	Typical Values					
Modern	5 to 10	-6 to -8	50 to 70	30 to 10^3	$c.10^{-7}$	7 to 12
10^4 yr	< 0.1	-7 to -10	< 10	30 to 10^2	10^{-7} to 10^{-5}	0 to 7
10^6 yr	< 0.1	> -6	< 0.2	<1 to 10^2	10^{-6} to 10^{-3}	>10

[1]Noble Gas Recharge Temperature

Table 3. Potential chemical constraints on flow models - summary based on experience at Sellafield, north-west England.

Constraint	Model Type		
	Numerical		Conceptual
	PA	'System Understanding[1]	
Location of salinity gradients	●	●	●
'Width' of salinity gradients	●	●	●
Density correction on heads (from salinity)	●	●	●
Mixing proportions		●	●
Stability of transition fresh-saline water		●	●
Sources of water		●	●
Boundary conditions		●	●

1: Numerical models not made as part of PA

Table 4. Comparison between the hydrogeological setting of Tono and Sellafield, UK.

Site	Country	Approx Dimensions of hydrogeological System (L x W x D)[1]	Approximate surface relief (Max. — Min. Altitude, m)	Main rock types[2]	Age range of rocks[2]	Maximum salinity of ground water[2]				Main drivers for change during the Quaternary	Key sources[3]
						Fresh (TDS <1000 mgl^{-1})	Brackish Water (1000< TDS <10,000 mgl^{-1})	Saline (10,000 < TDS < 100,000mgl^{-1})	Brine (TDS > 100,000 mgl^{-1})		
Tono	***Japan***	***30 km x 30 km x 3 km***	***475***	***Clastic sediments (typically volcaniclasti c-rich) overlying granite***	***Tertiary (c. 60 Ma) to Pleistocene***					***Tectonically driven uplift?***	***Yusa et al. 1993***
Sellafield	United Kingdom	60 km x 65 km x 4 km	1000	Red-bed sedimentary rocks (mainly sandstones) overlying volcaniclasic rocks	Ordovician to Quaternary				*	Glaciation	Bowden et al. 1998

[1]Largest area within which hydrogeological flow simulations undertaken
[2]This refers to rocks or waters that are encountered within the regional hydrogeology area and 'rocks' include any spatially extensive superficial deposits other than soils.
[3]Important overviews only listed
[4]South of the Toki River
L x W x D = Length x Width x Depth

Classification of salinity (Fresh, Brackish, Saline, Brine) is based on Carpenter (1978) (quoting Davis, 1964)

Table 5. Comparison between the principal geochemical approaches for interpreting past and present groundwater flow patterns employed at Sellafield, UK and the main geochemical approaches that have been used to interpret groundwater flow patterns in the Tono area. The only methods considered are those employed in the Tono before the end of 2001, outside the present Fellowship.

Locality	Geological Information			Rock Analyses			Mineralogical Information								Groundwater Chemical Information													Others		
	Lithological Evidence	Structural Evidence	Palaeontological Evidence	Whole-rock elemental analyses	Radiometric Dates on Rocks	U-series Isotope Measurements on Rocks	Mineral Distributions/Abundances	Mineral Parageneses	Elemental Compositions	Isotopic Compositions (Dates not calculated)	Radiometric or Fission Track Dates on Minerals	U-series Isotope Measurements on Minerals	Crystal Forms/Shapes	Fluid Inclusion Data	Gross salinity variations	Chemical type of water and/or chemical variations	$^{87}Sr/^{86}Sr$	^{36}Cl	Tritium	^{14}C	Stable $^{13}C/^{12}C$	Stable $^{34}S/^{32}S$	Stable $^{18}O/^{18}O$ and $^{2}H/^{1}H$	Noble Gas Concentations – Isotopes	U-series Isotopes	^{129}I	^{39}Ar	Chlorofluorocarbons	Hydrogeological Evidence (Heads, Conductivities Flow)	Geophysical Information	Palaeoclimatic Information
Tono																														
Sellafield	*	*	*	*		*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*				*	*	*

'Structural information' refers to both microstructural and macrostructural information.
'Isotopic Compositions (Dates not calculated)' also refers to ^{14}C data for calcite. Although these data indicate a limiting age for a component of the calcite (c. 50,000 years) they are not in themselves radiometric dates.

Table 6. Summary of information reported before the end of 2001 relevant to understanding the palaeohydrogeology of the Tono area.

Source	Geological Information			Rock Analyses			Mineralogical Information								Groundwater Chemical Information												Others		
	Lithological Evidence	Structural Evidence	Palaeontological Evidence	Whole-rock elemental analyses	Radiometric Dates on Rocks	U-series Isotope Measurements on Rocks	Mineral Distributions/Abundances	Mineral Parageneses	Elemental Compositions	Isotopic Compositions (Dates not calculated)	Radiometric or Fission Track Dates on Minerals	U-series Isotope Measurements on Minerals	Crystal Forms/Shapes	Fluid Inclusion Data	Gross salinity variations	Chemical type of water and/or chemical variations	^{36}Cl	Tritium	^{14}C	Stable $^{13}C/^{12}C$	Stable $^{18}O/^{18}O$ and $^{2}H/^{1}H$	Noble Gas Concentations – Isotopes	U-series Isotopes	^{129}I	^{39}Ar	Chlorofluorocarbons	Hydrogeological Evidence (Heads, Conductivities Flow)	Geophysical Information	Palaeoclimatic Information
Iwatsuki et al. 2002										P			N		N	S			P	P	P								
Iwatsuki et al. 2001										P						S		N, P	N, P	N, P	N, P						N		
Milodowski et al. 2001	N, S	N							N	N			N																
Morikawa, 2001				N																		N					S		
Gillespie et al. 2000	N, S	N		N			N	N	N	N.			N	N															
Iwatsuki et al. 2000a										N, S					N	S			P	P	P								
Iwatsuki et al. 2000b										N						S		N	N	N	N								
Iwatsuki and Yoshida 1999	S	N, S					N, S	N, S							N, S	N, S		N. S	S		N, S								
Milodowski et al. 1999	N. S	N					N	N					N																
Iwatsuki et al. 1995	S						N			N					N	N				N									
Seo & Yoshida 1994	S			S^u		S										S													
Yoshida, 1994	S	N, S		N^u		N, S			N			N				S													
Yoshida et al. 1994a	S	N, S		S^u		N, S			N			N																	
Yoshida et al. 1994b	S	N, S		N^u S^u																									

Table 6. continued

Source	Geological Information			Rock Analyses			Mineralogical Information								Groundwater Chemical Information											Others		
	Lithological Evidence	Structural Evidence	Palaeontological Evidence	Whole-rock elemental analyses	Radiometric Dates on Rocks	U-series Isotope Measurements on Rocks	Mineral Distributions/Abundances	Mineral Parageneses	Elemental Compositions	Isotopic Compositions (Dates not calculated)	Radiometric or Fission Track Dates on Minerals	U-series Isotope Measurements on Minerals	Crystal Forms/Shapes	Fluid Inclusion Data	Gross salinity variations	Chemical type of water and/or chemical variations	^{36}Cl	Tritium	^{14}C	Stable $^{13}C/^{12}C$	Stable $^{18}O/^{16}O$ and $^{2}H/^{1}H$	Noble Gas Concentations – Isotopes	U-series Isotopes	^{129}I	^{39}Ar	Chlorofluorocarbons	Hydrogeological Evidence (Heads, Conductivities Flow)	Geophysical Information	Palaeoclimatic Information
Yusa & Yoshida 1993	S	S		N^U		N, S									S	S			S		S							
Yusa et al. 1993	P, S	P. S	P, S			P									S	S		S	P		P							
Mizutani et al. 1992															N	N		N	N	N	N							
Nohara et al. 1992	S			N^U		N, S										S												
Kanai et al. 1991																							N					
Yamakawa 1991	S	S				N, P									S	S		S	S									
Kanai et al. 1990																							N					
Ochiai et al. 1989				N^U		N					N^F				N, S			P			N		N					
Sato et al. 1987				N^U		N									N	N		N										

Table 6. Continued.

N^F = New report of a Fission Track age
N^u = New report of uranium content of rock
S^u = Summary of previous determinations of uranium content of rock

N = New data reported and used for new palaeohydrogeological interpretation (Note: New data means no earlier reports of the data have been identified during the review. It is possible that earlier reports exist, but have not been identified. This situation is especially likely where the document referenced here is an English document. In this case, earlier publications probably exist in Japanese. Where there is a Japanese document and an English document with the same year of publication and containing similar information, the English document is listed, even though it is probably not the source document).
P = Previously reported data used for new palaeohydrogeological interpretation.
S = Summary of previously reported palaeohydrogeological *interpretation* (Note: references in this category are included only if the summary provides significant new insights or if the document also contains some new information in addition to the summarised information).
U = Unknown whether new data or data obtained prior to the referenced study.

References in italics are in Japanese

All references contain some new information and most also contain summaries of older information. In these cases where new and old data are summarised together, this table shows not only the new information, but also the information that is summarised. Documents that contain only duplicates of data or other information published elsewhere are not included in this table.

'Structural information' refers to both microstructural and macrostructural information.
Isotopic Compositions (Dates not calculated) also refers to ^{14}C data for calcite. Although these data indicate a limiting age for a component of the calcite (c. 50,000 years) they are not in themselves radiometric dates.

An interpretation is considered to be a palaeohydrogeological interpretation if it contains one or more of the following:

- estimates of *recharge times* for water;
- estimates of *residence times* for water;
- estimates of *residence times* for solutes ;
- information about stability of/ variations in boundary conditions, especially:
  - ⇒ locations of boundaries;
  - ⇒ fluxes across boundaries;
  - ⇒ recharge rates;

Table 6. Continued.

- information about stability of/variations in:
  - ⇒ past chemical conditions underground (levels and characteristics of salinity, pH and Eh);
  - ⇒ past driving forces for groundwater movement;
  - ⇒ past groundwater flow directions;
  - ⇒ past groundwater pathways (e.g. whether faults have acted as groundwater pathways).

Information about the *present* groundwater flow system is not included here, unless it gives particular insights into past stability or variations in groundwater movement and or chemistry. However, palaeohydrogeological information defined in this way would not be interpreted separately from information about the present groundwater flow system. Thus, for example, experimental data from in-diffusion experiments in Ota and Yoshida (1995) are not considered as palaeohydrogeological information, because they relate solely to the present flow paths available for solute migration.

Table 7. Summary of palaeohydrogeological information contained in studies of the Tono area reported before the end of 2001. Note, this table lists not only types of information that are mentioned explicitly in the referenced texts, but also information that is implicit.

Source	Type of Information																										
	Tono Mine[a]									Shobasama MIU Site									Elsewhere (See notes below)								
	Location of Recharge Zone	Timing of Recharge	Recharge Conditions (e.g. Temp, Rainfall)	Residence Time of Water in Formation	Residence Time of Solutes in Water	Timing of Flow and/or Solute Migration[b]	Identification of Groundwater Flow Paths[c]	Origins of Salinity[d]	Chemical Evolution of Groundwater	Location of Recharge Zone	Timing of Recharge	Recharge Conditions (e.g. Temp, Rainfall)	Residence Time of Water in Formation	Residence Time of Solutes in Water	Timing of Flow and/or Solute Migration[b]	Identification of Groundwater Flow Paths[c]	Origins of Salinity[d]	Chemical Evolution of Groundwater	Location	Location of Recharge Zone	Timing of Recharge	Recharge Conditions (e.g. Temp, Rainfall)	Residence Time of Water in Formation	Residence Time of Solutes in Water	Timing of Flow and/or Solute Migration[b]	Identification of Groundwater Flow Paths[c]	Origins of Salinity[d]	Chemical Evolution of Groundwater
Iwatsuki et al. 2002																			Tono Region[1] (DH-3,-5, -6,-7, -8, -9, -11)		G	G	G	G	G	G	G	G
Iwatsuki et al. 2001	M, G	A, TU, TL ,G	A, TU, TL , G	A, TU, TL , G	A, TU, TL , G	A, TU, TL , G	S, A, TU, TL , G	S, A, TU, TL , G	S, A, TU, TL , G																		
Milodowski et al. 2001						A, TU	A, TU	A, TU	A, TU						G	G	G	G									
Morikawa, 2001				S, A, TU, TL	S, A, TU, TL	S, A, TU, TL	S, A, TU, TL		S, A, TU, TL				S, A, TU, G	S, A, TU, G	S, A, TU, G	S, A, TU, G		S, A, TU, G	DH-3, DH-12, DH-13				A, TU G	A, TU G	A, TU G	A, TU G		A, TU G
Gillespie et al. 2000						TL ,G	TL ,G	TL ,G	TL ,G						G	G	G	G									
Iwatsuki et al. 2000a																			Tono Region[1] (DH-3,-5, -6,-7, -8, -9, -11)		G	G	G	G	G	G	G	G

Table 7. Continued.

Source	Type of Information: Tono Mine[a]									Shobasama MIU Site									Elsewhere (See notes below)									
	Location of Recharge Zone	Timing of Recharge	Recharge Conditions (e.g. Temp, Rainfall)	Residence Time of Water in Formation	Residence Time of Solutes in Water	Timing of Flow and/or Solute Migration[b]	Identification of Groundwater Flow Paths[c]	Origins of Salinity[d]	Chemical Evolution of Groundwater	Location of Recharge Zone	Timing of Recharge	Recharge Conditions (e.g. Temp, Rainfall)	Residence Time of Water in Formation	Residence Time of Solutes in Water	Timing of Flow and/or Solute Migration[b]	Identification of Groundwater Flow Paths[c]	Origins of Salinity[d]	Chemical Evolution of Groundwater	Location	Location of Recharge Zone	Timing of Recharge	Recharge Conditions (e.g. Temp, Rainfall)	Residence Time of Water in Formation	Residence Time of Solutes in Water	Timing of Flow and/or Solute Migration[b]	Identification of Groundwater Flow Paths[c]	Origins of Salinity[d]	Chemical Evolution of Groundwater
Iwatsuki et al. 2000b																			Tono Region[1] (DH-3, -5, -6, -7, -8)		G	G	G	G	G	G	G	G
Iwatsuki and Yoshida 1999																			DH-1, DH-2, DH-3, DH-4, AN-1		G	G	G	G	G	G	G	G
Milodowski et al. 1999						TL	TL	TL	TL																			
Iwatsuki et al. 1995				O, A, TU, TL.					O, A, TU, TL.																			
Seo & Yoshida 1994						TL	TL	S, M, G	S, M, G																			
Yoshida, 1994						TL	TL												AN-7 borehole						TL	TL		
Yoshida et al. 1994a						TL	TL																					
Yoshida et al. 1994b							TL																					
Yusa & Yoshida 1993		S, M, G	S, M, G	S, M, G	S, M, G	TL	TL	S, M, G	S, M, G																			

Table 7. Continued.

Source	Type of Information																										
	Tono Mine[a]									Shobasama MIU Site										Elsewhere (See notes below)								
	Location of Recharge Zone	Timing of Recharge	Recharge Conditions (e.g. Temp, Rainfall)	Residence Time of Water in Formation	Residence Time of Solutes in Water	Timing of Flow and/or Solute Migration[b]	Identification of Groundwater Flow Paths[c]	Origins of Salinity[d]	Chemical Evolution of Groundwater	Location of Recharge Zone	Timing of Recharge	Recharge Conditions (e.g. Temp, Rainfall)	Residence Time of Water in Formation	Residence Time of Solutes in Water	Timing of Flow and/or Solute Migration[b]	Identification of Groundwater Flow Paths[c]	Origins of Salinity[d]	Chemical Evolution of Groundwater	Location	Location of Recharge Zone	Timing of Recharge	Recharge Conditions (e.g. Temp, Rainfall)	Residence Time of Water in Formation	Residence Time of Solutes in Water	Timing of Flow and/or Solute Migration[b]	Identification of Groundwater Flow Paths[c]	Origins of Salinity[d]	Chemical Evolution of Groundwater
Mizutani et al. 1992		O, A, TU, TL, G	O, A, TU, TL, G	O, A, TU, TL, G	O, A, TU, TL, G	O, A, TU, TL, G	O, A, TU, TL, G	O, A, TU, TL, G	O, A, TU, TL, G										An-6A borehole		TU	TU	TU	TU	TU	TU	TU	TU
Nohara et al. 1992						TL	TL	S, M, G	S, M, G																			
Kanai et al. 1991					TL, G														Matsunoi-ke Nj1, Kimei 81, Kiguchi 81, Oniiwa Onsen						M, G			
Kanai et al. 1991					TL, G														Matsunoi-ke Nj1, Kimei 81, Kiguchi 81, Oniiwa Onsen						M, G			

Table 7. Continued.

Source	Type of Information																											
	Tono Mine[a]									Shobasama MIU Site									Elsewhere (See notes below)									
	Location of Recharge Zone	Timing of Recharge	Recharge Conditions (e.g. Temp, Rainfall)	Residence Time of Water in Formation	Residence Time of Solutes in Water	Timing of Flow and/or Solute Migration[b]	Identification of Groundwater Flow Paths[c]	Origins of Salinity[d]	Chemical Evolution of Groundwater	Location of Recharge Zone	Timing of Recharge	Recharge Conditions (e.g. Temp, Rainfall)	Residence Time of Water in Formation	Residence Time of Solutes in Water	Timing of Flow and/or Solute Migration	Identification of Groundwater Flow Paths	Origins of Salinity	Chemical Evolution of Groundwater	Location	Location of Recharge Zone	Timing of Recharge	Recharge Conditions (e.g. Temp, Rainfall)	Residence Time of Water in Formation	Residence Time of Solutes in Water	Timing of Flow and/or Solute Migration[b]	Identification of Groundwater Flow Paths[c]	Origins of Salinity[d]	Chemical Evolution of Groundwater
Yamakawa 1991		S, M, G	S, M, G	S, M, G		TL	TL	S, M, G	S, M, G										Tono Region[1], boreholes SN-2, AN-4 and AN-5						TL			
Kanai et al. 1990					TL, G														Matsunoi-ke N¡1, Kimei 81, Kiguchi 81, Oniiwa Onsen						M, G			
Ochiai et al. 1989		S, M, G	S, M, G	S, M, G		TL	TL	S, M, G	S, M, G																			
Sato et al. 1987		S, M, G	S, M, G	S, M, G		TL	TL	S, M, G	S, M, G										Tsukiyoshi Ore Body, boreholes SN-2, AI-12						TL			

Table 7. Continued.

S	Seto Group
M	Mizunami Group (undivided)
O	Oidawara Formation
A	Akeyo Formation
TU	Upper Toki lignite-bearing formation
TL	Lower Toki lignite-bearing formation
G	Toki Granite

References in italics are in Japanese

1 Here Region refers to the area covered by the regional geological project. Lithologies listed are a combination of all those occurring in the stated boreholes. For example, the column listing locations may contain DH-3 and DH-12. The corresponding lists of rock formations in the columns to the right could include the Toki Granite, Lower Toki Lignite, Akeyo Formation and Seto Group. In DH-3 there is only granite.

a Includes the mine compound, outside of the workings. Includes boreholes TH-1, TH-2, TH-3, TH-4, TH-6, TH-8

b Timing of flow and/or solute migration refers to evidence for the movement of water and/or solutes at some time in the past. For example, the presence of ^{14}C in calcite indicates that some of the calcite must have precipitated partly from water that recharged within the last 50,000 years. Thus, it can be concluded that groundwater flow to depth has occurred within the last 50,000 years.

c Identification of groundwater flow paths or solute migration paths refers to both macro-scale and micro-scale pathways.

d Origins of salinity means origins of past or present salinity

All references contain some new information and most also contain summaries of older information. In these cases where new and old data are summarised together, this table shows not only the new information, but also the information that is summarised. Table 6 should be consulted to determine which information is new. Documents that contain only duplicates of data or other information published elsewhere are not included in this table.

Table 8. Quantitative estimates of the timing of groundwater flow and chemical evolution in the Tono area, reported before the end of 2001. Note that only interpretations of the data actually reported in the quoted references are listed in this table.

Source	Locations studied (bold, underline constrains age)	Format -ions studied	Approx total depth range studied		Depths of smallest (s) and largest (l) age indicators		Location giving smallest (s) and largest (l) time	Formation giving smallest (s) and largest (l) time	Date	Process dated	Basis for date	Comment
			m above sea level	Equiv[1]. m below surface	m above sea level	m below surface			years			
Iwatsuki et al. 2002	**DH-5, DH-6, DH-7, DH-8, DH-9, DH-11**	G	92 to -557	184 to 897	92 to -557	184 897	N.A.	G	<50000	Fracture calcite precipitation	^{14}C of calcite	Limit only from calcite occurrence
Iwatsuki et al. 2001	**TH-3, TH-4, TH-6, TH-8**	O, A, TU, TL, G	251 to 116	46.5 to 160	209 (s) 155 (l)	104 (s) 121 (l)	TH-6 (s) TH-8 (l)	TL (s) TL (l)	4000 to 19000	Recharge	^{14}C of water	Correction made for dilution of ^{14}C by dead carbon; age s relative
Iwatsuki et al. 2000a	DH-3, **DH-5, DH-6,DH-7, DH-8, DH-9**, DH-11	G	92 to -708	183 to 978	67 to -483	203 to 802	N.A.	G	<50000	Fracture calcite precipitation	^{14}C of calcite	Limit only from calcite occurrence
Iwatsuki et al. 2000b	**DH-3,DH-5, DH-6,DH-7, DH-8**	G	148 to -708	209 to 978	148 (s) -602 (l)	209 (s) 872 (l)	N.A.	G	Modern to 14000	Recharge	^{14}C of water, Tritium	Assumes no dilution by dead carbon. Shallowest water with constraint has youngest recharge age; oldest recharge age from 873 m depth
Iwatsuki et al. 2000b	DH-3, **DH-5, DH 6,DH-7, DH-8**	G	67 to -461	203 to 780	67 to -305	203 to 624	N.A.	G	<50000	Fracture calcite precipitation	^{14}C of calcite	Limit only from calcite occurrence
Yoshida, 1994	**Tono Mine (KNA-3)**	TL	c. 150	c. 150	c. 150	c. 150	N.A.	TL	<3.5 x 10^5	U-migration	Variable $^{230}Th/^{234}U$ in minerals	Redistribution of U possibly only mineral grain-scale

Table 8. Continued.

Source	Locations studied (bold, underline constrains age)	Format -ions studied	Approx total depth range studied		Depths of smallest (s) and largest (l) age indicators		Location giving smallest (s) and largest (l) time	Formation giving smallest (s) and largest (l) time	Date	Process dated	Basis for date	Comment
			m above sea level	Equiv[1]. m below surface	m above sea level	m below surface			years			
Yoshida, 1994	**Tono Mine (KNA-3)**	TL	c. 150	c. 150	c. 150	c. 150	N.A.	TL	$<10^4$	Ra-migration	Variable $^{226}Ra/^{234}U$ in minerals	Redistribution of Ra, possibly only mineral grain-scale
Yoshida et al. 1994a	**Tono Mine (KNA-3) and AN-7**	TL	c. 150	c. 150	c. 150	c. 150	N.A.	TL	$>10^6$	U-migration	U-series isotope ratios c. 1 in rock	Possible limit on large-scale migration
Yoshida et al. 1994a	**Tono Mine (KNA-3) and AN-7**	TL	c. 150	c. 150	c. 150	c. 150	N.A.	TL	$< 3 \times 10^5$	U-migration	Variable $^{234}U/^{238}U$ and $^{230}U/^{238}U$ in minerals	Redistribution of U possibly only mineral grain-scale
Yusa et al. 1993	**Tono Mine (Gallery, c. 75 m from N¡1 drfit), SN-2, AI-12**	TL	c. 150	c. 150	c. 150	c. 150	N.A.	TL	$>10^6$	U-migration	U-series isotope ratios average c. 1 in rock	Possible limit on large-scale migration only — possibly only small-scale
Yusa et al. 1993	**Tono Mine (unstated)**	TL	c. 150	c. 150	c. 150	c. 150	N.A.	TL	$<10^6$	Ra-migration	Variable $^{226}Ra/^{238}U$	Possible limit on large-scale migration only — possibly only small-scale

Table 8. Continued.

Source	Locations studied (bold, underline constrains age)	Format -ions studied	Approx total depth range studied		Depths of smallest (s) and largest (l) age indicators		Location giving smallest (s) and largest (l) time	Formation giving smallest (s) and largest (l) time	Date	Process dated	Basis for date	Comment
			m above sea level	Equiv[1]. m below surface	m above sea level	m below surface			years			
Mizutani et al. 1992	**Tono Mine and AN-6A**	O, A, TU, TL, G	248 to 116	29 to 160	240 (s) c.160 (l)	14 (s) c.130 (l)	AN-6 (s) KS-1/ KNA-1 (l)	A/TU (s) TL (l)	c. 400 to c. 3400 and c. 14000 to c. 22000	Recharge	^{14}C analyses of water	Minimum and maximum ages are themselves given as ranges, reflecting the dependency of the ages on correction method
Nohara et al. 1992	**Tono Mine (unstated), and area near mine**	TL	c. 150	c. 150	c. 150	c. 150	N.A.	TL	$<10^6$	U-migration	Variable $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ in rock	Possible limit on large-scale migration only — possibly only small-scale
Nohara et al. 1992	**Tono Mine (unstated), and area near mine**	TL	c. 150	c. 150	c. 150	c. 150	N.A.	TL	$<10^6$	Ra-migration	Variable $^{226}Ra/^{230Th}$ in rock	Possible limit on large-scale migration only — possibly only small-scale
Yamakawa, 1991	**Tono Mine (unstated), and area near mine**	TL	c. 150	c. 150	c. 150	c. 150	N.A.	TL	$<10^6$	U-migration	Variable $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ in rock	Possible limit on large-scale migration only — possibly only small-scale
Yamakawa, 1991	**Tono Mine (unstated), and area near mine**	TL	c. 150	c. 150	c. 150	c. 150	N.A.	TL	$<10^6$	Ra-migration	Variable $^{226}Ra/^{238}U$ in rock	Possible limit on large-scale migration only — possibly only small-scale

Table 8. Continued.

Source	Locations studied (bold, underline constrains age)	Format -ions studied	Approx total depth range studied		Depths of smallest (s) and largest (l) age indicators		Location giving smallest (s) and largest (l) time	Formation giving smallest (s) and largest (l) time	Date	Process dated	Basis for date	Comment
			m above sea level	Equiv[1]. m below surface	m above sea level	m below surface			years			
Ochiai et al. 1989	Not reported	TL	N.R.	N.R.	N.R.	N.R.	N.A.	T.L.	c. 10^7	Fission Track on Zircon	U-ore deposit formed	May or may not be representative of entire deposit.
Sato et al. 1987	Tono Mine (Gallery, c. 75 m from N¡1 drfit), SN-2, AI-12	TL	c. 150	c. 150	c. 150	c. 150	N.A.	TL	$>10^6$	U-migration	U-series isotope ratios average c. 1 in rock	Possible limit on large-scale migration only
Sato et al. 1987	Tono Mine (Surface, N¡1 Shaft, Gallery)	S, O, A, TU, TL, G	c. 270 to c. 150	c. 0 to c. 150	> c. 260 (s) <c. 260 (l)	< c. 40 (s) >c. 40 (l)	Surface, N¡1 Shaft (s) Gallery (l)	S	< 40 to >40	Recharge	Tritium	Limit only from Tritium above detection

Table 8. Continued.

N.R. Not Reported
N.A. Not Applicable

1 These depths relative to the surface correspond to the elevations relative to sea level quoted in the column to the left. Owing to differences in surface elevation from place to place, this means that this column does not necessarily contain the overall depth range; a sample that is a relatively close to sea level is not necessarily from further below the surface than a sample at a higher elevation.

S Seto Group
O Oidawara Formation
A Akeyo Formation
TU Upper Toki lignite-bearing formation
TL Lower Toki lignite-bearing formation
G Toki Granite

References in italics are in Japanese

This table gives only apparently new interpretations of data in published sources, whether or not those data are newly reported in the same source as the interpretation or a summary of data reported earlier. Where an interpretation appears in several sources, only the earliest source is referenced. It is recognised that even these documents are not necessarily the original sources of the interpretations, which may appear in unpublished reports or Japanese language publications not available to the author. Where the referenced source is in English, this situation almost certainly occurs.

Table 9. Summary of stable isotopic compositions for groundwaters from the Tono area, based on data available at the end of 2001.

Water	Mean Values	
	δD	$\delta^{18}O$
	‰SMOW	‰SMOW
Rain Water	-55.6	-9.4
River Water	-52.5	-8.4
Sedimentary Rocks	-55.4	-8.5
Granite	-54.3	-8.4

(Means exclude those Tono Mine samples for which sampled lithologies not recorded).

Table 10. Summary data describing the Tsukiyoshi Fault in the boreholes examined, as available at the start of October 2001. Information taken mainly from British Geological Survey Technical Reports Gillespie et al. (2000) and Milodowski et al. (2001). See Appendix 5 for information about specific fault rock intersections.

Borehole	Nominal Borehole/Shaft orientation	Direction	Depth interval logged	Approx dip of fault plane, from horizontal		Top unconformity between Toki Granite and Sedimentary Rocks		Bottom unconformity between Toki Granite and Sedimentary Rocks		Main fault		Less Prominent fault		Overall envelope of strain indicators observed in vertical direction		Overall envelope of fault indicators (strain plus mineralisation) observed in vertical direction		Comments
			m along borehole	Magnitude (°)	Direction	m below surface	m relative to sea level	m below surface	m relative to sea level	m below surface	m relative to sea level	m below surface	m relative to sea level	m below surface	m relative to sea level	m below surface	m relative to sea level	
TM-2	Vertical	N/A	97 to 137	65 to 70	Southerly	Not seen	Not seen	130	125	118 to 124	138 to 131	103 to 103	152 to 152	103 to 124	152 to 131	103 to 124	152 to 131	
98FE-01	Vertical	N/A	90 to150	65 to 70	Southerly	100	168	139	137	107 to116	168 to 159	100 to 102	175 to 173	100 to 149	175 to 126	90 to 149	185 to 126	
KNA-6	Vertical	N/A	160 to 89	65 to 70	Southerly	Not calculated	158	Not calculated	125	Not calculated	127	None logged	N/A	Information for Main Fault Only	N/A	Information for Main Fault Only	N/A	Core inadequate quality to enable detailed logging of the full interval
SHAFT 2	Vertical	N/A	Not logged - records only examined	c. 60	Southerly	Shaft above unconformity	N/A	Shaft above unconformity	N/A	c.141	c.146	None logged	N/A	Information for Main Fault Only	N/A	Information for Main Fault Only	N/A	
TH-1	Vertical	N/A	127 to 182	60 to 65?	Southerly	166	121	Not seen	Not seen	179 to 182	108 to 105	148 to 149	139 to 138	127 to 182	160 to 105	127 to 182	160 to 105	
TH-2	Vertical	N/A	103 to 178	60 to 65?	Southerly	c.171	c.120	Not seen	Not seen	171 to 175	119 to 116	146 to 147	144 to 143	106 to 178	184 to 112	106 to 178	184 to 112	
TH-3	Vertical	N/A	129 to 201	60 to 65?	Southerly	160	138	c.177	c.122	188 to 192	110 to 107	171 to 173	128 to 126	129 to 196	170 to 103	129 to 196	170 to 103	
Gallery	N/A	N/A	Not logged, observations near main fault plane only	c. 60	Southerly	Gallery above unconformity	N/A	Gallery above unconformity	N/A	Not calculated	c.162	Main fault only seen	N/A	Information for Main Fault Only	N/A	Information for Main Fault Only	N/A	
98SI-03	5° Below Horizontal	Drilled southwards	18	c. 60	Southerly	Borehole entirely within sedimentary sequence	N/A	Borehole entirely within sedimentary sequence	N/A	Not calculated	c.162 to 158	Not calculated	c.155 to 151	Not calculated	c.162 to 149	Not calculated	c.162 to 149	
MIU2	Vertical	N/A	865 to 925	70 to 80	Southerly	Logged section entirely in granite	N/A	Logged section entirely in granite	N/A	911 to 915	-691 to -687	889 to 891 and 905 to 906	-665 to -667 and -681 to -682	865 to 925	-641 to -701	865 to 925	-641 to -701	Full interval of the fault not logged. Widest interval is interpreted to be the main fault. This is also the deepest interval. Within the interval for 'minor fault-rocks' are actually two intervals of faulting.
MIU3	Vertical	N/A	499 to 723	65 to 80	Southerly	Logged section entirely in granite	N/A	Logged section entirely in granite	N/A	704 to 707	-477 to -474	At least 10 fault strands within logged interval	At least 10 fault strands within logged interval	699 to 840	-487 to -610	699 to 840	-487 to -610	Not yet reported, preliminary observations only.
99SI-08	55° Below Horizontal	Drilled northwards	0 to 82	c. 60	Southerly	Borehole entirely within sedimentary sequence	N/A	Borehole entirely within sedimentary sequence	N/A	41 to 58	229 to 246	81 to 85	206 to 202	41 to 98	246 to 189	41 to 98	246 to 189	

NOTE: Depths have all been rounded to the nearest metre.
Where necessary, widths of the fault zone have been recalculated to be given in the vertical direction, rather than along a borehole axis.
Data shown were the latest available on 19/10/01

Table 11. Summary, simplified history of the Tsukiyoshi Fault, based on Milodowski et al. (2001, 1999) and Gillespie et al. (2000).

General Sequence	Features common throughout the fault	Features unique to granite	Features common to sediments, but not in granite	Features seen only in Toki Formation	Features seen only in Akeyo Formation
Oldest		Quartz, K-feldspar, albite, chlorite, epidote, fluorite, sphalerite, galena, annealed granulation seams			
			Early diagenetic alteration of glass to zeolite and smectite		
			Early diagenetic formation of pyrite		
				Formation of authigenic kaolinite	
				Major plastic deformation indicative of compaction	
	Main phase of faulting in sediments inferred to have been accompanied by at least some faulting in the granite				
					Fracture dilation and precipitation of traces of REE phosphate (possibly rhabdophane) in thin veinlets
			Evidence for post-main faulting fracture dilation with fluid flow (veining)	Dissolution of feldspar and smectite, replacement of smectite adjacent to fractures by Mg-chlorite	
	Evidence for post-main faulting episodic movement of over-pressured fluids through fault rocks (e.g. injection sediments in the Toki Granite and in the Akeyo Formation, cross-fibre calcite in the base of the Toki Formation)	Calcite, sericite vein mineralisation			
				A later generation of dilational calcite veining followed the fibre calcite veins but is relatively minor. This locally cuts the earlier calcite fabrics and is associated with minor zeolite and pyrite mineralisation.	
					Dissolution of pumice + smectite formation, possibly associated with bacterial activity and framboidal pyrite formation. This was possibly concurrent with the formation of pyrite in the injection sediments (see below) but the relationship is unclear. Major secondary porosity formation.
		Major host rock alteration. Smectite formation, Dissolution of plagioclase and alteration of biotite. Major secondary porosity generation.			
	Precipitation of calcite in open porosity (accompanied by smectite formation, and feldspar dissolution in the Toki Granite and Toki Formation and by pyrite formation in the Toki Granite only)				
					Late stage oxidation of pyrite locally in injection-sediment-filled fractures, and formation of secondary gypsum and iron oxides alteration products. This may be ongoing.
Youngest					

Table 12. Locations of groundwater samples for which both Br and Cl concentrations were reported to be above their respective detection limits (all data available on 2/10/01); compositions given in Table 13.

Location	Min.Depth mbgl	Max.Depth mbgl	Max. Elevation masl	Min. Elevation masl	Sampling or Analyzing Date	Temp. degC
Shizuhoragawa	N.R.	N.R.	N.R.	N.R.	29/8/88	N.R.
Takasago Onsen	N.R.	N.R.	N.R.	N.R.	2001.3.2	29.7
DH-4	185.5	188.5	81.08	78.08	1995.4.18	13..0
DH-12	345.90	387.18	-208.52	-249.79	2000.12.19	25.2
DH-12	388.90	429.68	-251.52	-292.29	2000.12.7	25.7
G 54	N.R.	101	132.6	N.R.	31/3/98	N.R.
G 55	N.R.	155	132.5	N.R.	30/3/98	N.R.
G 55	N.R.	155	132.5	N.R.	2/9/88	N.R.
G 58	N.R.	133	128.4	N.R.	26/3/98	N.R.
G 69	N.R.	317	157.8	N.R.	30/3/98	N.R.
G 69	N.R.	317	157.8	N.R.	13/9/88	N.R.
G 81	N.R.	261	137.6	N.R.	14/8/98	N.R.
G 81	N.R.	261	137.6	N.R.	9/9/88	N.R.
G 87	N.R.	200	190.0	N.R.	30/3/98	N.R.
G 87	N.R.	200	190.0	N.R.	2/9/88	N.R.
K 2	N.R.	53	134.6	N.R.	31/3/98	N.R.
MS 183	N.R.	131	229.2	N.R.	26/8/88	N.R.
MS 30	N.R.	148	167.4	N.R.	26/8/88	N.R.
MS 34	N.R.	219	158.2	N.R.	26/8/88	N.R.
S 116	N.R.	172	147.0	N.R.	23/3/98	N.R.
S 121	N.R.	96	142.8	N.R.	23/3/98	N.R.
S 121	N.R.	96	142.8	N.R.	29/8/88	N.R.
S 126	N.R.	38	147.7	N.R.	23/3/98	N.R.
S 128	N.R.	109	141.7	N.R.	23/3/98	N.R.
S 128	N.R.	109	141.7	N.R.	29/8/88	N.R.
Z 3	N.R.	63	145.3	N.R.	2/9/88	N.R.
Z 13	N.R.	105	151.1	N.R.	23/3/98	N.R.
Z 13	N.R.	105	151.1	N.R.	9/9/88	N.R.
Z 40	N.R.	185	144.1	N.R.	23/3/98	N.R.
Z 40	N.R.	185	144.1	N.R.	2/9/88	N.R.
Z 41	N.R.	195	159.7	N.R.	27/8/88	N.R.

Table 13. Compositions of groundwaters for which both Br and Cl were given (all data available on 2/10/01).

Location	pH	Na^+ ppm	K^+ ppm	Ca^{2+} ppm	Mg^{2+} ppm	IC ppm	F^- ppm	Cl^- ppm	Br^- ppm	Br/Cl Mass	Mg/Ca Mass	Na/Ca Mass	Na/K Mass
Shizuhoragawa	6.6	N.R.	N.R.	N.R.	N.R.	N.R.	0.04	1.7	0.02	1.18E-02	N.A.	N.A.	N.A.
Takasago Onsen	7.6	408	1.5	225	<0.2	1.8	7.30	916	2.2	2.40E-03	N.A.	2	272
DH-4	6.8	13.3	6.13	17.6	1.88	N.R.	4.99	2.74	0.08	2.92E-02	1.07E-01	1	2
DH-12	8.9	81.5	0.91	25.6	<0.2	3.82	9.79	137	0.32	2.34E-03	N.A.	3	90
DH-12	8.9	94.9	0.89	32.4	<0.2	3.13	9.40	175	0.37	2.11E-03	N.A.	3	107
G 54	9.0	168	0.56	13.52	0.03	N.R.	11.6	159.6	0.44	2.76E-03	2.22E-03	12	300
G 55	9.3	156	0.52	16.72	0.03	N.R.	10.2	202.9	0.52	2.56E-03	1.79E-03	9	300
G 55	9.2	N.R.	N.R.	N.R.	N.R.	N.R.	11.4	270.0	0.52	1.93E-03	N.A.	N.A.	N.A.
G 58	8.7	213	2.25	21.25	0.49	N.R.	8.25	295.8	0.73	2.47E-03	2.31E-02	10	95
G 69	9.4	141	0.91	2.41	0.05	N.R.	20.2	124.4	0.32	2.57E-03	2.07E-02	59	155
G 69	9.5	N.R.	N.R.	N.R.	N.R.	N.R.	20.9	177	0.25	1.41E-03	N.A.	N.A.	N.A.
G 81	8.6	288	1.90	93.5	0.37	N.R.	6.62	538	1.09	2.03E-03	3.96E-03	3	152
G 81	8.8	N.R.	N.R.	N.R.	N.R.	N.R.	8.6	600	0.79	1.32E-03	N.A.	N.A.	N.A.
G 87	9.8	58.0	0.35	1.73	<0.01	N.R.	15	17.7	0.04	2.26E-03	N.A.	34	166
G 87	9.8	N.R.	N.R.	N.R.	N.R.	N.R.	15.2	35.8	0.05	1.40E-03	N.A.	N.A.	N.A.
K 2	8.7	56.0	0.40	7.32	0.05	N.R.	11.3	35.2	0.08	2.27E-03	6.83E-03	8	140
MS 183	8.5	N.R.	N.R.	N.R.	N.R.	N.R.	2.94	1.0	0.02	2.04E-02	N.A.	N.A.	N.A.
MS 30	9.2	N.R.	N.R.	N.R.	N.R.	N.R.	8.54	3.0	0.01	3.37E-03	N.A.	N.A.	N.A.
MS 34	9.3	N.R.	N.R.	N.R.	N.R.	N.R.	16	6.6	0.01	1.53E-03	N.A.	N.A.	N.A.
S 116	9.3	41.3	0.51	1.59	0.02	N.R.	8.73	9.22	0.02	2.17E-03	1.19E-02	26	81
S 121	8.7	55.0	0.50	16.24	0.07	N.R.	5.96	76.9	0.13	1.69E-03	4.31E-03	3	110
S 121	8.7	N.R.	N.R.	N.R.	N.R.	N.R.	5.48	96.1	0.13	1.35E-03	N.A.	N.A.	N.A.
S 126	8.9	40.0	0.36	6.27	0.03	N.R.	8.77	9.5	0.03	3.15E-03	4.78E-03	6	111
S 128	9.2	75.5	0.76	3.91	0.03	N.R.	15.5	27.6	0.06	2.18E-03	7.67E-03	19	99
S 128	9.3	N.R.	N.R.	N.R.	N.R.	N.R.	14.8	36.8	0.05	1.36E-03	N.A.	N.A.	N.A.
Z 3	8.7	N.R.	N.R.	N.R.	N.R.	N.R.	8.26	56.7	0.08	1.41E-03	N.A.	N.A.	N.A.
Z 13	9.4	66.5	0.40	5.99	0.03	N.R.	10.3	73.2	0.13	1.78E-03	5.01E-03	11	166
Z 13	9.4	N.R.	N.R.	N.R.	N.R.	N.R.	11.3	54.7	0.07	1.28E-03	N.A.	N.A.	N.A.
Z 40	9.2	71.0	0.42	5.95	0.02	N.R.	13.8	76.0	0.13	1.71E-03	3.36E-03	12	169
Z 40	9.3	N.R.	N.R.	N.R.	N.R.	N.R.	12.8	74.8	0.12	1.60E-03	N.A.	N.A.	N.A.
Z 41	9.5	N.R.	N.R.	N.R.	N.R.	N.R.	19.1	104	0.29	2.79E-03	N.A.	N.A.	N.A.

Table 14. Estimated in-situ equilibrium $^{36}Cl/Cl$ ratios for different rock formations in the Tono area. Values are approximate owing to a lack of data required to make precise estimates.

		Formation							
		Oidawara	**Akeyo**	**Toki (upper)**	**Toki (lower)**	**Toki (lower)**	**Toki (lower)**	**Toki Granite**	**Toki Granite**
Location		Borehole SN-5	Borehole SN-5	Borehole TH-3	No.2 Shaft	No.2 Shaft	Borehole KNA-6	Borehole KNA-6	Borehole AN-1
Depth[1]	m	247.5	218.5	211	146	139	30.8	76.7	-114.1
Lithology		Tuffaceous siltstone	Tuffaceous medium sandstone	Tuffaceous mudstone	Arkosic fine-medium sandstone	Tuffaceous silt - fine sandstone (Approx Level of Ore Deposit)	Sandstone	Granite	Medium grained biotite granite
Source of Rock Analysis Data Used in Calculation		Yoshida et al. 1994	Yoshida et al. 1994	Yoshida et al. 1994	Yoshida et al. 1994	Yoshida et al. 1994	Tech Note 96-01	Tech Note 96-01	Yoshida et al. 1994
Approximate Equilibrium $^{36}Cl/Cl$ * 10^{-15}	Atomic Ratio	13	7	2	30501	163072	1812	217	45

Notes:

1. The data sources do not give a depth range. The depth quoted here is the only one given for each rock sample.

Sources

The whole-rock analytical data used in the calculations were obtained from the following sources:

Yoshida, H., Seo, T., Nohara, T., Ota, K., Hama, K., Kodama, K. and Iwatsuki, T. 1994. Data compilation of geoscientific studies of Tono uranium deposits, Central Japan. PNC Report TN7410 94-015.

Tech Note 96-01, 1996: Tono Natural Analogue Programme (PNC/NAGRA) - data compilation of field and lab activities June 1995-May 1996.

Table 15. Summary details of samples from the preliminary study in borehole KNA-6.

Sample	G-1	G-2	TL/G-1	TL/G-2
Comments	-	-	Duplicate analyses of same sample	
Sampled interval (m from top of borehole)	50.50 to 101.00	50.50 to 101.00	43.50 to 46.00	43.50 to 46.00
Lithology from which water sampled	Toki Granite	Toki Granite	Lower Toki Formation	Lower Toki Formation

Table 16. Summary of the rock compositions used to model equilibrium $^{36}Cl/Cl$ ratios (see next page for explanation).

Location		KNA-6		KNA-6		KNA-6		KNA-6		KNA-6		KNA-6		98FE-01		KNA-6		No.2 Shaft	
Model		26/1a		54/1a		66/1a		76/1a		89/1a		101/1a		1a		30/1a		139/1a	
Depth from Borehole Top		26.7		54.9		66.0		76.7		89.2		101.0		125.07 to 125.23		30.8		139.0	
Lithology		FG		WG		G		G		G		G		P/GC		Sst		S/FSst	
Element	Units	Conc^n	Source	Conc^n	Source	Conc^n	Source	Conc^n	Source	Conc^n	Source	Conc^n	Source	Conc^n	Source	Conc^n	Source	Conc^n	Source
Si	wt%	34.82	1	33.92	9	34.49	10	34.69	11	35.44	12	35.22	13	29.64	14	22.04	19	21.17	21
Ti	wt%	0.09	1	0.14	9	0.11	10	0.11	11	0.13	12	0.09	13	0.16	14	0.62	19	0.65	21
Al	wt%	6.67	1	7.13	9	7.07	10	6.89	11	7.14	12	6.78	13	7.20	14	8.87	19	9.24	21
Fe	wt%	1.54	1	1.83	9	1.32	10	1.40	11	0.54	12	1.21	13	2.43	14	4.83	19	2.62	21
Mn	wt%	0.04	1	0.04	9	0.04	10	0.04	11	0.04	12	0.05	13	0.03	14	0.04	19	0.04	21
Mg	wt%	0.26	1	0.25	9	0.16	10	0.19	11	0.11	12	0.18	13	0.54	14	1.44	19	0.63	21
Ca	wt%	0.35	1	0.76	9	0.46	10	0.79	11	0.09	12	1.04	13	0.66	14	8.12	19	5.24	21
Na	wt%	1.85	1	2.33	9	2.20	10	2.20	11	1.96	12	2.20	13	1.85	14	1.74	19	1.53	21
K	wt%	3.52	1	3.98	9	4.07	10	3.83	11	4.20	12	3.83	13	3.52	14	0.81	19	0.92	21
O	wt%	48.94	1	48.19	9	48.37	10	48.54	11	48.99	12	49.11	13	52.54	15	49.78	19	47.11	21
C	wt%	1.15	1	0.14	9	0.14	10	0.14	11	0.14	12	0.14	13	1.15	16	1.15	19	0.09	21
Cl	ppm	22	2	22	2	22	2	22	2	22	2	22	2	526	20	526	20	526	20
F	ppm	440	3	440	3	440	3	440	3	440	3	440	3	1000	17	1000	17	1000	17
Cr	ppm	10.3	4	10.3	4	10.3	4	10.3	4	10.3	4	10.3	4	22	14	22	14	119	22
Co	ppm	0.4	5	0.4	5	0.4	5	0.4	5	0.4	5	0.4	5	4	14	4	14	60	23
Ni	ppm	4	6	4	6	4	6	4	6	4	6	4	6	3	14	3	14	69	24
Sm	ppm	3.7	7	3.7	7	3.7	7	3.7	7	3.7	7	3.7	7	2.9	14	2.9	14	2.9	14
Gd	ppm	12.9	3	12.9	3	12.9	3	12.9	3	12.9	3	12.9	3	3.15	14	3.15	14	3.15	14
Be	ppm	5.5	3	5.5	3	5.5	3	5.5	3	5.5	3	5.5	3	3	18	3	18	3	18
N	ppm	20	3	20	3	20	3	20	3	20	3	20	3	600	18	600	18	600	18
Li	ppm	11	3	11	3	11	3	11	3	11	3	11	3	60	18	60	18	60	18
B	ppm	4	3	4	3	4	3	4	3	4	3	4	3	100	18	100	18	100	18
U	ppm	3.6	1	5.74	9	102	10	73.77	11	14.1	12	5.4	13	247	14	495	19	45000	21
Th	ppm	96	8	96	8	96	8	96	8	96	8	96	8	11.3	14	11.3	14	11.3	14
Total:	wt%	99.29		98.8		98.5		98.9		98.9		99.9		99.9		99.7		94.0	

Explanation of Table 16.

Shaded numbers are analyses actually reported for the rock being modelled; non-shaded numbers are analyses of similar rocks, which are used for calculations where actual data are not reported.

Abbreviations

Models with numbers ending in 'a' used exactly the same rock compositions as those reported in Table 16. Models with numbers ending in other letters were the same except for the specified changes in the table.

FG	Fractured Granite
WG	Weathered Granite
G	Granite
P/GC	Pebble/Gravel Conglomerate
Sst	Sandstone
S/FSst	Silt/Fine Sandstone
N/A	Not applicable

Data Sources

1 Analysis reported in JNC report TN96-01 for granite from 26.7 m in KNA-6
2 Cl reported for Toki Granite in AN-1, from an elevation of 30.2 m, in report PNC TN7410 94-015
3 Analyses reported for the Stripa Granite, Sweden in Andrews et al. 1989
4 Cr reported for Toki Granite in AN-1, from an elevation of -114.1 m, in report PNC TN7410 94-015
5 Co reported for Toki Granite in AN-1, from an elevation of -114.1 m, in report PNC TN7410 94-015
6 Ni reported for Toki Granite in AN-1, from an elevation of -114.1 m, in report PNC TN7410 94-015
7 Sm reported for Toki Granite in AN-1, from an elevation of -114.1 m, in report PNC TN7410 94-015
8 Maximum value reported for the Toki Granite in borehole DH-10 in TGRP hydrochemical database
9 Analysis reported in JNC report TN96-01 for granite from 54.9 m in KNA-6
10 Analysis reported in JNC report TN96-01 for granite from 66.0 m in KNA-6
11 Analysis reported in JNC report TN96-01 for granite from 76.7 m in KNA-6
12 Analysis reported in JNC report TN96-01 for granite from 89.2 m in KNA-6
13 Analysis reported in JNC report TN96-01 for granite from 101.0 m in KNA-6
14 Analysis reported in Excel file TFWRanalyses06546v2.xls, sample 98FE-01/7, supplied by BGS
15 Set to include H2O, such that total close to 100% is obtained, using reasonable maximum value for H2O in sandstone from KNA-6 in TN96-01
16 Value chosen to be near maximum reported for sandstone in TN96-01 and to give a total close to 100%
17 F reported for Lower Toki Formation in No.2 shaft from an elevation of 146m, in report PNC TN7410 94-015
18 Data for mean granite or shale/mudstone (as appropriate for rock type) Smith (1986)
19 Analysis reported in JNC report TN96-01 for sandstone from 30.8 m in KNA-6
20 Cl reported for Lower Toki Formation in KNA-3 from an elevation of 123 m, in report PNC TN7410 94-015
21 Analysis reported for Lower Toki Formation at an elevation of 139 m, No. 2 Shaft, in report PNC TN7410 94-015
22 Cr reported for Lower Toki Formation in No.2 shaft from an elevation of 146m, in report PNC TN7410 94-015
23 Co reported for Lower Toki Formation in No.2 shaft from an elevation of 146m, in report PNC TN7410 94-015
24 Ni reported for Lower Toki Formation in No.2 shaft from an elevation of 146m, in report PNC TN7410 94-015

Table 17. Raw $^{36}Cl/Cl$ ratios, with errors, and cycle numbers for each sample, reported by PRIME Lab. A 'Cycle' refers to a single measurement of an isotope ratio and a group of cycles on one sample is called a 'sequence'. During a cycle the stable isotope beam current and radionuclide beam current are alternated to obtain the $^{36}Cl/Cl$ ratio.

Run Letter and Cycle	Date	No. of Cycles Measured in a Sequence	Interference for ^{36}S Counts Per Second (cps)	Measured Background $^{36}Cl/Cl$ in Previous Blank Measured x 10^{-15}	Default Background Actually Subtracted for this Sample x 10^{-15}	Normalised Sample $^{36}Cl/Cl$ x 10^{-15}	Absolute 1_error on $^{36}Cl/Cl$ x 10^{-15}	% 1_ Error on $^{36}Cl/Cl$
G-1								
JQ2268	1/8/00	2	7123	6.97	3.00	110.2	+/-13.6	12%
JQ2291	1/8/00	2	3101	9.41	3.00	122.6	+/11.2	9.2%
JQ2314	1/8/00	2	41E3	4.32	3.00	110.8	+/-17.5	16%
JQ2320	1/8/00	2	1657	4.32	3.00	110.5	+/-13.0	12%
G-2								
JQ2265	1/8/00	2	8170	6.97	3.00	113.9	+/-14.5	13%
JQ2288	1/8/00	2	4229	9.41	3.00	107.1	+/-12.1	11%
JQ2305	1/8/00	2	3482	4.32	3.00	110.5	+/-10.7	9.6%
JQ2317	1/8/00	2	2550	4.32	3.00	117.1	+/-11.0	9.4%
TL/G-1								
JQ2262	1/8/00	2	3003	6.97	3.00	151.1	+/-11.7	7.7%
JQ2285	1/8/00	2	2081	9.41	3.00	151.0	+/-12.7	8.4%
JQ2311	1/8/00	2	2662	4.32	3.00	152.3	+/-12.8	8.4%
TLG-2								
JQ2255	1/8/00	2	2608	6.97	3.00	143.2	+/-11.6	8.1%
JQ2279	1/8/00	2	3482	9.41	3.00	137.3	+/-11.1	8.1%
JQ2302	1/8/00	2	3320	4.32	3.00	114.8	+/-11.8	10%

Table 18. Summary of mean $^{36}Cl/Cl$ ratios, with errors, for each sample, as reported before 1st August 2000.

Sample	G-1	G-2	TL/G-1	TL/G-2
Comments	-	-	Duplicate analyses of same sample	
Sampled interval (m from top of borehole)	50.50 to 101.00	50.50 to 101.00	43.50 to 46.00	43.50 to 46.00
Lithology from which water sampled	Toki Granite	Toki Granite	Lower Toki Formation	Lower Toki Formation
$^{36}Cl/Cl$ (atomic ratio) $x10^{-15}$	115	112.1	151	132
Error (1σ) $x10^{-15}$	7	5.9	7	7
Relative error (1σ %)	6.1	5.3	4.6	5.3

Table 19. Modelled equilibrium $^{36}Cl/Cl$ Atomic Ratio x 10^{-15}, based on data available on 1/8/01.

Details of Rocks Used as Basis of Calculations

Borehole/ Locality	KNA-6	KNA-6	KNA-6	KNA-6	KNA-6	KNA-6	KNA-6	KNA-6	98FE-01	98FE-01	KNA-6	No.2 Shaft
Lithology	FG	FG	FG	WG	G	G	G	G	P/GC	P/GC	Sst	S/FSst
Depth From Top Borehole/ Shaft	26.7	26.7	26.7	54.9	66.0	76.7	89.2	101.0	125.07 to 125.23	125.07 to 125.23	30.8	139.0

Equilibrium in-growth in water

Rock No.	26/1a	26/1a	26/1b	54/1a	66/1a	76/1a	89/1a	101/1a	1a	1a	30/1a	139/1a
Difference from XX/1a	N/A	N/A	Th Min for DH-10	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Cl in water (mg/l)	1	5	1	1	1	1	1	1	1	1	1	1
Porosity	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.3	0.1	0.3	0.3
$^{36}Cl/Cl$ x 10^{-15}	63	63	11	89	337	267	111	91	308	387	376	‡ 29571

Equilibrium in rock matrix

Rock No.	26/1a	26/1b	26/1c	54/1a	66/1a	76/1a	89/1a	101/1a	1a	1a	30/1a	139/1a
Difference from XX/1a	N/A	Th = Min DH-10 Cl = 1 ppm	Cl = 1 ppm	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Cl in water (mg/l)	1	1	1	1	1	1	1	1	1	N/A	1	1
Porosity	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.3	0*	0.3	0.3

Production of ^{36}Cl from Kα-n is neglected

$^{36}Cl/Cl$ x 10^{-15}	63	11	63	89	337	267	111	91	308	423	376	‡ 29571

Production of ^{36}Cl from Kα-n is included

$^{36}Cl/Cl$ x 10^{-15}	64	11	87	93	345	278	112	96	309	423	383	‡ 29893

See next page for explanation of terms

FG	Fractured Granite
WG	Weathered Granite
G	Granite
P/GC	Pebble/Gravel Conglomerate
Sst	Sandstone
S/FSst	Silt/Fine Sandstone
N/A	Not applicable

‡ Calculated using the largest U concentration reported for the Toki Formation in PNC (1994).
*Rock matrix only considered

Table 20. Summary of all ^{36}Cl data for groundwaters from the Tono area and analyses for other halides in the same samples, as available on 20/9/01.

Water Description	Location	Depth mbgl		Elevation masl		Lithology	$^{36}Cl/Cl$ Atomic Ratio		Cl ppm		Br ppm		F ppm	
		Minimum	Maximum	Minimum	Maximum		Estimate	2σ Error	Estimate	2σ Error	Estimate	2σ Error	Estimate	2σ Error
Shobagawa River Water	MIU-site, Shobagawa river	0	0	c. 210	c. 210	Runs over Akeyo Formation	409	36	1	N.R.	N.R.	N.R.	N.R.	N.R.
MIU-4 Water	Borehole MIU-4	71.45	76.77	145.54	140.22	Toki Lignite Formation	131	16	1.03	0.02	<0.1	0.02	6.67	0.02
MIU-4 Water	Borehole MIU-4	82.29	116.45	134.70	100.54	Toki Granite	141	14	0.86	0.02	<0.1	0.01	11.05	0.01
MIU-4 Water	Borehole MIU-4	272.75	274.49	-55.76	-57.50	Toki Granite	141	18	1.07	0.02	<0.1	0.02	11.95	0.02
DH-12 Water	Borehole DH-12	157.45	164.12	-20.07	-26.74	Toki Lignite (Conglomerate)	42	12	53.3	N.R.	<0.2	N.R.	14.8	N.R.
DH-12 Water	Borehole DH-12	279.40	344.67	-142.02	-207.29	Granite	41.6	11	99.9	N.R.	<0.2	N.R.	10.0	N.R.
DH-12 Water	Borehole DH-12	431.42	472.50	-294.04	-335.12	Granite	43	20	72.1	N.R.	<0.2	N.R.	12.8	N.R.
Water TLG/1 - Duplicate 1	Borehole KNA-6	157.76	159.53	129.10	127.33	Granite/Sediment	151	14	0.795	N.R.	<0.2	N.R.	4.35	N.R.
Water TLG/1 - Duplicate 2	Borehole KNA-6	157.76	159.53	129.10	127.33	Granite/Sediment	132	14	0.795	N.R.	<0.2	N.R.	4.35	N.R.
Water G-1	Borehole KNA-6	162.71	198.42	124.15	88.44	Granite	115	14	0.845	N.R.	<0.2	N.R.	3.73	N.R.
Water G-2	Borehole KNA-6	162.71	198.42	124.15	88.44	Granite	112.1	11.8	0.845	N.R.	<0.2	N.R.	3.73	N.R.

Note: Cl concentration for Shobagawa River water is not based on an analysis of this sample, but on the analysis of other groundwaters too
N.R. = Not Reported

Sources

The whole-rock analytical data used in the calculations were obtained from the following sources:

Yoshida, H., Seo, T., Nohara, T., Ota, K., Hama, K., Kodama, K. and Iwatsuki, T. 1994. Data compilation of geoscientific studies of Tono uranium deposits, Central Japan. PNC Report TN7410 94-015.

Tech Note 96-01, 1996: Tono Natural Analogue Programme (PNC/NAGRA) - data compilation of field and lab activities June 1995-May 1996.

Report from PRIMElab dated 29th September 2000 with references 000403 KHama and 000929 K.Hama rev. (Supplied by Hama san, 29th September 2000).

Table 21. Preliminary estimates of theoretical equilibrium $^{36}Cl/Cl$ ratios in the Toki Granite for different model conditions.

Description	U	Th	Cl		Porosity	$^{36}Cl/Cl \times 10^{-15}$: Rock matrix values allow for water-saturated porosity			$^{36}Cl/Cl \times 10^{-15}$: Rock matrix values exclude effect of water-saturated porosity	
			Granite	Water		Rock Matrix		Water	Rock Matrix	
	ppm	ppm	ppm	mg/l		Including Kα–n Reactions	Excluding Kα–n Reactions		Including Kα–n Reactions	Excluding Kα–n Reactions
[1]MIU-3 Average U and Th	9.34	14.40	[2]22	[3]1	[4]0.10	44	42	42	53	50
[1]MIU-3 Average U and Th	9.34	14.40	[2]22	[5]175	[4]0.10	44	42	42	53	50
[1]MIU-3 Average U and Th	9.34	14.40	[6]200	[3]1	[4]0.10	42	41	41	50	49
[1]MIU-3 Average U and Th	9.34	14.40	[2]22	[3]1	[7]0.05	48	46	46	53	50
[8]MIU-3 Max U, Max Th	16.64	22.27	[2]22	[3]1	[4]0.10	76.0	72	72	90.0	86
[9]MIU-3 Min U, Min Th	2.03	6.53	[2]22	[3]1	[4]0.10	13	12	12	15	15

Notes:

1 Here Average = Average of all analyses of U and Th in the Toki Granite from borehole MIU-3
2 Single analysis from the Toki Granite in borehole AN-1, reported in Yoshida et al. (1994)
3 Average Cl content of groundwater sampled from the Toki Granite in borehole MIU-4, as reported in Iwatsuki et al. (2001).
4 Porosity of Toki Granite reported in JNC (2001).
5 Maximum Cl concentration in DH-12, reported in Iwatsuki et al. (2001).
6 Average Cl content of 8 granite samples from Japan reported in Wedepohl et al. (1978).
7 Value of porosity chosen arbitrarily to illustrate sensitivity of calculation to porosity value.
8 Here Max U = Average + Standard Dev; Max Th = Average + Standard Dev
9 Here Min U = Average - Standard Dev; Min Th = Average - Standard Dev

Calculations were made on 27/11/01 before complete whole-rock analyses were available for the MIU- boreholes. Therefore, calculations were made using the following information:

- Mean values of SiO_2, TiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, MgO, CaO, Na_2O, and K_2O for the Toki Granite in DH-13.

The mean Loss-on-Ignition (LOI) for rocks in this borehole was assumed to be due entirely to H_2O.

Concentrations of the trace elements Cl, F, Cr, Co, Ni, Sm, Gd, Be, N, Li and B were for an average granite composition.

Uranium and Thorium values were based on analyses for MIU-3.

Table 22. Summary statistics for all exchangeable cation data obtained from the Tono area. Actual analyses are given in Appendix 5. Literature values are shown for comparison.

Summary statistics for data from the Tono area in Appendix 5.

Borehole		Exchangeable cations (Equivalent Fractions) Mg	Na	Ca	K
99SI-08(all)	Mean	0.04	0.08	0.87	0.02
99SI-08(all)	Stdev	0.02	0.02	0.03	0.01
99SI-08(Between U+L fault rock)	Mean	0.04	0.07	0.87	0.02
99SI-08(Between U+L fault rock)	Stdev	0.01	0.02	0.02	0.01
99SI-08(Above/Below U+L fault rock)	Mean	0.04	0.09	0.86	0.02
99SI-08(Above/Below U+L fault rock)	Stdev	0.03	0.04	0.03	0.01
MIU2(all)	Mean	0.06	0.04	0.87	0.03
MIU2(all)	Stdev	0.17	0.03	0.17	0.03
MIU2(Between U+L fault rock)	Mean	0.01	0.04	0.92	0.03
MIU2(Between U+L fault rock)	Stdev	0.00	0.00	0.02	0.01
MIU2(Above/Below U+L fault rock)	Mean	0.08	0.04	0.85	0.03
MIU2(Above/Below U+L fault rock)	Stdev	0.20	0.04	0.19	0.03
MIU3(all)	Mean	0.18	0.09	0.63	0.11
MIU3(all)	Stdev	0.27	0.06	0.21	0.10
MIU3(Between U+L fault rock)	Mean	0.18	0.09	0.63	0.11
MIU3(Between U+L fault rock)	Stdev	0.27	0.06	0.21	0.10
DH7(all)	Mean	0.62	0.01	0.37	0.00
DH7(all)	Stdev	0.00	0.00	0.00	0.00
DH13(all)	Mean	0.41	0.01	0.57	0.01
DH13(all)	Stdev	0.36	0.01	0.34	0.01
Fault rocks	Mean	0.22	0.04	0.73	0.02
Fault rocks	Stdev	0.30	0.02	0.28	0.02
Samples with fractures lined by clays	Mean	0.39	0.01	0.59	0.01
Samples with fractures lined by clays	Stdev	0.31	0.01	0.30	0.01
Fresh (i.e. unaltered) rock	Mean	0.03	0.08	0.85	0.04
Fresh (i.e. unaltered) rock	Stdev	0.02	0.04	0.09	0.06

Comparative analyses from the literature

Sample	CEC meq/100g	Exchangeable cations (Equivalent Fractions) Mg	Na	Ca	K	Source
Amazon River Sediment	N.R.	0.17	0.004	0.80	0.014	a
Amazon River Sediment After Equilibration with Seawater[2]	N.R.	0.38	0.16	0.38	0.08	a
Dakota Montmorillonite, After Equilibration with River Water[1]	54.3	0.28	0.03	0.66	0.002	b
Dakota Montmorillonite, After Equilibration with Seawater[2]	54.3	0.22	0.5	0.26	0.02	b
Texas Montmorillonite, After Equilibration with River Water[1]	80.9	0.23	0.03	0.71	0.007	b
Texas Montmorillonite, After Equilibration with Seawater[2]	80.9	0.22	0.55	0.19	0.03	b
Bath Kaolinite, After Equilibration with River Water[1]	6.2	0.18	0.06	0.51	0.008	b
Bath Kaolinite, After Equilibration with Seawater[2]	6.2	0.32	0.38	0.24	0.06	b
Wyoming Montmorillonite, Initial Dry Composition	70.2	0.18	0.46	0.27	0.02	b
Wyoming Montmorillonite, After Equilibration with Seawater[2]	70.2	0.39	0.53	0.04	0.04	b
Un-specified Mixed-layer Clay, Initial Dry Composition	38.5	0.23	0.01	0.39	0.08	b
Un-specified Mixed-layer Clay, After Equilibration with Seawater[2]	38.5	0.32	0.56	-	0.07	b
Un-specified Illite, Initial Dry Composition	16.8	0.01	0.01	0.74	0.15	b
Un-specified Illite, After Equilibration with Seawater[2]	16.8	0.24	0.47	0.11	0.17	b

Notes

1 Artificial 'mean world river water'
2 Seawater composition not specified. Presumed to be mean seawater.
All the seawater compositions in Sayles and Mangelsdorf (1977) are presumably the same.

Sources

a Sayles and Mangelsdorf (1979) - as quoted in Drever (1997)
b Sayles and Mangelsdorf (1977) - as quoted in Stumm and Morgan (1981)

Table 23. Summary of statistical models developed for the grounwater samples from Äspö.

Case	Determinands Considered	Water Compositions Used	Other Model Details
Model 1	Na, K, Ca, Mg, HCO_3, Cl, SO_4	All waters in Data Delivery 19, except for (Brine, Baltic Sea Water, Glacial Water and Meteoric Water, which were employed as end-members in the M3 modelling, and Sea Water, which was not employed in the latest M3 modelling)	Three separate models, using the different combination of water samples shown at the left Modelling was not carried out separately for high TDS samples as there were insufficient data in this group (6 samples)
		Samples in Data Delivery 19 with medium Total Dissolved Solid (TDS) contents (Cluster 1) (Brine, Baltic Sea Water, Glacial Water Meteoric Water, and Sea Water excluded from consideration)	
		Samples in Data Delivery 19 with low TDS contents (Cluster 2) (Brine, Baltic Sea Water, Glacial Water Meteoric Water, and Sea Water excluded from consideration)	
Model 2	Na, K, Ca, Mg, HCO_3, Cl, SO_4, D, Tr, $\delta^{18}O$	All waters in Data Delivery 19, except for (Brine, Baltic Sea Water, Glacial Water and Meteoric Water, which were employed as end-members in the M3 modelling, and Sea Water, which was not employed in the latest M3 modelling)	δD and δO18 values were multiplied by –1 to make them positive numbers.
Model 2 (v3)	Na, K, Ca, Mg, HCO_3, Cl, SO_4, δD, Tr, $\delta^{18}O$	All waters in Data Delivery 19, except for (Brine, Baltic Sea Water, Glacial Water and Meteoric Water, which were employed as end-members in the M3 modelling, and Sea Water, which was not employed in the latest M3 modelling)	Tritium data were used as reported. δD and $\delta^{18}O$ data were converted from per mil values to D/H and $^{18}O/^{16}O$ ratios for the purposes of the modelling and converted back to per mil values at the end
Model 2 (v5)	Na, K, Ca, Mg, HCO_3, Cl, SO_4, δD, Tr, $\delta^{18}O$ [8]	All waters in Data Delivery 19, INCLUDING Brine, Baltic Sea Water, Glacial Water and Meteoric Water, which were employed as end-members in the M3 modelling. Sea Water, which was not employed in the latest M3 modelling, was not included)	
Model 3	Na, K, Ca, Mg, HCO_3, Cl, SO_4, δD, $\delta^{18}O$	All waters in Data Delivery 19, except for (Brine, Baltic Sea Water, Glacial Water and Meteoric Water, which were employed as end-members in the M3 modelling, and Sea Water, which was not employed in the latest M3 modelling)	The model differs from Model 2(v3) only in that Tritium data were excluded

Table 24. Compositions of end-members used in M3 modelling, reported previously by Laaksoharju et al. (1999b) and the results of JNC's modelling.

Compositions of end-members reported previously (From M3 modelling, reported in SKB's data Delivery 19)											
	Na	K	Ca	Mg	HCO3	Cl	SO4	O18	D	Tr	Bal
Brine ref. w.	8500	45.5	19300	2.1	14.1	47200	906	-8.9	-44.9	4.2	-0.6
Baltic Sea ref. w.	1960	95	93.7	234	90	3760	325	-5.9	-53.3	42	-1.2
Glacial ref. w.	0.2	0.4	0.2	0.1	0.12	0.5	0.5	-21	-158	0	13.6
Meteoric ref. w.	0.4	0.3	0.2	0.1	12.2	0.2	1.4	-10.5	-80	100	-67.9

Model 1											
Chemical Component	Na	K	Ca	Mg	HCO3	Cl	SO4	O18	D	Tr	Bal
All Data											
1	641	23.8	0.00	270	507	0.00	0.00	N.I.	N.I.	N.I.	71.8
2	5663	0.00	10607	0.00	0.00	27529	742	N.I.	N.I.	N.I.	-1.0
3	2342	76.5	1227	214	0.00	6434	448	N.I.	N.I.	N.I.	-2.2
4	0.0	0.0	0.0	0.0	476	0.0	0.0	N.I.	N.I.	N.I.	-100.0
5	767	16.8	0.0	57.5	103	484	466	N.I.	N.I.	N.I.	21.2
Cluster 1 – Medium TDS Samples											
1	3896	0.0	4631	0.0	3367	12845	0.0	N.I.	N.I.	N.I.	-2.1
2	3168	242	0.0	593	242	6241	293	N.I.	N.I.	N.I.	1.8
3	2765	7.5	3759	9.9	0.0	10946	547	N.I.	N.I.	N.I.	-1.8
4	825	0.0	0.0	0.0	0.0	578	747	N.I.	N.I.	N.I.	6.0
5	1225	0.2	0.0	214	131	1615	0.0	N.I.	N.I.	N.I.	19.6
Cluster 2 – High TDS samples											
1	1730	8.5	1089	27.8	0.0	4864	149	N.I.	N.I.	N.I.	-3.0
2	0.00	0.0	0.0	0.0	335	0.0	1.2	N.I.	N.I.	N.I.	-100.0
3	889	2.0	448	0.0	534	1718	422	N.I.	N.I.	N.I.	-3.9
4	70.7	10.7	0.0	27.7	0.0	259	0.0	N.I.	N.I.	N.I.	-13.0
5	179	2.1	0.0	147	682	0.0	0.0	N.I.	N.I.	N.I.	28.2

N.I. = Not included. Values that appear to be zero are actually very small numbers.

Table 24. Continued.

Model 2											
Chemical Component	Na	K	Ca	Mg	HCO3	Cl	SO4	O18	D	Tr	Bal
1	8508.6	5.1	17235.0	0.0	47.1	44001.5	800.3	-11.8	-75.7	14.6	-1.1
2	2066.3	0.0	1379.1	169.1	225.4	6163.5	0.0	-8.8	-68.5	0.0	-1.4
3	456.9	5.5	258.4	16.7	0.0	1207.9	79.8	-12.4	-94.2	0.0	-2.1
Ω	0.0	1256.2	0.0	2020.1	505.6	0.0	0.0	0.0	0.0	492.0	92.0
5	0.0	0.0	0.0	0.0	22039.5	0.0	0.0	0.0	0.0	0.0	-100.0
6	0.0	0.0	0.0	0.0	298.8	0.0	0.0	0.0	0.0	391.5	-100.0
7	2021.3	17.8	205.4	8.0	0.0	3230.3	1284.4	-14.3	-107.9	0.0	-8.6

Model 2 V3											
Chemical Component	Na	K	Ca	Mg	HCO3	Cl	SO4	O18	D	Tr	Bal
1	11782.6	26.8	23756.3	0.0	0.0	60832.1	1119.8	-14.5	-92.4	0.0	-1.2
2	5107.0	43.7	0.0	729.7	247.5	7971.5	51.6	1.3	-6.0	0.0	10.4
3	3285.6	227.3	1689.9	371.9	53.1	9018.2	923.6	1.3	3.9	66.5	-2.0
4	20187.6	287.5	44808.2	0.0	58890.3	81067.1	66.0	128.7	1167.0	477.0	-2.1
5	4.0	0.0	0.0	0.0	112.4	0.0	0.0	-11.0	-82.6	8.7	-82.7
6	3135.7	0.0	0.0	185.5	0.0	0.0	1911.2	-15.2	-119.7	0.0	58.4
7	1664.1	24.3	4004.8	131.2	462.3	9300.7	385.0	17.0	114.4	1017.0	1.0

Model 2 V5											
Chemical Component	Na	K	Ca	Mg	HCO3	Cl	SO4	O18	D	Tr	Bal
1	9045.0	33.9	18802.0	0.8	42.0	47544.9	891.7	-10.7	-64.1	0.0	-1.0
2	1975.8	0.0	1228.7	169.6	231.8	5738.2	0.0	-8.5	-66.7	6.1	-1.4
3	433.4	6.0	243.4	15.7	0.0	1140.5	75.3	-12.7	-95.9	0.0	-2.0
4	0.0	0.0	0.0	0.0	9841.4	0.0	0.0	0.0	0.0	0.0	-100.0
5	3841.4	910.2	0.0	1683.6	315.1	0.0	327.6	0.0	0.0	0.0	93.0
6	1949.8	7.1	407.0	0.0	0.0	3528.3	1147.4	-14.3	-107.9	4.2	-7.9
7	0.0	0.0	0.0	0.0	213.1	0.0	0.0	0.0	0.0	436.4	-100.0

Values that appear to be zero are actually very small numbers.

Table 24. Continued.

Model 3											
Chemical Component	Na	K	Ca	Mg	HCO3	Cl	SO4	O18	D	Tr	Bal
1	11825.3	28.1	23723.5	0.0	0.0	60865.2	1121.2	-13.8	-87.9	N.I.	-1.2
2	3225.9	25.5	0.0	449.5	108.5	5046.4	47.6	-4.1	-40.5	N.I.	10.2
3	3483.6	246.3	2020.5	403.3	107.8	9950.1	960.1	3.9	22.4	N.I.	-1.8
4	39462.1	454.2	30364.5	3113.6	70548.1	90027.7	0.0	208. 7	1732.3	N.I.	-2.7
5	2071.4	0.0	0.0	78.2	0.0	0.0	1595.1	-15.9	-122.3	N.I.	48.8
6	1.7	0.5	0.0	0.0	125.3	0.0	0.0	-10.6	-80.1	N.I.	-91.9

N.I. = Not included. Values that appear to be zero are actually very small numbers.

Table 25. Flow diagram illustrating major activities in the development of Nirex 97, highlighting those stages where geochemistry was a major input.

APPENDIX 1

Publications produced during the Fellowship

Published

Metcalfe, R., Kunimaru, T., Hama, K., Amano, K., Iwatsuki, T., Milodowski, A.E. and Gillespie, M.R. 2001. Water-rock interactions around a fault: implications for waste disposal. In: Cidu, R. (ed) Water-Rock Interaction, 1643-1646.

Uchida, M., Dershowitz, B., **Metcalfe, R.,** Shuttle, D., Cave, M. and Takeuchi, S. 2001. Integrating groundwater flow and geochemistry – an example of Äspö hard rock laboratory, Sweden. Proceedings of Japan Society of Rock Mechanics.

Iwatsuki, T., Yoshida, H., Hama, K. and **Metcalfe, R.** 2000. Study on pH conditions deep underground by using isotopic analysis of carbonate minerals. Cycle Research Report, 8, 41-47.

Tsubota, K., Yoshida, H., Milodowski, A.E. and **Metcalfe, R.** The role of the Tsukiyoshi Fault as a control on nuclide migration in the Tono uranium deposit, central Japan. Proceedings of Natural Analogue Working Group Meeting, April 1999. 10pp.

Accepted for publication, in press

Hama, K, Amano, K, **Metcalfe, R.,** Yoshida, H., Iwatsuki, T., Milodowski, A.E. and Gillespie, M.R. 2002. Mineralogical and petrological evidence for the hydrogeological characteristics of the Tsukiyoshi Fault, Japan. Quarterly Journal of Engineering Geology and Hydrogeology, v 35(2). In press.

Iwatsuki, T., Satake, H., **Metcalfe, R.,** Yoshida, H. and Hama, K. Isotopic and morphological features of fracture calcite from granitic rocks of the Tono area, Japan: a promising palaeohydrogeological tool. Applied Geochemistry. In Press.

Arthur, R., Iwatsuki, T., Hama, K., Amano, K., **Metcalfe, R.** and Ota, K. 2002. The Redox Environment of Deep Groundwaters Associated with the Tono Uranium Deposit, Japan. Submitted for Publication in Proceedings of the Materials Research Society – reviewers' comments awaited.

Submitted for publication, awaiting reviewers' comments

Stenhouse, M.J., Arthur, R., Ota, K., Iwatsuki, T., **Metcalfe, R.** and Takase, H. 2002. Application of Systems Analysis to a Natural Analogue Project. Submitted for Publication in Proceedings of the Materials Research Society – reviewers' comments awaited.

Completed, being reviewed within JNC – submission planned before end of fellowship

Metcalfe, R., Uchida, M., Cave, M.R., Dershowitz, W., Shuttle, D. and Takeuchi, S. 2002. Refining models of disturbed groundwater flow using hydrogeochemistry. Paper prepared for submission to the international journal 'Groundwater'.

APPENDIX 2

Listing of conference and seminar abstracts produced during the Fellowship

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Explanation of presentations	A2-2
Geochemical approaches to understanding a deep groundwater flow system in the Tono area, Gifu, Japan	A2-4
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Explanation of presentations

Presentations were given at the following international conferences outside Japan:

- Water/rock Interaction 10, Vallasimius, Sardinia, Italy, 11th – 16th June 2001 (Title: Water-rock interaction around a fault: implications for waste disposal);
- American Geophysical Union, Western Pacific Meeting, Tokyo June 27th –30th , 2000 (Title: Characterising groundwater flow histories in faults: a case study of the Tsukiyoshi Fault, Tono Mine, Japan);
- Äspö Groundwater Modelling Task Force Working Group Meeting, Stockholm 28th-29th October 1999 (Title: Importance of hydrogeochemical uncertainty in JNC's modelling for Task 5).

Presentations were also given at the following conferences within Japan:

- Annual Conference of the Geological Society of Japan, Kanazawa, 21-23rd September 2001 (Title: Groundwater chemistry in the Toki Granite: new approaches for understanding a groundwater flow system using groundwater geochemistry (a case study of the Toki Granite);
- Fall Meeting of the Atomic Society of Japan, Hokkaido University, 20th September 2001 (Title: Some implications for site characterisation at Horonobe from experience at Sellafield, UK and Äspö, Sweden: constraining groundwater flow models using hydrogeochemistry));
- Japan Earth and Planetary Sciences Conference, Tokyo, 4th June 2001 (Geochemical approaches to evaluate groundwater flow system stability: implications of research at Sellafield, UK and Äspö, Sweden;
- Integrate 2001, JNC Tokai Works, 14th February 2001 (Title: Constraining groundwater flow models using hydrogeochemistry: some implications for site characterisation in Japan from experience at Sellafield, UK and Apso, Sweden);
- Annual Conference of the Geological Society of Japan, Nagoya, 10th October 1999 (Title: Meeting the challenge of deep geological waste disposal: some lessons from research into radioactive waste disposal in the UK).

Additionally, seminars have been given at:

- JNC Head Office (1);
- Tohoku University (1);
- Nagoya University (1);
- Tono Geoscience Center (3);
- Presentations were also given at two International Fellowship Review Meetings, one in October 2000 and one in October 2001.

An abstract has also been accepted for a paper to be presented at the International Symposium on Groundwater Problems related to Geo-Environment, to be held in Okoyama from May 28th to May 30th 2003.

In the case of the presentation at Water/rock Interaction 10, a paper was published and is reproduced in Appendix 1. In some other cases, there were no abstracts produced. The following pages reproduce all remaining abstracts.

Title:

Geochemical approaches to understanding a deep groundwater flow system in the Tono area, Gifu, Japan

[Submitted to: International Symposium on Groundwater Problems related to Geo-Environment Okayama, Japan May 28-30, 2003]

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Proposed Session Theme: Modelling and analysis of groundwater flow

Key Words: Groundwater flow, Geochemistry, Palaeohydrogeology, Waste isolation, Deep disposal

Abstract

Internationally, deep groundwater flow (several hundred metres to > 1000 m) is studied for reasons ranging from groundwater resource evaluation to deep geological disposal of radioactive wastes. Many investigations aim to model past groundwater flow patterns and fluxes over long time-scales (e.g. a million years or more if considering deep geological disposal of radioactive wastes). These models may then be extended to future flow. However, a limitation of basing models only on hydrogeological information like hydraulic conductivities and groundwater heads, is that these parameters are determined at the present. A flow system's current state may differ from past states and the system may not be at equilibrium with present driving forces (i.e. be transient). To account for these possibilities, geochemical information from groundwater and minerals can be used. Internationally, much recent research has shown that geochemistry can be used to constrain numerical flow models and to interpret past groundwater flow. Geochemistry was used in this way at Sellafield in northwest England and at Äspö in eastern Sweden. However, these and other international investigations, have focussed on saline groundwater (Total Dissolved Solids, TDS ≥ 10,000 mg/l) and brine (TDS ≥ 100,000 mg/l). Geochemistry has been less used to understand deep fresh and brackish groundwater flow (TDS < 10,000 mg/l). On-going generic research at Tono, Gifu-ken, central Japan, is therefore developing geochemical approaches to understand a deep (to c. 1000 m) freshwater flow system (generally TDS < 300 mg/l) the Cretaceous Toki Granite. Specialised methods have been developed to sample deep groundwater with little and quantified contamination. It has been possible to collect samples of sufficiently high quality to establish that variable groundwater chemistry may be related to setting within the flow system. Hydrogeological data suggest that flow is topographically-driven, deeper water flowing generally from high ground in the north-east towards the Toki river in the south-west. Shallower

water flow is more variable, being controlled by local topography. The variations in groundwater chemistry are consistent with this interpretation. In the main study area to the north of the Toki river progressive water/rock interactions are probably a major cause of variations in groundwater chemistry. Deeper, relatively Na- and F- enriched, higher pH waters may have resided in the granite longer than the shallower, relatively Ca-enriched, lower-pH waters. Data for ^{14}C from groundwaters and fracture-filling calcite are consistent with a component of the deep waters being recharged within the last few tens of thousands of years. This is also consistent with preliminary flow-time estimates from hydrogeological data. Just south of the Toki River, slightly more saline (to c. 1550 mg/l TDS) Na-Cl dominated groundwater of unknown origin occurs. Preliminary ^{36}Cl data imply that the chloride in this water may have resided for longer in the rock than has the chloride further north. The distribution of this Na-Cl water could indicate the southern limit of the flow-system north of the Toki River. The investigations have demonstrated the potential for using groundwater chemistry to understand groundwater flow in deep fresh groundwater systems.

Abstract for a presentation at the Second Review Meeting of JNC's International Fellowship, held at Tokai on October 18th and 19th 2001

Title: Geochemical methods for interpreting groundwater flow around Tono and their generic relevance to site characterisation and Performance Assessment

Name: Richard Metcalfe

Division: Tono Geoscience Centre

Subject of research: Hydrogeochemistry

Description of research

Background

Groundwater is the main medium by which radionuclides might be transported from any future deep, underground repository for radioactive wastes. Therefore, such a repository should be sited where groundwater flow conditions are presently suitable and are expected to remain suitable, for as long the waste remains hazardous. Generally, it should be shown that radionuclides would not return from the repository to the near surface biosphere in quantities that would cause unacceptably high risks. Therefore it is desirable to demonstrate that: 1. flow rates are sufficiently slow; 2. flow paths between the repository and the near-surface biosphere are adequately long; and 3. flow is away from potentially vulnerable parts of the biosphere, such as human populations.

In Japan, geochemistry has been used relatively little to interpret groundwater flow. Instead, research has focussed mainly on demonstrating the stability of chemical conditions (e.g. pH, Eh) deep underground. In contrast, internationally, geochemical information is more often used to constrain models for past and present flow. Spatial and/or temporal variations in groundwater chemistry, mineral chemistry and mineral distributions at a site can be used to develop and/or support general conceptual flow models (e.g. indicate general groundwater sources, flow directions etc). Alternatively, these variations can be used to calibrate numerical flow models. Both conceptual and numerical models are developed iteratively, with data acquisition, during site characterisation. Both types of model are also a basis for Performance Assessment (PA) modelling.

In other countries geochemical methods have tended to be applied to groundwater systems that contain saline groundwaters and brines. In these systems mixing is often a more important cause of chemical variations than water/rock interactions. In contrast, in Japan relatively fresh deep groundwater systems are common. In these systems water/rock interactions are likely to be proportionately more significant controls on chemical variations. This means that many methods employed in other countries need to be tested to establish their applicability in Japan and, where appropriate, the methods need to be adapted.

On-going investigations in the Tono area provide an opportunity to meet both these goals. This presentation will review some promising geochemical methods for constraining groundwater flow models in Japan, based upon research in the Tono area. The possible value of these methods in future site characterisation and Performance Assessment (PA) elsewhere in Japan will be highlighted.

Investigations in the Tono area

Investigations have focussed on an area of 10 km x 10 km (Figure 1). Here, Miocene to Pleistocene sedimentary rocks (ranging in age from c. 20 Ma to c. 0.7Ma before the present) fill hollows eroded into the Cretaceous Toki Granite (c. 70 Ma old). An approximately east-west trending reversed fault, the Tsukiyoshi Fault, lies in the middle of the area. Rocks on the southern side of the fault are displaced upwards by about 30 m, relative to rocks on its northern side.

Groundwaters and rocks have been sampled from boreholes up to about 1000 m deep. Investigations have also been undertaken in Tono mine, a uranium mine that was constructed for exploration in the 1970's (Figure 1), but which was never worked commercially. This mine is now a research facility of JNC.

Key activities

The research has involved working closely with Japanese colleagues at TGC and has included the following major activities:

- Contribution to the construction of a geochemical database for the Tono area.
- Interpretation of groundwater and mineralogical chemical data from the Tono area.
- Interpretation of rock chemical and mineralogical data from the Tsukiyoshi Fault zone.
- Review of investigations in a new, inclined deep borehole.
- Publication of results (two papers in press).
- Dissemination of results at conferences (presentations given at 5 conferences in the last year).

Key results

Major specific results of the research are summarised as follows:

- Variations in groundwater chemistry, though subtle, can be identified and are generally consistent with concepts of groundwater flow based on hydrogeological data (Figures 2, 3 and 4).
- Cation exchange reactions on clay minerals can explain much of the chemical variability of the HCO_3-dominated groundwaters in the Tono area, but recently Na-Cl dominated fresh groundwaters have also been discovered in the southern part of the area (Figures 2, 3 and 4).
- The origin of the Na-Cl dominated waters is uncertain, but may possibly reflect the presence of a small component of chemically modified relict seawater. Additional data are needed to test this hypothesis.
- Isotopic data from fracture-filling calcite crystals suggests that seawater was present in the deep Toki granite in the past, but has been flushed by more recent fresh meteoric water.
- The groundwater flow system in the Tono area is relatively young and at least a component of the deep waters (to depths of several hundred metres) was recharged within the last few tens of thousands of years.
- It has been possible to obtain useful ^{36}Cl data from groundwaters in the area, though interpretations are complicated by the possibility that significant chloride could have originated in the rock, rather than water sources.
- Groundwater from the base of the Lower Toki Formation contains ^{36}Cl that is probably not equilibrated with the in-situ production in any of the local rocks. The simplest explanation is

that the chloride in this Lower Toki water originated in the Toki Granite and has moved into the Lower Toki Formation geologically recently.

- Careful borehole design and specialist sampling strategies enabled evidence for post-faulting groundwater flow to be identified in the Tsukiyoshi Fault.
- The Tsukiyoshi Fault is not a simple planar discontinuity, but a deformation *zone*. This zone contains another zone of 'chemical damage', which records past groundwater flow. This zone's porosity, and by inference permeability, possibly evolved due to chemical processes after fault movement ceased.
- Hydraulic data acquired before the recent mineralogical study of the Tsukiyoshi Fault are not of sufficiently high resolution to allow comparison between measurements of rock permeability and inferences about presently permeable zones based on mineralogical data.

General implications of these results for site characterisation and PA elsewhere in Japan are:

- Available groundwater sampling and analytical methods can identify spatial variations in groundwater chemistry in fresh groundwater systems and could be valuable in future site characterisation exercises.
- Groundwater chemistry could be a useful tool for supporting (i.e. improving confidence in) groundwater flow models in fresh groundwater environments during future site characterisation exercises.
- Planning of hydrogeological investigations during site characterisation, notably the detailed design of hydraulic tests, should be integrated with the interpretation of mineralogical and structural features of rock core, to ensure that heterogeneity in the rock mass is adequately tested.
- Though more data are needed, the initial results suggest that mineralogical data have the potential to provide valuable records of past variations in groundwater chemistry. This could be valuable for developing scenario's for PA in the future.
- Apparently inactive faults should not necessarily be represented as planar, time-invariant features in flow-models underpinning PA.

Figure 1. Location map showing the boreholes drilled during JNC's regional hydrogeology programme and some of the boreholes drilled near Tono Mine.

Figure 2. Variations in cation ratios in the highest quality deep groundwaters from the Toki Granite. The variation is thought to be due to mainly cation exchange on clay minerals.

Figure 3. Variations in anion ratios in the hightest quality deep groundwaters from the Toki Granite. The relatively high Cl concentration in the DH-12 waters may reflect the presence of older, Na-Cl dominated water.

Figure 4. Schematic illustration of relationships of different groundwater types to the inferred flow system.

Groundwater geochemistry in the Toki granite

Richard Metcalfe, Tono Geoscience Center

New approaches for understanding a groundwater flow system using groundwater geochemistry (a case study of the Toki granite).

Richard Metcalfe, Kenji Amano, Katsuhiro Hama, Teruki Iwatsuki, Hiromitsu Saegusa, Japan Nuclear Cycle Development Institute. Randolph C. Arthur, Monitor Scientific, U.S.A. F. J. Pearson, Ground-Water Geochemistry, U.S.A.

1. Introduction

Much basic research into deep groundwater systems aims to develop approaches for predicting the extent to which water and solutes will move or remain immobile. Such predictions will be needed to evaluate the long-term safety of any future deep geological disposal. To make these predictions it is important to: 1. characterise present groundwater flow systems; and 2. determine their past stability. Internationally, geochemical information is often used to help meet these goals. Generally, spatial variations in groundwater composition, mineral distributions and mineral chemistry are used to interpret: 1. the origins of a water and its solutes; 2. mixing relationships between different waters; 3. groundwater residence times; and 4. past chemical conditions. However, most research internationally has focussed on groundwater systems containing saline water and/or brine. In contrast on-going research in the Tono area, by the Japan Nuclear Cycle Development Institute, is evaluating the general applicability of these approaches for characterising the relatively early evolution of a fresh groundwater system.

2. Results

Fresh groundwater flows through the fractured Toki granite (Figure 1). Hydrogeological data suggest that flow is topographically-driven, deeper water flowing generally from high ground in the north-east towards the Toki river in the south-west. Shallower water flow is more variable, being controlled by local topography (Figure 1). Groundwater was sampled from 25 intervals in the granite, in boreholes between c. 180 m and c. 1000 m deep. All these waters are fresh and are indicated by stable oxygen and hydrogen isotopes to be meteoric in origin. Deeper groundwater generally has a higher pH than shallower water, though below 200 m pH varies from c. 8 to 10, with no clear trend. Shallower groundwater is generally Ca-Na-HCO_3^- dominated and has relatively low F concentrations (< 5 ppm at < 500 m depth). Deeper water tends to be more Na-HCO_3^- dominated and to have relatively high F concentrations (deeper than 500 m, F > 6.5 ppm). Borehole DH12 is anomalous in that it produced relatively shallow (175 m deep)

Figure 1: Sketch map of the study area. Numbered boreholes gave water samples.

Na-Cl dominated groundwater with the highest F concentration (12.5 ppm). It is uncertain whether DH12 samples the same flow system as more northerly boreholes. However, regardless of whether or not the flow systems are different, DH12 is probably relatively close to a discharge zone while DH3, DH8 and DH13 are closer to recharge zones. These contrasting hydrogeological settings are reflected in the chemistry of the groundwaters sampled from these different boreholes. In the boreholes to the north of the Toki river it is likely that progressive water/rock interactions are the main cause of the chemical variations. The relatively Na- and F- enriched, higher pH waters may have resided in the granite longer than the shallower, relatively Ca-enriched, lower-pH waters. Data for ^{14}C from groundwaters and fracture-filling calcite are consistent with a component of the deep waters being recharged within the last few tens of thousands of years. This is also consistent with preliminary flow-time estimates from hydrogeological data. In contrast, mixing between fresh water and Cl-dominated water of presently unknown origin could possibly be more important in DH12.

3. Conclusions

Samples from the deep Toki granite were of sufficiently high quality, to establish that fresh groundwater chemistry is variable and may relate to setting within the sampled flow system. Qualitative and quantitative indicators of groundwater and solute residence times, coupled with mineralogical indicators of past groundwater chemistry are likely to be most useful for refining flow concepts, once more data become available.

Abstract for a presentation given at the Fall Meeting of the Atomic Society of Japan, Hokkaido University, 20th September 2001

SOME IMPLICATIONS FOR SITE CHARACTERISATION AT HORONOBE FROM EXPERIENCE AT SELLAFIELD, UK AND ÄSPÖ, SWEDEN: CONSTRAINING GROUNDWATER FLOW MODELS USING HYDROGEOCHEMISTRY

Japan Nuclear Cycle Development Institute **RICHARD METCALFE**

This paper shows how geochemistry can be used to understand groundwater flow, using examples from Sellafield, UK and Äspö, Sweden. The best interpretations of flow generally use both chemical and hydraulic data. Chemical data may indicate past flow. It is suggested that geochemistry may be valuable for interpreting groundwater flow at Horonobe.

Key words: Groundwater flow, water chemistry, mineralogy, site characterisation, hydrogeology, palaeohydrogeology

1. INTRODUCTION

One aim of basic research into deep groundwater systems is to develop approaches for predicting the future movement of water and dissolved solutes. These approaches will be needed to establish the safety of any future deep geological waste repository. To do this, it is important to establish the characteristics of present groundwater flow systems (e.g. directions and rates of flow) and to determine their past stability. Knowledge of the past impact of phenomena such as climate change, uplift etc can be used to predict future responses to similar phenomena.

2. GENERAL PRINCIPLES

Spatial variations in groundwater composition and spatial variations in mineral distributions and chemistry can be used to develop *conceptual* models for past groundwater flow [1](Fig.1, Fig.2). This information can also be used to *constrain* numerical groundwater flow models [2][3]. This second approach may involve applying geochemistry to: 1. define the initial numerical model, for example by suggesting boundary conditions; and 2. test model output, for example by comparing modelled and observed salinity variations. Constituents of the water (^{3}H, $^{2}H/^{1}H$, $^{18}O/^{16}O$), certain dissolved solutes (e.g. noble gases, ^{36}Cl) and mineral sequences can be used to constrain a groundwater's flow history.

3. EXAMPLES FROM SELLAFIELD, UK AND ÄSPÖ, SWEDEN

At Sellafield, Br and Cl data were valuable for deducing salinity origins and groundwater mixing proportions. Most dissolved Cl is thought to originate in sedimentary halite to the west. Mixing between Cl-enriched water from the west and fresh groundwater recharged more recently to the east are thought to be the main cause of variations in Cl within the area (Fig. 2). These water sources suggested boundaries for flow models, using computer codes like SUTRA. Computer simulations were adjusted until their output matched observed Cl variations. Mineral data suggest that deep groundwaters had similar distributions to the present for a long time. In contrast, variations in groundwater chemistry at Äspö are mixtures of at least 4 waters. Multivariate statistics may distinguish chemical variations due to mixing between these waters, from variations due to water/rock reactions. The former may constrain flow models.

4. SOME IMPLICATIONS FOR HORONOBE

Results from Sellafield and Äspö show that geochemistry can greatly improve confidence in groundwater flow models. Initial studies at Horonobe found variations in groundwater chemistry, with shallower, fresh Ca-HCO_3 groundwater lying above deeper, saline Na-Cl water. It is expected that there will be transitions between the different water types. Therefore methods similar to those used at Sellafield and Äspö may prove useful at Horonobe.

5. REFERENCES

Fig. 1: Gradients in salinity, represented by chloride, in three boreholes from Sellafield, U.K.

Fig. 2: A conceptual model for groundwater flow at Sellafield constructed to be consistent with the salinity gradients Fig. 1.

[1] Nirex, Nirex Science Report S/97/012 (1997), 4 vol. [2]. M. Laaksoharju and I. Rhen, Use of hydrogeochemical information in testing groundwater flow models. Workshop Proceedings, Borgholm, Sweden, 1-3 September, (1997). pp. 65-78. [3] A.K. Littleboy D.J. Noy and R. Metcalfe, High Level Radioactive Waste Management, 7th Annual International Conference, American Nuclear Society, Las Vegas, 29 April - 3 May (1996). pp. 135-140.

Abstract for a presentation given at the Japan Earth and Planetary Sciences Conference, Tokyo, 4th June 2001

Geochemical approaches to evaluate groundwater flow system stability: implications of research at Sellafield, UK and Äspö, Sweden

Key Words:

Waste isolation, deep disposal, groundwater chemistry, groundwater flow, radioactive waste

Abstract

Groundwater flow will affect the movement of radionuclides from any future deep geological waste repository. To assess the safety of such a repository it will be important to evaluate the extent to which the surrounding groundwater flow system has been stable. Investigations at Sellafield in northwest England and at Äspö, in eastern Sweden, have demonstrated that geochemical information can improve our understanding of groundwater flow patterns and their stability.

Geochemical constraints on flow-system stability may be either quantitative (e.g. data for the radioactive isotopes ^{36}Cl and ^{14}C may indicate the timing of past water flow) or qualitative (e.g. the presence of pyrite may support any suggestion that deep groundwaters have remained reducing). Sequences of mineral precipitates can also constrain the geochemical evolution of a groundwater system. This quantitative or qualitative information can be used to develop and/or support *conceptual* models for past groundwater flow (e.g. indicate general flow directions, sources of water etc). Alternatively, this information can be used to *constrain* numerical groundwater flow models, designed to scope the sensitivity of the flow system to varying conditions. Two important aspects of this second approach are: 1. the use of geochemistry to define the initial numerical model, for example by suggesting boundary conditions; and 2. the application of geochemistry to test model output. Different kinds of chemical information can be used to suggest boundary conditions and to test model output. For example, chemical data for groundwaters may suggest boundary conditions, while mineral distributions might suggest past groundwater distributions, that can be compared with the simulation.

These approaches were adopted at Sellafield. The value of halide chemistry (notably variations in Br and Cl) to deduce the origins of groundwater salinity and mixing relationships was demonstrated. Most of the groundwaters' Cl was attributed to sedimentary halite dissolution to the west of the investigated area. It was concluded that variations in Cl concentrations within the area were caused dominantly by Cl-enriched water from the west mixing with more recently recharged, fresh groundwaters originating to the east. These water sources were used to set boundaries for groundwater flow models, using computer codes such as SUTRA. Computer simulations were adjusted until they matched the observed variations in groundwater Cl. The general consistency between the flow models and variations in water Cl concentrations was supported by isotopic data such as ^{36}Cl, $^{34}S/^{32}S$, $^{87}Sr/^{86}Sr$, and by the distributions of minerals, notably Fe/Mn-oxyhydroxides, pyrite, calcite and anhydrite. The mineralogical data suggest that the present deep groundwaters have been distributed similarly to the present for a long time, possibly from the Tertiary.

In contrast to Sellafield, variations in groundwater chemistry at Äspö are due to mixing between at least 4 different waters, each with a different Cl concentration. A particular groundwater Cl

concentration at Äspö can be explained by several alternative mixing schemes. This limits the use of variations in Cl concentrations alone to constrain groundwater flow models. However, multivariate statistical techniques may distinguish, for a range of solutes, chemical variations due to mixing, from variations due to water/rock reactions. The mixing-related variations may be valuable constraints on groundwater flow models, enabling the effects of fracture zones on groundwater flow to be constrained.

- In Japan, a focus of basic research concerned with radioactive waste disposal has been the stability of chemical conditions deep underground. Compared to programmes in many other countries, there has been less use of geochemical information to constrain the stability of groundwater flow systems. It is suggested that in future such an application of geochemistry may become more important in Japan.

Abstract for a seminar given at the Tono Geoscience Center, 23rd March 2001

Geochemical methods for interpreting groundwater flow around Tono and their generic relevance to site characterisation and Performance Assessment

A presentation by Richard Metcalfe, 23rd March 2001

Internationally, geochemical information is often used as a powerful tool to constrain models for past and present groundwater flow. Spatial and/or temporal variations in groundwater chemistry, mineral chemistry and mineral distributions at a site can be used to develop and/or support general *conceptual* models for groundwater flow (e.g. indicate general directions of groundwater flow, sources of groundwater etc). Alternatively, these variations can be used to *calibrate* numerical groundwater flow models. Both conceptual and numerical models are developed iteratively, with data acquisition, during site characterisation. Both types of model also form a basis for Performance Assessment (PA) modelling.

Compared to research related to rad-waste in many other countries, Japanese research has made less use of geochemical information to constrain the groundwater flow models. Intead, a focus of basic research in Japan has been the stability of chemical conditions deep underground. It is suggested that in future, more use could be made in Japan of geochemical methods for constraining groundwater flow models.

However, the geochemical methods employed in other countries have tended to be applied to groundwater systems that contain saline groundwaters and brines. In these systems groundwater mixing is often a relatively large cause of chemical variations compared to water/rock interactions. In contrast, in Japan relatively fresh deep groundwater systems are common and in these systems water/rock interactions are likely to exert a proportionately greater control on chemical variations. This means that many methods employed in other countries need to be tested to establish their applicability to typical fresh Japanese deep groundwater systems and, where appropriate, the methods need to be adapted.

The on-going investigations in the Tono area provide an opportunity to meet both these goals. In this presentation, the applications of geochemistry elsewhere in the world will be reviewed and an overview will be given of some promising geochemical methods for constraining groundwater flow models in Japan, based upon research in the Tono area. The possible value of these methods in any future site characterisation and PA elsewhere in Japan will be highlighted.

Abstract for a presentation given at a joint workshop on integrating groundwater flow models and Performance Assessment (Integrate 2001), held at JNC Tokai Works, 14th February 2001

Constraining groundwater flow models using hydrogeochemistry: some implications for site characterisation in Japan from experience at Sellafield, UK and Apso, Sweden

Spatial and/or temporal variations in groundwater chemistry, mineral chemistry and mineral distributions at a site can be used to develop and/or support general *conceptual* models of groundwater flow (e.g. indicate general directions of groundwater flow, sources of groundwater etc). Alternatively, these variations can be used to *calibrate* numerical groundwater flow models. To use groundwater chemistry to constrain flow models, chemical variations due to mixing must be distinguished from variations due to reactions between water and rock. Variations due to the first of these processes depend most directly upon groundwater flow and are therefore the most useful constraints on numerical groundwater flow models.

At Sellafield in north-east England the spatial variations in groundwater salinity and chemical characteristics (notably variations in the trace element Br) were used to deduce the origins of groundwater salinity. This approach enabled most of the Cl in the groundwaters to be attributed to halite dissolution in sedimentary rocks to the west of the investigated site. Thus, it was concluded that variations in Cl concentrations *within* this site were caused dominantly by Cl-enriched water from the west mixing with more recent low-Cl fresh groundwaters originating to the east. Consequently, variations in Cl concentration could be used to calibrate models for groundwater flow, using computer codes such as SUTRA and NAMMU. The basic approach was to adjust computer simulations until they matched the observed variations in groundwater Cl. The general consistency between the flow models and variations in water chloride was further supported by variations in isotopic data such as ^{36}Cl, $^{34}S/^{32}S$, $^{87}Sr/^{86}Sr$, and by variations in the distributions of minerals, such as Fe/Mn-oxyhydroxides, pyrite, calcite and anhydrite. Furthermore, the mineralogical observations suggest that the present distributions of the deep groundwaters may have been broadly similar to the present for a considerable period in the past, possibly from the Tertiary.

Compared to Sellafield, the variations in groundwater chemistry at Äspö, Sweden, are due to much more complex mixing processes, involving at least 4 different chemically distinct groundwaters (meteoric water, 'glacial' water, Baltic Sea water and 'basement brine'), each containing a different concentration of Cl. Thus, a particular observed Cl concentration at Äspö could be interpreted to be caused by several alternative mixing schemes. This means that, in the absence of other information, variations in Cl concentrations are of more limited value for constraining groundwater flow models than is the case at Sellafield. Therefore, during collaborative research at Äspö, JNC has developed a new multivariate statistical approach, which attempts to distinguish, for a range of dissolved constituents of the groundwaters, the variations attributable to mixing, from variations attributable to water/rock reactions. The aim is to use the former to constrain groundwater flow models.

In Japan, most groundwaters that have been encountered to date are fresh. Compared to the saline waters and brines of the UK and Sweden, a greater proportion of the salinity of these fresh groundwaters is expected to reflect water/rock interactions and contamination during sampling and analysis. It is suggested that the multivariate approach developed at Äspö has potential to be used to distinguish these effects from groundwater mixing effects. The experience at Sellafield

demonstrates the value of integraring data for trace constituents, isotopes that are often considered 'non-routine' (particularly ^{36}Cl, $^{34}S/^{32}S$, $^{87}Sr/^{86}Sr$) and mineralogical information for demonstrating consistency between concepts of groundwater flow and hydrogeochemical interpretations. It is suggested that such information could also be valuable in Japanese fresh groundwater systems.

Abstract for Presentation at the Review Meeting of JNC's International Fellowship, held at Tokai on December 6th 2000

Title: Geochemical approaches for evaluating groundwater flow and chemical evolution: application to radioactive waste management

Name: Richard Metcalfe

Division: Tono Geoscience Centre

Subject of research: Hydrogeochemistry

Description of research

Background

Groundwater is the main medium by which radionuclides might be transported from any future deep, underground repository for radioactive wastes. Therefore, it is important that such repository is sited where groundwater flow conditions are suitable at the present and are expected to remain suitable in the future, for as long the waste remains hazardous. Suitable groundwater flow conditions will be specific to a particular repository site and design concept. However, generally it is necessary to show that radionuclides will not return from the repository to the near surface biosphere in quantities that would cause an unacceptably high risk. To meet this goal it is desirable to demonstrate in particular that: 1. flow rates are sufficiently slow; 2. flow paths between the repository and the near-surface biosphere are sufficiently long; and 3. flow directions are directed away from potentially vulnerableparts of the biosphere, such as human population centres.

One important approach for determining flow rates, paths and directions involves hydraulic testing in boreholes, to deduce groundwater pressures (heads) and rock permeabilities (hydraulic conductivities). This information is then used to calibrate theoretical models for groundwater flow (Figure 1). The basic approach is to use the hydraulic conductivites deduced from adjust conditions (e.g. heads, fluxes) at the boundaries of the model until the observed groundwater heads are reproduced.

However, if used on its own, this approach tells us only about the present state of the groundwater system. Groundwater heads can change relatively rapidly and may change considerably over the time scales considered by safety assessments for radioactive waste repositories (often up to around 1 million years). Additionally, inevitably it is possible to test only a very small proportion of an area. Therefore, groundwater flow paths and system boundaries must be deduced indirectly, by methods involving considerable spatial extrapolation.

Geochemical information from groundwaters, rocks and minerals can complement the hydraulic data (Figure 1). Major advantages of using geochemical data are:

- The past history of groundwater movement may be deduced from certain kinds of geochemical information. This information can be used in turn as a constraint on system stability, and for testing theoretical flow models that can then be used to predict future

groundwater flow.

- Groundwater chemistry may provide an independent check on groundwater flow directions and flow rates that are calculated from the groundwater head data.
- Geochemical information is a useful in scenario development for repository performance assessments, because it places

In any event, it is essential to demonstrate that concepts for groundwater flow and evolution are consistent with both the available geochemical data and with the hydraulic information. Unexplained discrepancies will be used by parties opposed to any proposed radioactive waste disposal as evidence for a lack of understanding about a site.

In most other research programmes related to radioactive waste management, groundwater chemistry is used to evaluate groundwater flow at the present and in the past (e.g. Sellafield, UK, Apso, Sweden, Whiteshell, Canada). However, to date research into groundwater chemistry by JNC has focussed upon determining the geochemical conditions deep underground (e.g. pH and redox conditions), and the influence of these conditions on radionuclide migration. Much less emphasis has been given to using groundwater chemistry to constrain groundwater flow. Methods and approaches for using geochemistry to constrain groundwater flow that have been developed at sites elsewhere in the world may not be directly applicable to many groundwater systems in Japan, but may require modification. Potentially, new methods may need to be developed. For example, in Europe many methods and approaches have been developed in saline groundwater systems at sites where glaciation has been a major cause of change in groundwater flow systems. In contrast, in Japan, saline groundwater systems are apparently much rarer (except near to the coasts; H12 report) and plate tectonic processes (e.g. uplift and subsidence) have been a much more important source of change.

For these reasons, research is being undertaken in the Tono area to evaluate and develop geochemical methods for evaluating past and present groundwater flow. In this area, groundwaters are fresh (to a few hundred mgl^{-1} total dissolved solids) to depths of at least 1000 m. Within the Quaternary period (the last 1.8 million years) there is thought to have been several hundred metres of uplift. A range of different rock types (sedimentary rocks with a sub-economic grade uranium deposit near their base overlie a granite) are cut by an inactive reverse fault, the Tsukiyoshi Fault, with a throw of around 30 m. Faults of such a scale might well occur near to any future repository site elsewhere in Japan. A large quantity of various kinds of geoscientific data, including geochemical data, has been (and is being) produced by on-going research programmes involving: 1. deep borehole drilling at various sites distributed throughout the area; 2. geoscientific research in Tono Mine, located predominantly at the stratigraphical level of the uranium deposits; and 3. investigations related to the proposed construction of the Mizunami Underground Research Laboratory (MIU).

Thus, the area is particularly suitable to test and develop geochemical methods for evaluating groundwater flow systems in a range of rock types and in a general hydrogeological environment with features that might be expected to occur in many places in Japan.

Major research activities during the fellowship are as follows:

- Review of aspects of the H12 report concerning geochemical conditions in deep geological

environments, coupled with assistance in writing the English language version of the report.

- Review of approaches used in other programmes world-wide, to use groundwater chemistry for constraining models of groundwater flow.
- Evaluation of the applicability of these methods to Japan, and particularly fresh groundwater systems, like that in the Tono area.
- Development of generic methods for using geochemistry to constrain present groundwater flow models, using a knowledge of the geochemical disturbance caused by construction of underground research facilities. Use data from Aspo, Sweden to develop basic method, with a view to applying this in the MIU site and making it more applicable for specifically Japanese hydrogeological settings.
- Development of approaches for interpretation of past groundwater movement in a fault, the 'Tsukiyoshi Fault', which cuts Tono mine.
- Assistance with planning data acquisition so that groundwater chemical information suitable for interpreting regional groundwater flow at the present and in the past.
- Evaluation of the application of ^{36}Cl isotopes for tracing groundwater movement and residence times.

Key results:

- During acquisition of high quality geochemical data in areas like Tono where there are fresh groundwaters, contamination of groundwaters during drilling is a proportionately greater problem than in areas where there are more saline waters. Thus, there is a need to focus on determinands that are likely to show large changes in fresh groundwater systems, such as stable oxygen and hydrogen isotopes, tritium, ^{14}C, ^{36}Cl..
- Multi-variate statistics can be used to separate contamination and water-rock interactions effects from chemical variations due to mixing between chemically distinct groundwaters.
- Theoretical calculations indicate that there should be large variations in equilibrium $^{36}Cl/Cl$ activities in groundwaters in the Tono area.
- It is possible to obtain ^{36}Cl data from fresh groundwaters like those occurring in the Tono area.
- Careful borehole design coupled and specialist sampling strategies has enabled evidence for post-faulting groundwater flow to be identified in the Tsukiyoshi Fault.

The Tsukiyoshi Fault is not a simple planar discontinuity, but a zone of deformation. Within this zone, there is a zone of 'chemical damage', which records the movement of groundwater through the zone in the past. The porosity, and by inference the permeability of this zone has possibly continued to evolve as a consequence of chemical processes long after fault movement ceased.

Figure 1. Cartoon illustrating how geochemical evidence from groundwaters for past groundwater flow can constrain groundwater flow models. Groundwater head measurements in two boreholes, and knowledge of rock permeability allow a groundwater flow rate and direction to be calculated. The chemistry of water sampled from the same two boreholes allows an independent estimate of these parameters. The flow rate can be calculated from the recharge time ('age')of the groundwater, determined from the chemistry. The salinity variation can also be used to infer a groundwater flow direction (e.g. groundwater becomes less saline towards the recharge zone, because nearer the recharge zone the water had less time to react with the rock). The flow directions and rates calculated from the hydraulic tests and geochemistry may be different if conditions have changed (for example the recharge rate or the angle of tilt of the aquifer has varied).

Figure 2. Cartoon illustrating how the variation of groundwater flowing into a tunnel can be used to help calibrate groundwater flow models. In A. the groundwater system is undisturbed and there are groundwaters with three different chemistries, 1., 2. and 3. In B. a tunnel has been constructed and water flows into the tunnel along various different flow paths, a., b., c. Initially the lengths of these paths are short and the water sampled is only of type 2. and 3., from near to the tunnel. C. illustrates the situaion at a later time. Here, the flow paths are longer. All three water types are now intersected by the flow paths and a mixture of the three types flows into the tunnel. D. illustrates the general change in the chemistry of water flowing into the tunnel over time. E. shows how comparisons between theoretical predictions of these calculated chemical variations and observed chemical variations can be used to refine the flow model underpinning the predictions.

Abstract for a presentation given at the American Geophysical Union, Western Pacific Meeting, Tokyo June 27th –30th, 2000

Characterising Groundwater Flow Histories in Faults: a Case Study of the Tsukiyoshi Fault, Tono Mine, Japan

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The chemistry and movement of groundwater affect the migration of a wide variety of substances, including pollutants, through rocks deep underground. Groundwater flow will be controlled partly by the hydraulic properties of any faults that are present. Groundwater chemistry may be influenced by processes within these faults, such as water/rock interactions and mixing between chemically distinct waters. However, there have been relatively few integrated studies of hydrogeology, structural 3-dimensionality, hydraulic anisotropy and hydrogeochemistry in reverse fault zones. Consequently, possible coupled temporal variations in fault properties, particularly over times relevant to predicting pollutant migration (up to c. 1 million years for certain radioactive wastes) require a better understanding. Therefore, as part of an on-going natural analogue study at Tono Mine, Gifu Prefecture, Japan, the Japan Nuclear Cycle Development Institute (JNC) is developing generic methods for determining the history of groundwater and solute flow in the reverse Tsukiyoshi Fault. This fault cuts a Cretaceous granite and overlying sedimentary rocks, deposited between c. 20 Ma and c. 15 Ma. Uranium deposits, which formed c. 10 million years ago in the lowest sedimentary rocks, are also displaced. The fault dips at 60° to 70°, has an overall reverse displacement of c. 30 m and moved over a period of up to c. 10 million years, although it has been inactive for several million years. There is no indication of significant uranium migration connected with this displacement or with later groundwater movement. Mine outcrops and 9 borehole cores were sampled for detailed petrographical, mineralogical and chemical analysis. The impact of the Tsukiyoshi fault on groundwater flow was also studied during the construction of a shaft. The draw down on the piezometric head in the surrounding rocks was observed in 14 boreholes and allowed the fault's hydraulic properties to be inferred. The study has demonstrated that the Tsukiyoshi Fault is not a single planar fracture, but a zone of fracturing containing several fault strands. In the sedimentary rocks, fault strands apparently vary in width from 4 m to at least 20 m over a lateral distance of < 50 m. In the granite the maximum width is at least 60 m. The hanging wall and foot wall of the fault zone apparently had differing hydraulic properties for at least part of the fault's history. Mineralogical data suggest that some of these properties may have changed over time due to both a structural control and to water/rock interactions. The full implications are still to be assessed. However, there are generic implications for the underground disposal of radioactive wastes. Performance Assessments (PA) for underground waste repositories have tended to represent such faults as temporally invariant, open planar features and to assume that repositories can be designed to avoid faults with permeable crush zones that could act as nuclide

transfer paths (e.g. Second Progress Report, JNC, 2000). This study demonstrates that these representations are simplistic. To assign reasonable hydraulic properties to such faults, and to define appropriate separation distances from crush zones, the 3D variability in fault zones may need to be investigated over lateral distances of only a few metres. The possibility that these properties may change on the time scale of PA (c.1 million years) cannot be ruled out.

Abstract for a seminar given at the Tono Geoscience Center on 21st June 2000

Researching groundwater movement histories in fractured rocks: advances from the ongoing Tsukiyoshi Fault Project

Richard Metcalfe, Tono Geoscience Center

Internationally, research relevant to the deep geological disposal of radioactive wastes has included detailed investigations of fractured rocks. A major aim at many research sites has been to investigate how fractures have functioned as pathways for groundwater and solute migration in the past. The information obtained has been used to constrain predictive models for future groundwater and solute movement, for example during Performance Assessments (PA). However, it is desirable to develop improved methods for characterising groundwater movement histories in fracture networks that are genetically related to presently inactive faults. In paricular, it is desirable to be able to:

- distinguish features of the fracture-networks that occurred during the faulting, from more recent features that developed after faulting stopped, due to processes such as regional uplift or subsidence, and/or water/rock interactions within the fracture network.
- determine the spatial extent of fractures genetically related to ancient faulting, from fractures caused by other phenomena;
- determine the spatial extent of hydraulically conductive fractures that are genetically related to faulting.

Such an improved capability will enable safe separation distances between any future deep waste repository and inactive faults to be defined more confidently. It will also allow PA scenarios to be defined that are more demonstrably conservative.

The ongoing Tsuikiyoshi Fault Project has the potential to develop such improved methods. Work to date has highlighted the importance of core recovery using methods such as 'CorePack', to acquire high quality information on the distributions of fractures and the minerals filling these fractures. The faulting and associated water/rock interactions apparently occurred at relatively low temperatures, probably less than 150 °C and possibly much lower than this temperature. The Tsukiyoshi Fault is not a single planar fracture, but a zone of fracturing containing several fault strands. In the sedimentary rocks, fault strands apparently vary in width from 4 m to at least 20 m over a lateral distance of < 50 m. In the underlying granite the maximum width is at least 60 m, but could be much wider. The hanging wall and foot wall of the fault zone apparently had differing hydraulic properties for at least part of the fault's history. In the borehole studied in most detail, the hanging wall of the fault has been the most conductive pathway for mineralisation in the past, controlling the distribution of chlorite and calcite mineralisation. However, chemical buffering of the fluids by water/rock interactions has apparently prevented any significant large-scale movement of uranium. Outside the fractured zone in the hanging wall, there is little evidence that mineralising fluids could penetrate into or circulate within, the rock's matrix. Mineralogical data suggest that some of these properties may have changed over time due to both a structural control and to water/rock interactions. The two most important aspects of this are:

- a change in the sense of movement of the fault from reverse to normal may have influenced the hydraulic conductivity of the fault, notably by reducing permeability normal to the fault plane, and possibly by generating porosity in the hanging wall;
- water/rock interactions probably included a combination of dissolution/precipitation reactions that affected the distribution of open porosity and, by inference, the hydraulic properties of the fault.

This second mechanism is important because it could influence the permeability of a fault zone even after tectonic activity has ceased.

Abstract for a presentation at the Annual Conference of the Geological Society of Japan, Nagoya, 10th October 1999

Meeting the challenge of deep geological waste disposal: some lessons from research into radioactive waste disposal in the UK

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In the United Kingdom, 'geological disposal' is used to describe the placement of many types of waste within a geological environment without any intention to disturb the waste in the future. The environments may be near to the surface or deep underground, but it is always aimed to contain the waste for as long as it is potentially harmful. Many types of underground disposal systems have been used or proposed. The waste may be placed in an artificially excavated cavity (or repository), or it may be pumped directly into artificial or natural pore space in the rocks. Many types of barrier have been used or proposed to prevent pollution leaking from the disposal environments. The type of barrier depends upon the type of waste and the nature of the disposal environment. Sometimes, artificial barriers (engineered barriers) are needed (Fig. 1A). In other cases, the only barrier is the rock around the waste (Fig. 1B).

In the United Kingdom, there has been extensive research into geological disposal for many types of waste, ranging from radioactive wastes to CO_2 generated by power stations. However, during the last 25 years, geological disposal of radioactive wastes has received most attention. A goal of this research has been to identify sites that have the characteristics in Table 1. At the same time as potential repository sites have been studied, research has also been done on artificial barriers. Initially, all kinds of radioactive waste were considered. However, since 1982, there has been little research into the geological disposal of the most potentially harmful waste, High Level Waste (which includes spent fuel), partly due to public opposition. Since then, the policy has been to store High Level Waste on the surface for 50 years, while a final disposal solution is sought. Instead, research into geological disposal has concentrated on other types of radioactive waste (Low- and Intermediate- level wastes). Both shallow and deep geological disposal have been considered. However, in 1987 the government decided that most Low- and Intermediate-level wastes should be placed in a deep repository. From 1989 investigations focussed upon deep geological environments at Sellafield, in northwest England and at Dounreay in northern Scotland, but after 1991 investigations concentrated on Sellafield. By the start of 1997, extensive geological and hydrogeological investigations had been done here and 29 deep (up to c. 2 km) boreholes had been drilled. In the next stage an underground laboratory was to have been constructed. If investigations in the laboratory were favourable, a repository, including several artificial barriers (Fig. 1A), would have been constructed at the same site. However, in March 1997, the government refused permission to build the laboratory, thereby ending the site's evaluation. The main reasons were: 1. planning objections (e.g. appearance of spoil heaps); 2. further hydrogeological and geological studies were thought necessary; 3. the laboratory's location was not thought to be the best site for the repository; 4. it was thought that the laboratory's construction might damage the rock around a future repository. As a consequence, since March 1997, no site has been evaluated for the geological disposal of radioactive wastes in the United Kingdom. However, the research at Sellafield was not stopped because the site was shown to be technically unsuitable. Instead, planning procedures, public opinion, politics and the fact that the progress of technical investigations was out of step with these factors, all

contributed to the investigations being ended. In fact, the research done at Sellafield and elsewhere in the United Kingdom made considerable advances. Many technologies and approaches were developed to investigate the deep geological environment (Table 1). Perhaps the greatest achievement was to integrate many different types of research successfully. It was also demonstrated that deep geological environments are likely to exist in the United Kingdom at which radioactive wastes could be disposed of safely. Additionally, there now exists an understanding of deep geological environments and the basic technologies required to investigate them adequately. Thus, in March 1999, the Science and Technology Committee of the United Kingdom's parliament was able to recommend that deep geological disposal remains the best disposal option for all the main types of radioactive wastes, including High Level Waste.

An important lesson is that scientific investigations related to radioactive waste disposal should be synchronised effectively with other processes, such as planning procedures or political processes. This challenges earth scientists to ensure that technical issues are reported clearly and transparently to regulators, politicians, planners and public. On the other hand, earth scientists should target their investigations at issues that concern these groups of people.

These principles also apply to other types of waste disposal. Other wastes for which deep geological disposal might be appropriate include highly toxic wastes, like some chemical wastes and wastes that are physically unsuitable for disposal close to the surface, such as CO_2 generated by power stations. However, in all cases, it is important to keep the regulators, politicians, planning an public informed about the scientific issues that determine the safety of the proposed disposal. The nuclear waste management industry has gained unparalleled expertise in presenting scientific information to these groups of people. Organisations involved in other types of waste disposal could learn from this experience.

Different wastes will require very different types of disposal. In some cases, it will be necessary to excavate an underground cavity, whereas in other cases, it will be possible to pump waste underground into the natural pores in the rock (Fig. 1). Sometimes, it will be necessary to construct an artificial barrier (Fig. 1A), but sometimes it will be possible to rely on the natural barrier provided by the rocks (Fig. 1B). However, many of the general approaches and technologies developed by the radioactive waste management industry can contribute to the disposal of many very different types of waste. For example, in the United Kingdom, there has been significant research into the possible disposal of CO_2 from power stations, by pumping the CO_2 underground in a similar fashion to that illustrated by Fig. 1B. In this case, the proposal is to change the pressure and temperature of the CO_2 so that it behaves as a liquid-like fluid (the CO_2 in this state is said to be a 'supercritical fluid'). Under these conditions, the fluid will be more dense than many groundwaters. This is a very different disposal situation to the one usually proposed for radioactive wastes, as shown in Fig. 1A. However, in both cases it is important to predict how fluid flowing from the disposal site (CO_2 or water flowing through the radioactive waste repository) will react with rocks. Approaches to numerical predictions and investigations of water/rock interactions by laboratory experiments that have been developed by the radioactive waste management industry have been adapted to predict the chemical effects of CO_2 disposal in the rocks around a disposal site.

In conclusion, research into radioactive waste disposal has significantly improved our understanding of the deep geological environment. This research has also developed effective approaches for investigating the deep geological environment. Earth scientists are challenged to apply this understanding and these approaches to the disposal of other types of waste.

Table 1. Some general features of potential deep disposal sites and approaches to investigating these features in the United Kingdom.

Typical Features of a Deep Disposal Environment		Some Major Items to be Determined	Some Approaches
Generic	• High potential to retard and attenuate pollutants • Low geothermal gradients • Low groundwater fluxes • Large chemical buffering capacity • No natural resources • Little potential for future change • Predictable	• Lithologies (Rock types) • Rock Structure • Geological History • Groundwater chemistry • Rock chemistry • Mineralogy • Rock permeability • Hydraulic heads (forces driving groundwater flow) • Distances from natural hazards • Distances from natural resources	• Geological mapping • Borehole investigations • Investigations in underground laboratories • Laboratory testing/experiments • Geophysical investigations (e.g. seismic, borehole geophysics) • Investigations of natural features with some similarities to wastes (e.g. uranium deposits) • Theoretical geochemical modelling, • Hydrogeological modelling (models for groundwater flow)
Depends on Waste and Barrier	• Suitable rock strength • Suitable rock porosity		

Fig. 1 Schematic illustrations of two contrasting potential deep disposal situations. A. is based loosely on proposals by United Kingdom Nirex Ltd for an engineered barrier system in a repository for Low- and Intermediate- level radioactive wastes in the United Kingdom.

Abstract for a seminar given at the Tono Geoscience Center on 23rd April 1999

USING GEOCHEMISTRY IN PERFORMANCE ASSESSMENTS FOR RADIOACTIVE WASTE DISPOSAL: SOME ASPECTS RELEVANT TO INVESTIGATIONS IN TONO MINE AND THE MIU AREA

Abstract for a Presentation by

Richard Metcalfe

JNC International Fellow, Tono Geoscience Center

Performance Assessment (PA) for a potential underground radioactive waste repository is based directly and/or indirectly upon a wide variety of information types, but principally upon hydraulic, geological and hydrogeochemical information. However, PA tends to use the first two types of information more directly than hydrogeochemical information. Hydrogeochemical data tend to be used to help develop conceptual models underpinning PA, rather than to provide direct inputs to numerical PA models. An evaluation will be made of the extent to which hydrogeochemical information could be applied, or should be applied, more directly in PA. As an illustration, results from recent investigations at Sellafield in the United Kingdom will be presented and wider implications of these results will be drawn, including implications for on-going studies in Japan.

Hydrogeochemical information can be used to:

- describe the present spatial distributions of distinct groundwater masses within an area;
- constrain the history of past groundwater movement;
- constrain the present chemical conditions in the deep geosphere;
- constrain the temporal evolution of chemical conditions in the deep geosphere.

In practice, PA tends to take a very conservative approach that emphasizes the first application. However, there is scope for giving the other applications more prominence. In particular, PA would be enhanced if the timing of groundwater movements implied by the groundwater flow models is corroborated independently. In principal, evidence from groundwater chemistry can provide such corroboration. However, in practice, such hydrochemical data may give only a very general indication of the timing of groundwater movements. This limitation reflects factors such as contamination during sampling and mixing between different groundwaters.

A major advance of the Sellafield study was an integrated interpretation of both the mineralogical and hydrochemical datasets. This integration provided important qualitative constraints on the stability of the groundwater system and past groundwater flow patterns. Potentially, a more complete integration of these types of information in any other site investigation elsewhere, coupled to improved mineral dating techniques, could constrain the absolute timing of groundwater movements. This approach is likely to be particularly valuable in areas such as the Tono Mine and MIU, where the groundwaters are fresh and show relatively little geochemical variation. In these cases, mineralogical information could provide a particularly valuable constraint upon past groundwater movements.

The findings at Sellafield also imply that the hydraulic properties of the rock mass changed over time, due to water/rock interactions. PA does not normally consider this factor. Recent investigations in Tono mine suggest that such variations in hydraulic properties may have occurred there in then past.

It is necessary to design information management procedures carefully, to ensure that modellers involved directly in PA are appraised adequately about site characterization issues. Similarly, the workers involved in PA must articulate their requirements clearly to workers operating in the fields of data acquisition and interpretation.

APPENDIX 3

Computer programme to calculate in-situ production of ^{36}Cl

This appendix contains major parts of the code Clip36, which was written to calculate equilibrium $^{36}Cl/Cl$ ratios at depths of more than a few 10's of metres, where near surface production from muon-pion reactions are unimportant.

Microsoft Visual Basic for Applications™, within Microsoft Excel 98™ for Apple Macintosh computers. It is designed to use the in-built features of Excel and therefore variables refer to cells within Excel.

The program is included on the CD ROM that accompanies this report.

Data describing a rock's composition and porosity and the coexisting water composition are entered into appropriate cells in the 'Model' worksheet within Excel. The 'Start' button on the worksheet 'StartPage' is then pressed and the results are written to the 'TempResult' worksheet.

It is stressed that the code was written specifically for the purpose of calculating theoretical equilibrium $^{36}Cl/Cl$ ratios in rocks and for performing scoping calculations for the Tono area. The code is therefore not very user-friendly. Additionally, there is considerable redundancy in the code presented. This is because it was written with expansion in mind.

```
Sub Startbutton_Click()                    'Contains calls to subroutines below, which are invoked when the start
                                            button is pressed.

Rockmove
NabsXsect
Alphaneut
Fissneut
Fisandalpha
Cl36prod

End Sub

Option Private Module  ' Indicate that the variables declared public can be used anywhere in this project
'Define variables to hold references to cells in the work book; procedure-specific variables are declared within the procedure to
which they refer

'Values that are constant within a calculation

Public Rocktitle As String                 'Holds identity of the rock being considered
Public Location As String                  'Holds the location of for which the model is being calculated
Public Waterswitch As String               'Holds the answer (Yes/No) to the question Water 36Cl/Cl?
Public WClconc As Double                   'Holds  the  Cl concentration in the sampled water
Public WCl36 As Double                     'Holds the number of atoms of 36Cl in the sampled water
Public WCl36Cl As Double                   'Holds the 36Cl/Cl ratio in the sampled water
Public IClconc As Double                   'Holds  the  Cl concentration in the water that flows into the formation of
                                            interest
Public ICl36 As Double                     'Holds the number of atoms of 36Cl in the water that flows into the
                                             formation of interest
Public ICl36Cl As Double                   'Holds the 36Cl/Cl ratio in the water that flows into the formation of
                                            interest
Public ClconcRk As Double                  'Holds the Cl concentration in the rock
Public KconcRk As Double                   'Holds the K concentration in the rock
Public Latitude As Double                  'Holds the latitude of the location for which the model is being calculated
Public Longitude As Double                 'Holds the longitude of the location for which the model is being
                                            calculated
Public Altitude As Double                  'Holds the longitude of the location for which the model is being
                                             calculated
Public Rkdensity As Double                 'Holds the density of the rock for which the model is being calculated
Public Rkporosity As Double                'Holds the porosity of the rock for which the model is being calculated
Public Frac238 As Double                   'Holds fraction of U that is U238
Public Mass238 As Double                   'Holds atomic mass of U238
Public Dconst238 As Double                 'Holds decay constant of U238
Public Nutperfis As Double                 'Holds number of neutrons emitted on average per fission of U-238
Public PI As Double                        'Holds the value of PI
Public BasicDataDepths As Double           'Holds the number of the column containing the depth data in the basic
                                            data sheet
Public Nprodepth As Double '               'Holds column in Tempresults sheet that contains the depths of the neutron
                                            production calculations
Public Nprodval As Double                  'Holds column in Tempresults sheet that contains the total neutron production
Public Nproderr As Double                  'Holds column in Tempresults sheet that contains the error on the total
                                             neutron production
Public Nfluxval As Double                  'Holds column in Tempresults sheet that contains the total neutron flux
Public Nfluxerr As Double                  'Holds column in Tempresults sheet that contains the error on the total
                                            neutron flux
Public Cl36ratdepth As Double              'Holds column in Tempresults sheet that contains the deths for which in-
                                             situ 36Cl/Cl ratios are calculated
Public Cl36Rratio As Double                'Holds column in Tempresults sheet that contains the in-situ 36Cl/Cl ratios
                                             in the rock matrix
Public Cl36Rratioerr As Double             'Holds column in Tempresults sheet that contains the error on in-situ
                                            36Cl/Cl ratios in the rock matrix
Public Cl36RratioKno As Double             'Holds column in Tempresults sheet that contains the rock ratio, calculated
                                            with the Kna component
Public Cl36RratioKnoerr As Double          'Holds column in Tempresults sheet that contains the error on the rock
                                            ratio, calculated without Kna component
```

```
Public Cl36Wratio As Double                'Holds column in Tempresults sheet that contains the in-situ 36Cl/Cl ratios
                                            in the water
Public Cl36Wratioerr As Double             'Holds column in Tempresults sheet that contains the error on in-situ
                                            36Cl/Cl ratios in the water
Public Cl36Datdepth As Double              'Holds the column in the Tempresults sheet that contains the depth for
                                            which 36Cl ages are calculated
Public Cl36Date As Double                  'Holds the column in the Tempresults sheet that contains the model 36Cl
                                            ages
Public Cl36Daterr As Double                'Holds the column in the Tempresults sheet that contains the errors on the
                                            model 36Cl ages
Public Modanalstart As Double              'Holds the number of the row in which the rock analysis starts in the Model
                                            spreadsheet
Public Tempanalstart As Double             'Holds the number of the row in which the rock analysis starts in the
                                            Tempresult spreadsheet
Public Modanalend As Double                'Holds the number of the row in which the rock analysis ends in the Model
                                            spreadsheet
Public Tempanalend As Double               'Holds the number of the row in which the rock analysis ends in the
                                            Temporary Results spreadsheet

'Values that may vary within a calculation

Public Sumfract As String                  'Holds the name of the cell containing the sum of the fractional data
Public Sumsect As String                   'Holds the name of the cell containing the sum of the cross-sections
Public Errsumsect As String                'Holds the name of the cell containing the error on the sum of the cross-
                                            sections
Public Nutgyr As String                    'Holds the name of the cell containing the neutron production per year per
                                            gramme of rock by fission
Public Errnutgyr As String                 'Holds the name of the cell containing the error on the neutron production
                                            per year per gramme of rock
Public Nutuguyr As String                  'Holds the name of the cell containing the neutrons produced per year per
                                            microgramme of uranium
Public Totnutprod As String                'Holds the name of the cell containing the total production of neutrons per
                                            gramme of rock per year
Public Errtotnutprod As String             'Holds the name of the cell containing the error on the total production of
                                            neutrons per gramme of rock per year
Public UANnutgyr As String                 'Holds the name of the cell containing the neutrons produced per year per microgramme of
uranium, from alpha-neutron reactions
Public ErrUANnutgyr As String              'Holds the name of the cell containing the error on the neutrons produced
                                            per year per microgramme of uranium, from alpha-neutron reactions
Public TANnutgyr As String                 'Holds the name of the cell containing the neutrons produced per year per
                                            microgramme of thorium, from alpha-neutron reactions
Public ErrTANnutgyr As String              'Holds the name of the cell containing the error on the neutrons produced
                                            per year per microgramme of thorium, from alpha-neutron reactions
Public UANnutgyrg As String                'Holds the name of the cell containing the neutrons produced by alpha-
                                            neutron reactions per year, per gramme of rock, the neutrons arising from
                                            uranium
Public ErrUANnutgyrg As String             'Holds the name of the cell containing the error on the neutrons produced
                                            by alpha-neutron reactions per year, per gramme of rock, the neutrons
                                            arising from uranium
Public TANnutgyrg As String                'Holds the name of the cell containing the neutrons produced by alpha-
                                            neutron reactions per year, per gramme of rock, the neutrons arising from
                                            thorium
Public ErrTANnutgyrg As String             'Holds the name of the cell containing the error on the neutrons produced
                                            by alpha-neutron reactions per year, per gramme of rock, the neutrons
                                            arising from thorium
Public Chloride As String                  'Holds the name of the cell containing the chloride abundance in fractional
                                            form
Public ChlorideE As String                 'Holds the name of the cell containing the error on the chloride abundance
                                            in fractional form
Public Sodium As String                    'Holds the name of the cell containing the sodium abundance in fractional
                                            form
Public SodiumE As String                   'Holds the name of the cell containing the error on the sodium abundance
                                            in fractional form
Public Oxygen As String                    'Holds the name of the cell containing the oxygen abundance in fractional
                                            form
Public OxygenE As String                   'Holds the name of the cell containing the error on the oxygen abundance
                                            in fractional form
```

```
Public Hydrogen As String                'Holds the name of the cell containing the hydrogen abundance in
                                          fractional form
Public HydrogenE As String               'Holds the name of the cell containing the error on the hydrogen abundance
                                          in fractional form
Public Calcium As String                 'Holds the name of the cell containing the calcium abundance in fractional
                                          form
Public Potassium As String               'Holds the name of the cell containing the chloride abundance in fractional
                                          form
Public Geomaglat As String               'Holds the name of the cell Tempresults sheet that contains the
                                          geomagnetic latitude
Public Pionlatcorr As String             'Holds name of cell in Tempresults sheet that contains the latitude
                                          correction for pion production
Public Pionaltcorr As String             'Holds name of cell in Tempresults sheet that contains the altitude
                                          correction for pion production
Public Fallout As String                 'Holds name of cell in Tempresults sheet that contains the atoms of 36Cl
                                          fallout in precipitation
Public Evaporation As String             'Holds name of cell in Tempresults sheet that contains the amount of
                                          evaporation/transpiration in mm
Public Rechgconc As String               'Holds the name of cell in Tempresults sheet that contains the
                                          concentration of Cl-36 in recharge
Public Uconcug As Double                 'Holds U abundance in microgrammes per gramme, ppm
Public Uconerr As Double                 'Holds error on U abundance in microgrammes per gramme, ppm
Public Thconug As Double                 'Holds Th abundance in microgrammes per gramme, ppm
Public Thconerr As Double                'Holds error on Th abundance in microgrammes per gramme, ppm
Public AtU238 As Double                  'Contains number of atoms of uranium 238


Sub Assvar()                             'Assigns values to variables, from the spreadsheet information

 'Constants within the calculations - may be varied from model to model, but constant within a calculation

 Rocktitle = Worksheets("Model").Range("Rocktitle").Value
 Waterswitch = Worksheets("Model").Range("Watercalc").Value
 Frac238 = Worksheets("Basic Data").Range("Frac238").Value
 Mass238 = Worksheets("Basic Data").Range("Mass238").Value
 Dconst238 = Worksheets("Basic Data").Range("Dconst238").Value
 Nutperfis = Worksheets("Basic Data").Range("Nutperfis").Value
 Location = Worksheets("Model").Range("Location").Value
 Latitude = Worksheets("Model").Range("Latitude").Value
 Longitude = Worksheets("Model").Range("Longitude").Value
 Altitude = Worksheets("Model").Range("Altitude").Value
 Rkdensity = Worksheets("Model").Range("Rkdensity").Value
 Rkporosity = Worksheets("Model").Range("Rkporosity").Value / 100 'Rock porosity input as a percentage, but used here as a
fractional value
 Rainfall = Worksheets("Model").Range("Rainfall").Value
 Evapotrans = Worksheets("Model").Range("Evapotrans").Value
 WClconc = Worksheets("Model").Range("WClconc").Value
 ClconcRk = Worksheets("Model").Range("ClconcRk").Value
 CaconcRk = Worksheets("Model").Range("CaconcRk").Value
 KconcRk = Worksheets("Model").Range("KconcRk").Value
 WCl36 = Worksheets("Model").Range("WCl36").Value
 WCl36Cl = Worksheets("Model").Range("WCl36Cl").Value
 ICl conc = Worksheets("Model").Range("ICl conc").Value
 ICl36 = Worksheets("Model").Range("ICl36").Value
 ICl36Cl = Worksheets("Model").Range("ICl36Cl").Value
 PI = 3.141593
 BasicDataDepths = 38
 Nprodepth = 50
 Nprodval = 51
 Nproderr = 52
 Nfluxval = 53
 Nfluxerr = 54
 Cl36ratdepth = 56
 Cl36Rratio = 57
 Cl36Rratioerr = 58
 Cl36RratioKno = 59
 Cl36RratioKnoerr = 60
```

```
Cl36Wratio = 61
Cl36Wratioerr = 62
Cl36Datdepth = 63
Cl36Date = 64
Cl36Daterr = 74
Modanalstart = 51
Modanalend = 75
Tempanalstart = 7
Tempanalend = 31

'Variables - vary in the course of the calculations

Sumfract = "Sumfract"
Sumsect = "Sumsect"
Errsumsect = "Errsumsect"
Nutgyr = "Nutgyr"
Errnutgyr = "Errnutgyr"
Nutuguyr = "Nutuguyr"
UANnutgyr = "UANnutgyr"
ErrUANnutgyr = "ErrUANnutgyr"
TANnutgyr = "TANnutgyr"
ErrTANnutgyr = "ErrTANnutgyr"
UANnutgyrg = "UANnutgyrg"
ErrUANnutgyrg = "ErrUANnutgyrg"
TANnutgyrg = "TANnutgyrg"
ErrTANnutgyrg = "ErrTANnutgyrg"
Totnutprod = "Totnutprod"
Errtotnutprod = "Errtotnutprod"
Chloride = "Chloride"
ChlorideE = "ChlorideE"
Sodium = "Sodium"
SodiumE = "SodiumE"
Oxygen = "Oxygen"
OxygenE = "OxygenE"
Hydrogen = "Hydrogen"
HydrogenE = "HydrogenE"
Calcium = "Calcium"
Potassium = "Potassium"
Geomaglat = "Geomaglat"
Pionlatcorr = "Pionlatcorr"
Pionaltcorr = "Pionaltcorr"
Fallout = "Fallout"
Evaporation = "Evaporation"
Rechgconc = "Rechgconc"

'Take U and Th fractional abundances and convert to microgrammes per gramme

Uconcug = Worksheets("TempResult").Range("Uconcug").Value * 1000000
Uconerr = Worksheets("TempResult").Range("Uconerr").Value * 1000000

If Uconerr < 0.001 Then

  Uconerr = Uconerr * 0.05

End If

Thconug = Worksheets("TempResult").Range("Thconug").Value * 1000000
Thconerr = Worksheets("TempResult").Range("Thconerr").Value * 1000000

If Thconerr < 0.001 Then

  Thconerr = Thconerr * 0.05

End If

End Sub
```

```
Option Private Module 'Means that the module can only be used in this project
Private Rowcount As Integer 'Means that this variable can be used only in this module - variable simply a counter to count through rows in the spreadsheet
```

Sub Rockmove() 'Cycles through the rock composition provided in the model, with constituents in wt% or ppm, recalculates the compositions in fractional abundances

```
 Dim Sumabund As Double  'A variable within which the abundances of rock components are summed
 Dim Waterdensity As Double 'A variable which holds the density of the water, approximated by the sum of the mass of water (density assumed 1 kg/l, no temperature correction) and
                            'the mass of solute present, assumed to be just Na Cl for simplicity, the concentration of Na Cl being calculated assuming all Cl is present as Na Cl
 Dim Fracsolid As Double 'A variable that holds the fraction of the rock mass that is solid
 Dim FracCl As Double 'A variable that holds the fraction of the solution's mass that is Cl
 Dim FracNa As Double 'A variable that holds the fraction of the solution's mass that is Na
 Dim FracH As Double 'A variable that holds the fraction of the solution's mass that is H
 Dim FracO As Double 'A variable that holds the fraction of the solution' mass that is O

 Sumabund = 0
 Waterdensity = 0
 Fracsolid = 0

 Assvar 'Assigns variables

 Worksheets("TempResult").Cells(4, 3).Value = Rocktitle 'Enters title for rock type into the temporary result work sheet
 Worksheets("TempResult").Cells(4, 7).Value = Rocktitle 'Enters title for rock type into the temporary result work sheet

 For Rowcount = Modanalstart To (Modanalstart + 11) 'Cycles through the rock composition provided in the model, with constituents in wt%,  recalculates the compositions in fractional abundances

   Worksheets("TempResult").Cells(Rowcount - (Modanalstart - Tempanalstart), 3).Value = Worksheets("Model").Cells(Rowcount, 3).Value * 0.01 'Converts estimate of value
   Worksheets("TempResult").Cells(Rowcount - (Modanalstart - Tempanalstart), 4).Value = Worksheets("Model").Cells(Rowcount, 4).Value * 0.01 'Converts error on value
   Sumabund = Sumabund + Worksheets("TempResult").Cells(Rowcount - (Modanalstart - Tempanalstart), 3).Value 'Calculates a running total of the fractional abundances

   If Worksheets("TempResult").Cells(Rowcount - (Modanalstart - Tempanalstart), 4).Value < 0.00000001 Then

     Worksheets("TempResult").Cells(Rowcount - (Modanalstart - Tempanalstart), 4).Value = Worksheets("TempResult").Cells(Rowcount - (Modanalstart - Tempanalstart), 3).Value / 10

   End If

 Next

 For Rowcount = (Modanalstart + 12) To Modanalend 'Cycles through the rock composition provided in the model, with constituents in ppm,  recalculates the compositions in fractional abundances

   Worksheets("TempResult").Cells(Rowcount - (Modanalstart - Tempanalstart), 3).Value = Worksheets("Model").Cells(Rowcount, 3).Value * 0.000001 'Converts estimate of value
   Worksheets("TempResult").Cells(Rowcount - (Modanalstart - Tempanalstart), 4).Value = Worksheets("Model").Cells(Rowcount, 4).Value * 0.000001 'Converts error on value
   Sumabund = Sumabund + Worksheets("TempResult").Cells(Rowcount - (Modanalstart - Tempanalstart), 3).Value 'Calculates a running total of the fractional abundances

   If Worksheets("TempResult").Cells(Rowcount - (Modanalstart - Tempanalstart), 4).Value < 0.00000001 Then

     Worksheets("TempResult").Cells(Rowcount - (Modanalstart - Tempanalstart), 4).Value = Worksheets("TempResult").Cells(Rowcount - (Modanalstart - Tempanalstart), 3).Value / 10

   End If

 Next
```

```
 Worksheets("TempResult").Range(Sumfract).Value = Sumabund 'Enters the total fractional abundance in the temporary results worksheet

 If Waterswitch = "Yes" Then

   Sumabund = 0
   Waterdensity = 1 + (WClconc + Worksheets("Basic Data").Cells(14, 2).Value * WClconc / Worksheets("Basic Data").Cells(19, 2).Value) / 1000000 'Calculates an approximate value for the density of the groundwater
   Fracsolid = 1 - (Waterdensity / (Waterdensity + (Rkdensity / Rkporosity) - Rkdensity)) 'Calculate the mass fraction of the rock which is solid

   For Rowcount = Tempanalstart To Tempanalend  'Cycles through the rock composition in the spreadsheet 'TempResult' and modifies the composition to allow for the fact that a unit mass of rock contains water-filled space

     Worksheets("TempResult").Cells(Rowcount, 3).Value = Worksheets("TempResult").Cells(Rowcount, 3).Value * Fracsolid
     Worksheets("TempResult").Cells(Rowcount, 4).Value = Worksheets("TempResult").Cells(Rowcount, 4).Value * Fracsolid
     Sumabund = Sumabund + Worksheets("TempResult").Cells(Rowcount, 3).Value 'Calculates a running total of the fractional abundances

   Next

   Worksheets("TempResult").Range(Sumfract).Value = Sumabund 'Enters the total fractional abundance in the temporary results worksheet

   'Calculate mass fraction of the water that is Cl, Na, O, H, taking the input Cl value with units in mg/l and assuming that 1 l of solution has the same volume as the water that it contains

    FracCl = (WClconc / Waterdensity) / 1000000
    FracNa = ((WClconc / Waterdensity) * Worksheets("Basic Data").Cells(14, 2).Value / Worksheets("Basic Data").Cells(19, 2).Value) / 1000000
    FracH = (2 * Worksheets("Basic Data").Cells(17, 2).Value / (2 * Worksheets("Basic Data").Cells(17, 2).Value + Worksheets("Basic Data").Cells(16, 2).Value)) * (1000000 - (WClconc / Waterdensity) - ((WClconc / Waterdensity) * Worksheets("Basic Data").Cells(14, 2).Value / Worksheets("Basic Data").Cells(19, 2).Value)) / 1000000
    FracO = (Worksheets("Basic Data").Cells(16, 2).Value / (2 * Worksheets("Basic Data").Cells(17, 2).Value + Worksheets("Basic Data").Cells(16, 2).Value)) * (1000000 - (WClconc / Waterdensity) - ((WClconc / Waterdensity) * Worksheets("Basic Data").Cells(14, 2).Value / Worksheets("Basic Data").Cells(19, 2).Value)) / 1000000

   'Add the mass fractions of Cl, Na, O and H in the water, to the modified mass fractions in the rock

    Worksheets("TempResult").Range(Chloride).Value = Worksheets("TempResult").Range(Chloride).Value + (FracCl * (1 - Fracsolid))
    Worksheets("TempResult").Range(Sodium).Value = Worksheets("TempResult").Range(Sodium).Value + (FracNa * (1 - Fracsolid))
    Worksheets("TempResult").Range(Oxygen).Value = Worksheets("TempResult").Range(Oxygen).Value + (FracO * (1 - Fracsolid))
    Worksheets("TempResult").Range(Hydrogen).Value = Worksheets("TempResult").Range(Hydrogen).Value + (FracH * (1 - Fracsolid))
    Worksheets("TempResult").Range(Sumfract).Value = Worksheets("TempResult").Range(Sumfract).Value + ((FracCl + FracNa + FracO + FracH) * (1 - Fracsolid))

 End If

End Sub
```

Sub NabsXsect() 'Calculates the neutron absorption cross-section of the rock

```
 Dim SumXsect As Double 'A variable within which the cross-sections for each component of the rock are summed
 Dim Sumerrxsect As Double  'A variable within which the errors on the cross-sections for each component of the rock are summed

 SumXsect = 0
 Sumerrxsect = 0

 Assvar
```

```
For Rowcount = Tempanalstart To Tempanalend 'Cycles through the rock composition provided in the model, with consituents in fractional proportions

  Worksheets("TempResult").Cells(Rowcount, 7).Value = Worksheets("Basic Data").Cells(Rowcount, 3).Value * (Worksheets("TempResult").Cells(Rowcount, 3).Value / Worksheets("Basic Data").Cells(Rowcount, 2).Value)

  SumXsect = SumXsect + Worksheets("TempResult").Cells(Rowcount, 7).Value

  If Worksheets("TempResult").Cells(Rowcount, 7).Value > 0 Then 'If the actual value of the cross-section is positive, that is non-zero, calculate an error on the cross-section

    If IsNumeric(Worksheets("Basic Data").Cells(Rowcount, 4).Value) Then 'Check to see if there is an error reported for the absolute absorption cross-section, if so calculate an error on the contribution to the total absorption cross-section from the element that takes into account both the error on the analysis and the error on the absolute cross-section

      Worksheets("TempResult").Cells(Rowcount, 8).Value = Worksheets("TempResult").Cells(Rowcount, 7).Value * (((Worksheets("TempResult").Cells(Rowcount, 4).Value / Worksheets("TempResult").Cells(Rowcount, 3).Value) ^ 2 + (Worksheets("Basic Data").Cells(Rowcount, 4).Value / Worksheets("Basic Data").Cells(Rowcount, 3).Value) ^ 2) ^ 0.5)

      Sumerrxsect = Sumerrxsect + (Worksheets("TempResult").Cells(Rowcount, 8).Value) ^ 2

    Else 'If there is no error reported for the absolute cross-section, calculate a minimum error on the contribution of the element to the cross-section using only the error on the analysis

      Worksheets("TempResult").Cells(Rowcount, 8).Value = Worksheets("TempResult").Cells(Rowcount, 7).Value * (((Worksheets("TempResult").Cells(Rowcount, 4).Value / Worksheets("TempResult").Cells(Rowcount, 3).Value) ^ 2) ^ 0.5)

      Sumerrxsect = Sumerrxsect + (Worksheets("TempResult").Cells(Rowcount, 8).Value) ^ 2

    End If

  Else

    Worksheets("TempResult").Cells(Rowcount, 7).Value = 0 'If the cross-section is zero or negative, set the error on the cross-section to be zero

  End If

Next

Sumerrxsect = Sumerrxsect ^ 0.5 'Calculates a total error

Worksheets("TempResult").Range(Sumsect).Value = SumXsect * 0.6023 'Required units are cm2/g, therefore multiply by 6.023 x 10^23 (to obtain cross section in barns) and then x 10^-24 to obtain in cm2/g - this is equivalent to multiplying by 0.6023 below.
Worksheets("TempResult").Range(Errsumsect).Value = Sumerrxsect * 0.6023 'Required units are cm2/g, therefore multiply by 6.023 x 10^23 (to obtain cross section in barns) and then x 10^-24 to obtain in cm2/g - this is equivalent to multiplying by 0.6023 below.

End Sub
```

Sub Alphaneut() 'Calculates neutron production rate resulting from alpha-neutron reactions, caused by neutrons originating from the U-Th series

```
Dim Uyielderr As Double 'Variable holding error on SiFiYiU, for each element
Dim Thyielderr As Double 'Variable holding error on SumSiFiYiTh for each element
Dim SumMstop As Double 'Variable holding sum  of mass stopping powers
Dim SumSiFiYiU As Double 'Variable holding sum of SumSiFiYiU
Dim SumSiFiYiTh As Double  'Variable holding sum of SumSiFiYiTh
Dim SumMstoperr As Double 'Variable holding the error on the sum of mass stopping powers
Dim SumSiFiYiUerr As Double 'Variable holding the error on SumSiFiYiU
Dim SumSiFiYiTherr As Double 'Variable holding the error on SumSiFiYiTh
Dim Nuturanalpha As Double 'Contains number of neutrons from alpha-neutron reactions due to U-derived alpha particles
```

```
 Dim Nuturanalphaerr As Double 'Contains error on number of neutrons from alpha-neutron reactions due to U-derived alpha particles
 Dim Nutthoralpha As Double 'Contains number of neutrons from alpha-neutron reactions due to Th-derived alpha particles
 Dim Nutthoralphaerr As Double 'Contains error on number of neutrons from alpha-neutron reactions due to Th-derived alpha particles

 SumMstop = 0
 SumSiFiYiU = 0
 SumSiFiYiTh = 0
 SumMstoperr = 0
 SumSiFiYiUerr = 0
 SumSiFiYiTherr = 0

 Assvar

 'Cycle through Basic data table containing mass stopping powers and neutron yields for Th and U

 For Rowcount = Tempanalstart To Tempanalend

  If IsNumeric(Worksheets("Basic Data").Cells(Rowcount, 6).Value) Then

   'Stopping power, Si x Fi in equations 2 and 3 of Andrews et al. 1989

   Worksheets("TempResult").Cells(Rowcount, 10).Value = "MeV g-1 cm-2" 'Writes units for stopping power
   Worksheets("TempResult").Cells(Rowcount, 10).Characters(6, 2).Font.Superscript = True 'Superscripts parts of units for stopping power
   Worksheets("TempResult").Cells(Rowcount, 10).Characters(11, 2).Font.Superscript = True 'Superscripts parts of units for stopping power
   Worksheets("TempResult").Cells(Rowcount, 11).Value = Worksheets("Basic Data").Cells(Rowcount, 6).Value * Worksheets("TempResult").Cells(Rowcount, 3).Value 'Stopping power
   Worksheets("TempResult").Cells(Rowcount, 12).Value = Worksheets("Basic Data").Cells(Rowcount, 6).Value * Worksheets("TempResult").Cells(Rowcount, 4).Value 'Error stopping power
   SumMstop = SumMstop + Worksheets("TempResult").Cells(Rowcount, 11).Value
   SumMstoperr = SumMstoperr + Worksheets("TempResult").Cells(Rowcount, 12).Value ^ 2

   'n-yield U, Si x Fi x YiU in equation 2 of Andrews et al. 1989

   Worksheets("TempResult").Cells(Rowcount, 14).Value = "MeV N ppm U-1 g-2 a-1 cm-2" 'Writes units for neutron yield
   Worksheets("TempResult").Cells(Rowcount, 14).Characters(12, 2).Font.Superscript = True 'Superscripts parts of units for Si x Fi x YiU
   Worksheets("TempResult").Cells(Rowcount, 14).Characters(16, 2).Font.Superscript = True 'Superscripts parts of units Si x Fi x YiU
   Worksheets("TempResult").Cells(Rowcount, 14).Characters(20, 2).Font.Superscript = True 'Superscripts parts of units Si x Fi x YiU
   Uyielderr = Worksheets("Basic Data").Cells(Rowcount, 7).Value * 0.8 'Holds error on neutron yield generated by alpha radiation from uranium fission
   Worksheets("TempResult").Cells(Rowcount, 15).Value = Worksheets("Basic Data").Cells(Rowcount, 6).Value * Worksheets("TempResult").Cells(Rowcount, 3).Value * Worksheets("Basic Data").Cells(Rowcount, 7).Value 'Si x Fi x YiU, reflecting neutron yield for alpha particles derived by U fission
   Worksheets("TempResult").Cells(Rowcount, 16).Value = Worksheets("TempResult").Cells(Rowcount, 15).Value * ((Worksheets("TempResult").Cells(Rowcount, 5).Value / Worksheets("TempResult").Cells(Rowcount, 4).Value) ^ 2 + (Uyielderr / Worksheets("Basic Data").Cells(Rowcount, 6).Value) ^ 2) ^ 0.5 'Error in Si x Fi x YiU
   SumSiFiYiU = SumSiFiYiU + Worksheets("TempResult").Cells(Rowcount, 15).Value
   SumSiFiYiUerr = SumSiFiYiUerr + Worksheets("TempResult").Cells(Rowcount, 16).Value ^ 2

   'n-yield Th, Si x Fi x YiTh in equation 2 of Andrews et al. 1989

   Worksheets("TempResult").Cells(Rowcount, 18).Value = "MeV N ppm Th-1 g-2 a-1 cm-2" 'Writes units for neutron yield
   Worksheets("TempResult").Cells(Rowcount, 18).Characters(13, 2).Font.Superscript = True 'Superscripts parts of units for Si x Fi x YiTh
   Worksheets("TempResult").Cells(Rowcount, 18).Characters(17, 2).Font.Superscript = True 'Superscripts parts of units for Si x Fi x YiTh
   Worksheets("TempResult").Cells(Rowcount, 18).Characters(21, 2).Font.Superscript = True 'Superscripts parts of units for Si x Fi x YiTh
   Worksheets("TempResult").Cells(Rowcount, 18).Characters(26, 2).Font.Superscript = True 'Superscripts parts of units for Si x Fi x YiTh
```

```
    Thyielderr = Worksheets("Basic Data").Cells(Rowcount, 8).Value * 0.8 'Holds error on neutron yield generated by alpha radiation from uranium fission
    Worksheets("TempResult").Cells(Rowcount, 19).Value = Worksheets("Basic Data").Cells(Rowcount, 6).Value * Worksheets("TempResult").Cells(Rowcount, 3).Value * Worksheets("Basic Data").Cells(Rowcount, 8).Value 'Si x Fi x YiTh, reflecting neutron yield for alpha particles derived by Th fission
    Worksheets("TempResult").Cells(Rowcount, 20).Value = Worksheets("TempResult").Cells(Rowcount, 19).Value * ((Worksheets("TempResult").Cells(Rowcount, 5).Value / Worksheets("TempResult").Cells(Rowcount, 4).Value) ^ 2 + (Thyielderr / Worksheets("Basic Data").Cells(Rowcount, 7).Value) ^ 2) ^ 0.5 'Error in Si x Fi x YiTh
    SumSiFiYiTh = SumSiFiYiTh + Worksheets("TempResult").Cells(Rowcount, 19).Value
    SumSiFiYiTherr = SumSiFiYiTherr + Worksheets("TempResult").Cells(Rowcount, 20).Value ^ 2

    End If

  Next

  'Calculates stopping power and terms Si x Fi x YiU and Si x Fi x YiTh, with corresponding errors

  Worksheets("TempResult").Cells((Tempanalend + 2), 11).Value = SumMstop 'Places sum of stopping powers 2 rows below analysis in TempResult
  Worksheets("TempResult").Cells((Tempanalend + 2), 12).Value = SumMstoperr ^ 0.5 'Places error on sum of stopping powers i2 rows below analysis in TempResult
  Worksheets("TempResult").Cells((Tempanalend + 2), 15).Value = SumSiFiYiU 'Places sum of Si x Fi x YiU 2 rows below analysis in TempResult
  Worksheets("TempResult").Cells((Tempanalend + 2), 16).Value = SumSiFiYiUerr ^ 0.5 'Places error on sum of Si x Fi x YiU 2 rows below analysis in TempResult
  Worksheets("TempResult").Cells((Tempanalend + 2), 19).Value = SumSiFiYiTh 'Places sum of Si x Fi x YiTh 2 rows below analysis in TempResult
  Worksheets("TempResult").Cells((Tempanalend + 2), 20).Value = SumSiFiYiTherr ^ 0.5 'Places error on sum of Si x Fi x YiTh 2 rows below analysis in TempResult

  'Calculates neutrons due to unit concentration of U and Th per unit mass of rock per year

  Worksheets("TempResult").Cells(Tempanalstart, 23).Value = SumSiFiYiU / SumMstop 'Places neutrons per g of rock per microg of U in row 7, column 23 of TempResult
  Worksheets("TempResult").Cells(Tempanalstart, 24).Value = (SumSiFiYiU / SumMstop) * (((SumSiFiYiUerr ^ 0.5) / SumSiFiYiU) ^ 2 + ((SumMstoperr ^ 0.5) / SumMstop) ^ 2) ^ 0.5 'Places error on neutrons per g of rock per microg of U in row 7, column 24 of TempResult
  Worksheets("TempResult").Cells(Tempanalstart, 27).Value = SumSiFiYiTh / SumMstop 'Places neutrons per g of rock per microg of Th in row 7, column 27 of TempResult
  Worksheets("TempResult").Cells(Tempanalstart, 28).Value = (SumSiFiYiTh / SumMstop) * (((SumSiFiYiTherr ^ 0.5) / SumSiFiYiTh) ^ 2 + ((SumMstoperr ^ 0.5) / SumMstop) ^ 2) ^ 0.5 'Places error on neutrons per g of rock per microg of U in row 7, column 28 of TempResult

  'Calculate neutrons from alpha-neutron reactions per g of rock per year

  Nuturanalpha = Uconcug * Worksheets("TempResult").Cells(Tempanalstart, 23).Value 'Neutrons per year per g of rock from U-alpha-neutron reactions
  Nuturanalphaerr = Nuturanalpha * ((Worksheets("TempResult").Cells(Tempanalstart, 24).Value / Worksheets("TempResult").Cells(7, 23).Value) ^ 2 + (Uconerr / Uconcug) ^ 2) ^ 0.5 'Error on neutrons per year per g of rock from U-alpha-neutron reactions
  Nutthoralpha = Thconug * Worksheets("TempResult").Cells(Tempanalstart, 27).Value 'Neutrons per year per g of rock from Th-alpha-neutron reactions
  Nutthoralphaerr = Nutthoralpha * ((Worksheets("TempResult").Cells(Tempanalstart, 28).Value / Worksheets("TempResult").Cells(7, 27).Value) ^ 2 + (Thconerr / Thconug) ^ 2) ^ 0.5 'Error on neutrons per year per g of rock from U-alpha-neutron reactions
  Worksheets("TempResult").Range(UANnutgyrg).Value = Nuturanalpha 'Places neutrons per year per g of rock from U-alpha-neutron reactions, in TempResult
  Worksheets("TempResult").Range(ErrUANnutgyrg).Value = Nuturanalphaerr 'Places error on neutrons per year per g of rock from U-alpha-neutron reactions, in TempResult
  Worksheets("TempResult").Range(TANnutgyrg).Value = Nutthoralpha 'Places neutrons per year per g of rock from U-alpha-neutron reactions, in TempResult
  Worksheets("TempResult").Range(ErrTANnutgyrg).Value = Nutthoralphaerr 'Places error on neutrons per year per g of rock from U-alpha-neutron reactions, in TempResult

End Sub
```

Sub Fissneut()

```
Dim NSponF As Double 'Contains neutrons generated by spontaneous U238 fission, per gramme of rock
Dim NSponFerr As Double 'Contains error on neutrons generated by spontaneous U238 fission per gramme of rock
Dim NSponFU As Double 'Contains neutrons generated by spontaneous fission per microgramme of uranium

Assvar

'Calculate atoms of U-238

AtU238 = Uconcug * 6.02 * 10 ^ 17 * Frac238 / Mass238 'U concentration in ppm in microgrammes per gramme, therefore
use 6.02E17 NOT 6.02E23

'Calculate neutrons from spontaneous fission of U-238, neutrons per year per g of rock

NSponF = AtU238 * Dconst238 * Nutperfis
NSponFerr = (((Uconerr / Uconcug) ^ 2 + 0.025 ^ 2) ^ 0.5) * NSponF 'Error on neutron production rate from spontaneous
fission of U-238, neutrons per year, per g of rock. 0.025 represents the ratio of the error on 8.5E-17*6.02E+17 * .9927 / 238.03
to the value of this ratio, taken from Neutflux
Worksheets("TempResult").Range(Nutgyr).Value = NSponF
Worksheets("TempResult").Range(Errnutgyr).Value = NSponFerr

'Calculate neutrons from spontaneous fission of U-238, neutrons per year per microgramme of U

NSponFU = NSponF / Uconcug
Worksheets("TempResult").Range(Nutuguyr).Value = NSponFU

End Sub
```

Sub Fisandalpha() 'Calculate the total fission and alpha-neutron reaction production rate

```
Dim Nutfromalpha As Double 'Contains total number of neutrons from alpha-neutron reactions
Dim Totnut As Double 'Contains total neutron production rate produced by alpha-neutron reactions and fission
Dim Errtotnut As Double 'Contains error on total neutron production rate produced by alpha-neutron reactions and fission

Assvar

'Calculate neutron production by alpha-neutron reactions

Nutfromalpha = Worksheets("TempResult").Range(UANnutgyr).Value * Uconcug +
Worksheets("TempResult").Range(TANnutgyr).Value * Thconug

'Total neutron flux, resulting from spontaneous fission decay of 238U and alpha/neutron reactions, involving alpha particles
produced by the decay of uranium and thorium and light atom constituents of the rock
'units neutrons per year per gramme, effectively equation 1 of Andrews et al 1989.

Totnut = Nutfromalpha + Worksheets("TempResult").Range(Nutgyr).Value

Errtotnut = (Worksheets("TempResult").Range(ErrUANnutgyrg).Value ^ 2 +
Worksheets("TempResult").Range(ErrTANnutgyrg).Value ^ 2 + Worksheets("TempResult").Range(Errnutgyr).Value ^ 2) ^ 0.5

'Write total neutron production and error on the total neutron production to the worksheet TempResult

Worksheets("TempResult").Range(Totnutprod).Value = Totnut

Worksheets("TempResult").Range(Errtotnutprod).Value = Errtotnut

End Sub
Sub PiMuApf() 'Calcs neutron production from spallation and neutron induced reactions,correcting for latitude and altitude.

Dim Gmaglat As Double 'Geomagnetic latitude
Dim AngfromNR As Double 'Angle from north in radians
Dim Longmag As Double 'Longitude relative to geomagnetic north pole in radians
```

```
Dim Latmag As Double 'Latitude relative to geomagnetic north pole in degrees
Dim Latmagcp As Double 'Compliment of the latitude relative to the geomagnetic north pole in radians
Dim Magpolelat As Double 'Latitude of the geomagnetic north pole in radians, measured from north pole
Dim Intercos As Double 'An intermediate result, used to split the equations below to make them easier to write
Dim Intertan As Double 'An intermediate result, used to split the equations below to make them easier to write
Dim Rkthickness As Double 'Term expressing the effect of rock density on attenuation of muons and pions
Dim Faclatpi As Double 'Latitude factor for pion/proton production
Dim Facaltpi As Double 'Altitude factor for pion/proton production
Dim Faclatmu As Double 'Latitude factor for muon production
Dim Facaltmu As Double 'Altitude factor for muon production
Dim Npiandmu As Double 'Contains neutrons produced in the near-surface from pions and muons
Dim Npi As Double 'Contains neutrons produced in the near-surface from pions
Dim Totneut As Double 'Contains the total neutrons produced at any depth
Dim Noneqcorr As Double 'Contains a correction for the non-equilibrium region
Dim Totnflux As Double 'Contains the total neutron flux at any depth

Assvar

  Totneut = Worksheets("TempResult").Range(Totnutprod).Value

  'Neutron flux is the neutron production rate divided by the macroscopic neutron absorption cross section.
  'The division by 3600*24*365 is to convert the resultant flux into a flux per second.

  Totnflux = Totneut / (Worksheets("TempResult").Range(Sumsect).Value * 3600 * 24 * 365) 'Units of flux are neutrons per
cm2 per second

  'Calculate for the non equilibrium region as O'BRIEN et al 1978 - this is because, within a short distance of the surface,
  'the production of neutrons is not exactly balanced by absorption within the rock

  Worksheets("TempResult").Cells(7, Nprodepth).Value = 100
  Worksheets("TempResult").Cells(7, Nprodval).Value = Totneut
  Worksheets("TempResult").Cells(7, Nproderr).Value = "Not Calc"
  Worksheets("TempResult").Cells(7, Nfluxval).Value = Totnflux
  Worksheets("TempResult").Cells(7, Nfluxerr).Value = "Not Calc"

End Sub


Option Private Module 'Means that the module can only be used in this project
Private Rowcount As Integer 'Means that this variable can be used only in this module - variable simply a counter to count
through rows in the spreadsheet
```

Sub Cl36prod()

```
Dim RClconc As Double 'Contains Cl concentration in rock in fractional form, g/g
Dim RKconc As Double "Contains Cl concentration in fractional form, g/g
Dim Cl36Deconst As Single 'Contains 36-Cl decay constant USED
Dim RCl3537At As Double 'Contains the total number of chloride atoms present in the solid rock
Dim WCl3537At As Double 'Contains the total number of chloride atoms present in the water
Dim RCl36Kna As Double 'Contains atoms per gramme of 36-Cl producted by neutron-alpha reactions on 39-K in the solid
rock
Dim Cl36n As Double 'Contains atoms per gramme of 36-Cl produced by neutrons on Cl in the solid rock or water (depending
upon option selected)
Dim Cl36ClRrat As Double 'Contains the equilibrium ratio, 36-Cl/Cl in the solid rock, INCLUDING 36-Cl produced by
neutron-alpha reactions on 39-K
Dim Cl36ClRratnoKna As Double 'Contains the equilibrium ratio, 36-Cl/Cl in the solid rock, EXCLUDING 36-Cl produced by
neutron-alpha reactions on 39-K
Dim Cl36ClWrat As Double 'Contains the equilibrium ratio, 36-Cl/Cl in the water USED
Dim Waterdensity As Double 'A variable which holds the density of the water, approximated by the sum of the mass of water
(density assumed 1 kg/l, no temperature correction) and
                                    'the mass of solute present, assumed to be just Na Cl for simplicity, the concentration of Na Cl
being calculated assuming all Cl is present as Na Cl

Assvar
```

```
  Cl36Deconst = 7.204881E-14

  Waterdensity = 0

 'Variables used to calculate Cl-36 production in the rock, including matrix Cl and K and Ca (from K and Ca by spallation) - as
in  Yoyama et al 1977

  RClconc = ClconcRk * 0.000001
  RKconc = CaconcRk * 0.01
  RCaconc = KconcRk * 0.01

  'Calculates the total number of atoms of chloride present

  RCl3537At = RClconc * 6.02E+23 / 35.453

  Cl36n = (RClconc * 0.76 * 6.02E+23 / 35.453) * 4.36E-23 * Worksheets("TempResult").Cells(7, Nfluxval).Value /
Cl36Deconst 'Cl36 atoms due to n-irrad. 0.76 is the proportion of natural Cl that is 35Cl; 4.36E-23 is the reaction cross-section of
Cl35 (from Andrews et al. 1989 - given as 43.6±0.4 b; note this is the value for 35Cl rather than bulk Cl, which is 33.6 b, owing
to 37Cl having a very low cross-section of 0.433)

  RCl36Kna = (RKconc * 0.93 * 6.02E+23 / 39.1) * 4.3E-27 * Worksheets("TempResult").Cells(7, Nfluxval).Value /
Cl36Deconst 'K39(n,a)Cl36 production; 0.93 is the proportion of natural K that is K39; 4.3E-27 is the reaction cross section of
K39 (from Andrews et al. 1989 - given as 4.3±0.5mb; note this is different to the value given in Neutron News 1992, v 3, No. 3,
29-37, which is 2.1 b)
  Cl36ClRrat = (RCl36Kna + Cl36n) / RCl3537At
  Cl36ClRratnoKna = (Cl36n) / RCl3537At 'This is uses the total amount of Cl present in the rock to calculate the ratio - not the
same as the amount of Cl in the water.
  Worksheets("TempResult").Cells(7, Cl36ratdepth).Value = 100
  Worksheets("TempResult").Cells(7, Cl36Rratio).Value = Cl36ClRrat * 1E+15
  Worksheets("TempResult").Cells(7, Cl36Rratioerr).Value = "Not Calc"
  Worksheets("TempResult").Cells(7, Cl36RratioKno).Value = Cl36ClRratnoKna * 1E+15
  Worksheets("TempResult").Cells(7, Cl36RratioKnoerr).Value = "Not Calc"
  Worksheets("TempResult").Cells(7, Cl36Wratio).Value = "Rock Model"
  Worksheets("TempResult").Cells(7, Cl36Wratioerr).Value = "Not Calc"

  If Waterswitch = "Yes" Then

    Waterdensity = 1 + (WClconc + Worksheets("Basic Data").Cells(14, 2).Value * WClconc / Worksheets("Basic
Data").Cells(19, 2).Value) / 1000000
    WCl3537At = (WClconc / Waterdensity) * 6.02E+23 / 35.453

    For Rowcount = Tempanalstart To (Tempanalstart + 6)

      Cl36n = ((WClconc / Waterdensity) * 0.76 * 6.02E+23 / 35.453) * 4.36E-23 * Worksheets("TempResult").Cells(Rowcount,
Nfluxval).Value / Cl36Deconst 'Cl36 atoms due to n-irrad. 0.76 is the proportion of natural Cl that is 35Cl; 4.36E-23 is the
reaction cross-section of Cl35 (from Andrews et al. 1989 - given as 43.6±0.4 b; note this is the value for 35Cl rather than bulk Cl,
which is 33.6 b, owing to 37Cl having a very low cross-section of 0.433)
      Cl36ClWrat = Cl36n / WCl3537At
      Worksheets("TempResult").Cells(Rowcount, Cl36Wratio).Value = Cl36ClWrat * 1E+15
      Worksheets("TempResult").Cells(Rowcount, Cl36Wratioerr).Value = "Not Calc"

    Next

  End If

End Sub
```

APPENDIX 4

Compilations of data produced during the Fellowship

During the Fellowship contributions were made to the following compilations of data:

- Iwatsuki, T., Metcalfe, R., Amano, K., Hama, K., Noda, N., Arthur, R.C. and Sasamoto, H. 2001. Data book on groundwater chemistry in the Tono area. JNC Report JNC TN 7450 2001-003.
- Iwatsuki, T., Metcalfe, R., Amano, K., Hama, K., Arthur, R.C. and Sasamoto, H. 2000. TGRP Hydrochemical database.
- Sasamoto, H., Metcalfe, and R., Arthur, R. 2000. ThemoTRGP.dat, a thermodynamic database for use in geochemical calculations (also reprinted with Iwatsuki et al. 2000).

These compilations are available as separate reports and are not reproduced here.

In addition, the following smaller compilations of data were produced:

- summary of information about the Tsukiyoshi Fault;
- plots comparing hydraulic test intervals in boreholes with the distributions of fault rocks in the same boreholes;
- compilation of water compositions from the Tsukiyoshi Fault zone;
- exchangeable cation data.

SUMMARY DATA FOR THE TSUKIYOSHI FAULT

TH1, TH2, TH3 and TM2 Borehole surface elevations are taken from Geosurf Version 1, as implemented on 1st March 2000. Geosurf is a sub-database of the GeoBase database system that is being constructed to hold all key geoscientific data acquired by JNC in the Tono/MIU areas.

Elevation of the top of the Borehole MIU2 is taken from Appendix 1-2 of the Working Programme for dated August 1999 (JNC Report TN7410 99-007)

Elevation of the top of the Borehole MIU3 is taken from the summary log of MIU-3, prepared by Ota san MIU-4 borehole investigations, 28th July 2001

Elevation of top of Boreholes 98SI-03, TFA-1, KNA-6 and 99SI-08 were calculated from depth information on un-named 1/1000 mine plan, supplied by K. Ota (dated 17/10/98) and by making an assumption that the gradient of the mine drifts is 1 m per 100 m, an increase in elevation above sea level corresponding to an increase in distance away from N°1 shaft (based on a personal communication by H. Yoshida, 27/3/00).

Elevation of the top of Borehole 98FE-01 was supplied by Azuma san, manager of the borehole drilling exercise, March 2000.

Data for 99SI-08 and MIU-3 from BGS report CR/01/17 (Report April 2001, based on logging by A.E. Milodowski and M.R. Gillespie in September 2000).

Data for TH-1, TH-2, TH-3, TM-2, 98FE-01, KNA-6 and MIU2 from BGS report CR/00/37 (Report August 2000, based on logging by A.E. Milodowski and M.R. Gillespie in August 1999; additional information for KNA-6 from Ota and Hanamuro, 1996).

Data for TFA-1 and 98SI-03 from BGS report WG/99/23C (Report August 1999, based on logging by A.E. Milodowski and R. Metcalfe in September 1998).

Notes

N/A Not Applicable
N/L Not Logged
N/R Not Recorded

Borehole Borehole Orientation Elevation of the START of the Borehole (maSL)			Logged Interval		Depths of Fault Rocks	
			Closest to START of borehole (m along borehole axis)	Furthest from START of borehole (m along borehole axis)	Top (m from START of hole along borehole axis)	Bottom (m from START of hole along borehole axis)
TH1	Vertical	287.01	127.0	182.0	178.82	179.08
TH1	Vertical	287.01	127.0	182.0	179.09	179.12
TH1	Vertical	287.01	127.0	182.0	179.14	N/R
TH1	Vertical	287.01	127.0	182.0	179.20	N/R
TH1	Vertical	287.01	127.0	182.0	180.55	>182
TH2	Vertical	290.18	103.0	177.7	171.24	N/R
TH2	Vertical	290.18	103.0	177.7	171.90	172.10
TH2	Vertical	290.18	187.2	112.5	172.65	N/R
TH2	Vertical	290.18	187.2	112.5	172.87	173.25
TH2	Vertical	290.18	103.0	177.7	174.60	N/R
TH3	Vertical	298.61	128.8	200.5	170.60	170.76
TH3	Vertical	298.61	128.8	200.5	172.60	N/R
TH3	Vertical	298.61	128.8	200.5	188.40	189.60
TH3	Vertical	298.61	128.8	200.5	191.50	N/R
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	2.43	N/R
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	3.17	N/R
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	3.18	N/R
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	10.00	N/R
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	10.05	N/R

Borehole Borehole Orientation Elevation of the START of the Borehole (maSL)			Logged Interval		Depths of Fault Rocks	
			Closest to START of borehole (m along borehole axis)	Furthest from START of borehole (m along borehole axis)	Top (m from START of hole along borehole axis)	Bottom (m from START of hole along borehole axis)
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	10.06	N/R
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	11.01	N/R
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	11.38	N/R
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	11.46	N/R
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	11.59	N/R
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	11.60	N/R
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	11.63	N/R
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	11.76	N/R
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	13.28	N/R

Borehole	Borehole Orientation	Elevation of the START of the Borehole (maSL)	Logged Interval		Depths of Fault Rocks	
			Closest to START of borehole (m along borehole axis)	Furthest from START of borehole (m along borehole axis)	Top (m from START of hole along borehole axis)	Bottom (m from START of hole along borehole axis)
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	13.45	N/R
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	13.95	14.01
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	14.50	14.61
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	14.63	14.67
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	15.74	N/R
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	15.85	N/R
98SI-03	Drilled in direction 180°, 5° below the horizontal	162.77	0.0	18.1	16.00	N/R
TFA-1	Drilled in direction 180°, 5° below the horizontal	162.77	0	29.96	14.60	15.30
KNA-6	Drilled in direction 340°, 45° below horizontal	159.86	0.0	100.15	28.33	28.37

Borehole Borehole Orientation Elevation of the START of the Borehole (maSL)			Logged Interval		Depths of Fault Rocks	
			Closest to START of borehole (m along borehole axis)	Furthest from START of borehole (m along borehole axis)	Top (m from START of hole along borehole axis)	Bottom (m from START of hole along borehole axis)
98FE-01	Vertical	275.267	90.0	150.0	100.12	100.62
98FE-01	Vertical	275.267	90.0	150.0	102.27	102.29
98FE-01	Vertical	275.267	90.0	150.0	107.15	107.21
98FE-01	Vertical	275.267	90.0	150.0	109.27	109.28
98FE-01	Vertical	275.267	90.0	150.0	109.36	109.37
98FE-01	Vertical	275.267	90.0	150.0	111.06	111.12
98FE-01	Vertical	275.267	90.0	150.0	111.12	111.54
98FE-01	Vertical	275.267	90.0	150.0	111.54	111.58
98FE-01	Vertical	275.267	90.0	150.0	111.35	113.69
98FE-01	Vertical	275.267	90.0	150.0	116.34	N/R
TM2	Vertical	255	97.0	136.9	103.30	104.40
TM2	Vertical	255	97.0	136.9	117.53	117.63
TM2	Vertical	255	97.0	136.9	117.63	118.40
TM2	Vertical	255	97.0	136.9	118.40	119.16
TM2	Vertical	255	97.0	136.9	119.16	119.45
TM2	Vertical	255	97.0	136.9	119.45	120.50
TM2	Vertical	255	97.0	136.9	120.50	121.17
TM2	Vertical	255	97.0	136.9	120.60	120.63
TM2	Vertical	255	97.0	136.9	121.17	121.70
TM2	Vertical	255	97.0	136.9	121.70	122.48
TM2	Vertical	255	97.0	136.9	122.48	122.50
TM2	Vertical	255	97.0	136.9	122.50	122.55
TM2	Vertical	255	97.0	136.9	122.55	123.02
TM2	Vertical	255	97.0	136.9	123.02	123.04
TM2	Vertical	255	97.0	136.9	123.10	123.15
TM2	Vertical	255	97.0	136.9	123.15	123.24
TM2	Vertical	255	97.0	136.9	123.24	123.36
TM2	Vertical	255	97.0	136.9	123.49	123.61
MIU2	Vertical	223.755	865	925	867.2	870.0
MIU2	Vertical	223.755	865	925	870.0	872.3
MIU2	Vertical	223.755	865	925	870.0	870.8
MIU2	Vertical	223.755	865	925	876.7	882.0
MIU2	Vertical	223.755	865	925	882.0	882.4
MIU2	Vertical	223.755	865	925	882.4	889.9
MIU2	Vertical	223.755	865	925	889.0	890.04
MIU2	Vertical	223.755	865	925	890.04	890.06
MIU2	Vertical	223.755	865	925	890.06	890.14
MIU2	Vertical	223.755	865	925	890.14	890.24
MIU2	Vertical	223.755	865	925	890.24	890.66

Borehole Borehole Orientation Elevation of the START of the Borehole (maSL)	Logged Interval	Depths of Fault Rocks

			Closest to START of borehole (m along borehole axis)	Furthest from START of borehole (m along borehole axis)	Top (m from START of hole along borehole axis)	Bottom (m from START of hole along borehole axis)
MIU2	Vertical	223.755	865	925	890.66	890.69
MIU2	Vertical	223.755	865	925	890.7	893.3
MIU2	Vertical	223.755	865	925	893.3	894.6
MIU2	Vertical	223.755	865	925	894.6	904.7
MIU2	Vertical	223.755	865	925	904.7	904.95
MIU2	Vertical	223.755	865	925	904.95	905.10
MIU2	Vertical	223.755	865	925	905.10	905.46
MIU2	Vertical	223.755	865	925	905.46	905.80
MIU2	Vertical	223.755	865	925	905.8	911.2
MIU2	Vertical	223.755	865	925	911.2	911.7
MIU2	Vertical	223.755	865	925	911.7	914.0
MIU2	Vertical	223.755	865	925	914.0	914.3
MIU2	Vertical	223.755	865	925	914.3	914.7
MIU2	Vertical	223.755	865	925	914.7	914.9
MIU2	Vertical	223.755	865	925	914.90	914.95
MIU3	Vertical	230.476	498	879	522.50	522.52
MIU3	Vertical	230.476	498	879	532.80	532.83
MIU3	Vertical	230.476	498	879	557.60	560.00
MIU3	Vertical	230.476	498	879	564.50	564.52
MIU3	Vertical	230.476	498	879	600.12	N/R
MIU3	Vertical	230.476	498	879	606.80	607.50
MIU3	Vertical	230.476	498	879	609.50	609.95
MIU3	Vertical	230.476	498	879	613.70	N/R
MIU3	Vertical	230.476	498	879	627.50	N/R
MIU3	Vertical	230.476	498	879	643.35	643.60
MIU3	Vertical	230.476	498	879	644.40	644.60
MIU3	Vertical	230.476	498	879	645.70	646.00
MIU3	Vertical	230.476	498	879	649.75	N/R
MIU3	Vertical	230.476	498	879	652.40	N/R
MIU3	Vertical	230.476	498	879	663.65	663.45
MIU3	Vertical	230.476	498	879	667.30	N/R
MIU3	Vertical	230.476	498	879	669.50	669.80
MIU3	Vertical	230.476	498	879	670.30	670.55
MIU3	Vertical	230.476	498	879	672.10	N/R
MIU3	Vertical	230.476	498	879	674.30	N/R
MIU3	Vertical	230.476	498	879	674.80	N/R
MIU3	Vertical	230.476	498	879	675.30	N/R
MIU3	Vertical	230.476	498	879	676.20	N/R
MIU3	Vertical	230.476	498	879	676.50	N/R
MIU3	Vertical	230.476	498	879	676.90	N/R

Borehole Borehole Orientation Elevation of the START of the Borehole (maSL)	Logged Interval	Depths of Fault Rocks

			Closest to START of borehole (m along borehole axis)	Furthest from START of borehole (m along borehole axis)	Top (m from START of hole along borehole axis)	Bottom (m from START of hole along borehole axis)
MIU3	Vertical	230.476	498	879	678.20	N/R
MIU3	Vertical	230.476	498	879	680.40	N/R
MIU3	Vertical	230.476	498	879	682.85	683.10
MIU3	Vertical	230.476	498	879	693.20	N/R
MIU3	Vertical	230.476	498	879	693.30	693.50
MIU3	Vertical	230.476	498	879	694.20	N/R
MIU3	Vertical	230.476	498	879	694.35	N/R
MIU3	Vertical	230.476	498	879	694.65	N/R
MIU3	Vertical	230.476	498	879	695.10	N/R
MIU3	Vertical	230.476	498	879	696.70	N/R
MIU3	Vertical	230.476	498	879	697.15	697.45
MIU3	Vertical	230.476	498	879	699.25	N/R
MIU3	Vertical	230.476	498	879	699.70	699.80
MIU3	Vertical	230.476	498	879	700.00	700.50
MIU3	Vertical	230.476	498	879	702.30	702.70
MIU3	Vertical	230.476	498	879	700.50	707.60
MIU3	Vertical	230.476	498	879	710.45	711.35
MIU3	Vertical	230.476	498	879	718.43	718.60
MIU3	Vertical	230.476	498	879	719.12	719.42
MIU3	Vertical	230.476	498	879	719.46	719.87
MIU3	Vertical	230.476	498	879	725.72	725.80
MIU3	Vertical	230.476	498	879	727.80	727.85
MIU3	Vertical	230.476	498	879	731.22	731.29
MIU3	Vertical	230.476	498	879	740.62	740.72
MIU3	Vertical	230.476	498	879	745.18	N/R
MIU3	Vertical	230.476	498	879	745.40	745.42
MIU3	Vertical	230.476	498	879	745.60	746.60
MIU3	Vertical	230.476	498	879	746.87	N/R
MIU3	Vertical	230.476	498	879	747.18	747.25
MIU3	Vertical	230.476	498	879	747.50	747.53
MIU3	Vertical	230.476	498	879	747.84	747.86
MIU3	Vertical	230.476	498	879	749.28	749.45
MIU3	Vertical	230.476	498	879	758.57	758.70
MIU3	Vertical	230.476	498	879	763.21	763.47
MIU3	Vertical	230.476	498	879	764.20	764.35
MIU3	Vertical	230.476	498	879	765.00	765.12
MIU3	Vertical	230.476	498	879	767.20	767.30
MIU3	Vertical	230.476	498	879	767.55	767.80

MIU3	Vertical	230.476	498	879	769.90	770.14
MIU3	Vertical	230.476	498	879	779.60	779.67
MIU3	Vertical	230.476	498	879	780.57	781.13
MIU3	Vertical	230.476	498	879	786.50	786.60
MIU3	Vertical	230.476	498	879	803.12	803.50
MIU3	Vertical	230.476	498	879	812.10	812.90
MIU3	Vertical	230.476	498	879	827.10	827.40
MIU3	Vertical	230.476	498	879	863.00	864.00
MIU3	Vertical	230.476	498	879	864.00	865.00
MIU3	Vertical	230.476	498	879	865.00	867.00
MIU3	Vertical	230.476	498	879	869.00	870.00
99SI-08	55° below horizontal in direction due north	240.50	1.40	82.60	11.76	13.20
99SI-08	55° below horizontal in direction due north	240.50	1.40	82.60	17.20	21.70
99SI-08	55° below horizontal in direction due north	240.50	1.40	82.60	25.75	26.95
99SI-08	55° below horizontal in direction due north	240.50	1.40	82.60	49.80	54.10

PLOTS COMPARING HYDRAULIC TEST INTERVALS IN BOREHOLES WITH THE DISTRIBUTIONS OF FAULT ROCKS

TH-2: Hydraulic Conductivity Versus Depth (From Lugeon Tests)

TH-3: Hydraulic Conductivity Versus Depth (From Lugeon Tests)

MIU-2: Hydraulic Conductivity Versus Depth (From Slug Tests)

MIU-3: Hydraulic Conductivity Versus Depth (From Slug Tests)

MIU-3: Hydraulic Conductivity Versus Depth (From Pump Tests)

Compositions of groundwater samples that lie between the uppermost and lowermost fault rocks within the Tsukiyoshi Fault zone.

Borehole	Rock/Formation	Min. Depth	Max. Depth	Elev.	T	pH	Eh	Cond.	Na^+
		mabh	mabh	masl	°C		mv	µS/cm	ppm
TH-1	Akeyo Formation	-33.8		*253.2*	***13.7***	7.6		147	18
TH-2	Akeyo Formation	-32.8		*257.4*		7.2		130	13.7
TH-3	Akeyo Formation	-46.5		*252.1*	***16.7***	7.5		143	16.3
TH-1	Upper Toki Lignite-Bearing Formation	-70.8		*216.2*	***15.7***	8.0		257	50.5
TH-2	Upper Toki Lignite-Bearing Formation	-74.8		*215.4*		8.2		311	65
TH-3	Upper Toki Lignite-Bearing Formation	-85.5		*213.1*	***17.1***	8.4		271	62
TH-1	Lower Toki Lignite-Bearing Formation	-138.3		*148.1*	***18.4***	9.5		181	38.7
TH-2	Lower Toki Lignite-Bearing Formation	-109.8		*179.5*		8.6		210	45
TH-3	Lower Toki Lignite-Bearing Formation	-124		*173.6*	***18.0***	8.8		200	40.7
KNA-6 sediments	Lower Toki Lignite-Bearing Formation	-32.05	-33.05	*137.0*		9.5		202	45.5
KNA-6 near unconformity	Lower Toki Lignite-Bearing Formation	-43.5	-46.0	*128.4*		9.2	-360	180	42.5
KNA-2 (? But uncertain)	Lower Toki Lignite-Bearing Formation	-153	-155		18.5	9.2	-300	168	45
TFA-1	Lower Toki Lignite-Bearing Formation	-14.6	-14.79			8.14			49.9
TFA-1	Lower Toki Lignite-Bearing Formation	-14.79	-15.04			7.96			31.9
TFA-1	Lower Toki Lignite-Bearing Formation	-15.04	-15.3			7.47			62.9
TH-1	Toki Granite	-166.3		*120.1*	***18.9***	7.9		145	36.3
KNA-6 granite	Toki Granite	-50.5	-101	*-106.4*		8.2	0	180	29.3

Compositions of groundwater samples that lie between the uppermost and lowermost fault rocks within the Tsukiyoshi Fault zone…continued.

Borehole	Rock/ Formation	Min. Depth mabh	Max. Depth mabh	K^+ ppm	Ca^{2+} ppm	Mg^{2+} ppm	Sr^{2+} ppm	TC ppm	IC ppm	TOC ppm
TH-1	Akeyo Formation	-33.8		1.61	12.1	1.07	0.09		16.52	
TH-2	Akeyo Formation	-32.8		1.52	12.1	1.28	<0.01		*13.77*	
TH-3	Akeyo Formation	-46.5		1.07	12.5	1.17	0.06		*17.31*	
TH-1	Upper Toki Lignite-Bearing Formation	-70.8		1.81	4.3	0.21	0.02		*26.36*	
TH-2	Upper Toki Lignite-Bearing Formation	-74.8		1.36	5.23	0.23	0.02		*35.61*	
TH-3	Upper Toki Lignite-Bearing Formation	-85.5		1.33	4.13	0.17	0.01		*31.28*	
TH-1	Lower Toki Lignite-Bearing Formation	-138.3		0.28	1.45	0.03	<0.01		*10.03*	
TH-2	Lower Toki Lignite-Bearing Formation	-109.8		0.54	1.87	0.04	<0.01		*20.85*	
TH-3	Lower Toki Lignite-Bearing Formation	-124		0.43	1.54	0.03	<0.01		*15.54*	
KNA-6 sediments	Lower Toki Lignite-Bearing Formation	-32.05	-33.05	0.38	1.7	0.03	<0.01		17.9	
KNA-6 near unconformity	Lower Toki Lignite-Bearing Formation	-43.5	-46.0	0.25	2.34	0.02	<0.01		21.42	
KNA-2 (? But uncertain)	Lower Toki Lignite-Bearing Formation	-153	-155	0.29	1.98	0.02				
TFA-1	Lower Toki Lignite-Bearing Formation	-14.6	-14.79	<1.0	0.76	0.32	0.016		13.4	9.03
TFA-1	Lower Toki Lignite-Bearing Formation	-14.79	-15.04	<1.0	0.25	0.29	0.008		8.59	9.10
TFA-1	Lower Toki Lignite-Bearing Formation	-15.04	-15.3	<1.67	1.44	0.58	0.022		6.43	6.35
TH-1	Toki Granite	-166.3		0.9	7	0.31	0.02		*23.41*	
KNA-6 granite	Toki Granite	-50.5	-101	0.43	12.26	0.18	0.08	24.5	23.4	1.1

Compositions of groundwater samples that lie between the uppermost and lowermost fault rocks within the Tsukiyoshi Fault zone…continued.

Borehole	Rock/ Formation	Min. Depth	Max. Depth	CO_3^{2-}	HCO_3^-	alk.	SO_4^{2-}	HS^-	F^-	Cl^-
		mabh	mabh	ppm	ppm	meq/l	ppm	ppm	ppm	ppm
TH-1	Akeyo Formation	-33.8			84		4.23	*<0.1*	0.18	1.04
TH-2	Akeyo Formation	-32.8			70		4.93	*<0.1*	0.16	0.86
TH-3	Akeyo Formation	-46.5			88		5.8	*<0.1*	0.19	1.93
TH-1	Upper Toki Lignite-Bearing Formation	-70.8			134		10.7	*<0.1*	2.85	3.34
TH-2	Upper Toki Lignite-Bearing Formation	-74.8			181		1.14	*0.2*	2.76	1.11
TH-3	Upper Toki Lignite-Bearing Formation	-85.5			159		1.32	*30.1*	4.77	1.49
TH-1	Lower Toki Lignite-Bearing Formation	-138.3			51		12.2	*0.92*	3.01	1.94
TH-2	Lower Toki Lignite-Bearing Formation	-109.8			106		9.73	*<0.1*	2.66	2.02
TH-3	Lower Toki Lignite-Bearing Formation	-124			79		17.1	*25.7*	3.08	3.9
KNA-6 sediments	Lower Toki Lignite-Bearing Formation	-32.05	-33.05	*22.4*	*67.5*		0.86	<0.05	4.55	1.02
KNA-6 near unconformity	Lower Toki Lignite-Bearing Formation	-43.5	-46.0	*107.1*	*<1*		0.05		4.29	0.87
KNA-2 (? But uncertain)	Lower Toki Lignite-Bearing Formation	-153	-155	8	79.0		1.26		4.10	1.06
TFA-1	Lower Toki Lignite-Bearing Formation	-14.6	-14.79		79.0		7.42		12.0	6.33
TFA-1	Lower Toki Lignite-Bearing Formation	-14.79	-15.04		48.3		10.4		5.09	2.62
TFA-1	Lower Toki Lignite-Bearing Formation	-15.04	-15.3		30.6		97.5		4.26	3.67
TH-1	Toki Granite	-166.3			119		14.7		1.55	2.5
KNA-6 granite	Toki Granite	-50.5	-101	*<1*	*110.4*		0.17	<0.05	3.78	1.06

Compositions of groundwater samples that lie between the uppermost and lowermost fault rocks within the Tsukiyoshi Fault zone…continued.

Borehole	Rock/ Formation	Min. Depth mabh	Max. Depth mabh	NO_2^- ppm	NO_3^- ppm	NH_4^+ ppm	PO_4^{3-} ppm	Si ppm	Al ppm	ΣFe ppm
TH-1	Akeyo Formation	-33.8		<0.02	<0.02		0.51	36	<0.02	0.07
TH-2	Akeyo Formation	-32.8		<0.02	<0.02		0.25	36.3	<0.02	0.58
TH-3	Akeyo Formation	-46.5		<0.02	<0.02		0.53	36.3	<0.02	0.04
TH-1	Upper Toki Lignite-Bearing Formation	-70.8		<0.02	<0.02		0.45	26.7	<0.02	0.09
TH-2	Upper Toki Lignite-Bearing Formation	-74.8		<0.02	<0.02		0.78	24.6	<0.02	<0.02
TH-3	Upper Toki Lignite-Bearing Formation	-85.5		<0.02	<0.02		<0.02	29.7	<0.02	<0.02
TH-1	Lower Toki Lignite-Bearing Formation	-138.3		<0.02	<0.02		0.04	12.9	<0.02	<0.02
TH-2	Lower Toki Lignite-Bearing Formation	-109.8		<0.02	<0.02		0.14	9.57	<0.02	<0.02
TH-3	Lower Toki Lignite-Bearing Formation	-124		<0.02	<0.02		0.11	14.1	<0.02	<0.02
KNA-6 sediments	Lower Toki Lignite-Bearing Formation	-32.05	-33.05	<0.02	0.04		<0.02	7.41	<0.1	0.04
KNA-6 near unconformity	Lower Toki Lignite-Bearing Formation	-43.5	-46.0	<0.02	<0.02		<0.02	7.51	<0.1	<0.02
KNA-2 (? But uncertain)	Lower Toki Lignite-Bearing Formation	-153	-155					8.1	<0.02	
TFA-1	Lower Toki Lignite-Bearing Formation	-14.6	-14.79	1.24	1.84			6.87	0.23	<0.02
TFA-1	Lower Toki Lignite-Bearing Formation	-14.79	-15.04	0.40	0.67			6.07	0.12	<0.02
TFA-1	Lower Toki Lignite-Bearing Formation	-15.04	-15.3	0.19	<0.2			5.8	0.16	<0.03
TH-1	Toki Granite	-166.3		<0.02	<0.02		0.16	9.63	<0.02	<0.02
KNA-6 granite.	Toki Granite	-50.5	-101	<0.02	<0.02	<0.01	<0.02	10.73	<0.1	<0.02

Compositions of groundwater samples that lie between the uppermost and lowermost fault rocks within the Tsukiyoshi Fault zone…continued.

Borehole	Rock/ Formation	Min. Depth	Max. Depth	Fe^{2+}	Fe^{3+}	ΣMn	δD	$\delta^{18}O$	$\delta^{13}C$
		mabh	mabh	ppm	ppm	ppm	‰SMOW	‰SMOW	‰
TH-1	Akeyo Formation	-33.8		<0.02	<0.02	0.17	-52.6	-8.4	
TH-2	Akeyo Formation	-32.8		<0.02	<0.02	0.25	-53.7	-8.4	
TH-3	Akeyo Formation	-46.5		<0.02	<0.02	0.19	-53.5	-8.4	-20.1
TH-1	Upper Toki Lignite-Bearing Formation	-70.8		<0.02	<0.02	<0.01	-55.7	-8.5	
TH-2	Upper Toki Lignite-Bearing Formation	-74.8		<0.02	<0.02	<0.01	-55.9	-8.8	*-7.8*
TH-3	Upper Toki Lignite-Bearing Formation	-85.5		<0.02	<0.02	<0.01	-59.2	-8.8	-5.2
TH-1	Lower Toki Lignite-Bearing Formation	-138.3		<0.02	<0.02	<0.01	-55.6	-8.6	*-16.1*
TH-2	Lower Toki Lignite-Bearing Formation	-109.8		<0.02	<0.02	<0.01	-57.3	-8.8	
TH-3	Lower Toki Lignite-Bearing Formation	-124		<0.02	<0.02	<0.01	-58.7	-8.5	-12.6
KNA-6 sediments	Lower Toki Lignite-Bearing Formation	-32.05	-33.05	<0.05	<0.05	<0.01	-59.4	-9.0	
KNA-6 near unconformity	Lower Toki Lignite-Bearing Formation	-43.5	-46.0	<0.05	<0.05	<0.01			
KNA-2 (? But uncertain)	Lower Toki Lignite-Bearing Formation	-153	-155	<0.02	<0.02	<0.01			
TFA-1	Lower Toki Lignite-Bearing Formation	-14.6	-14.79			<0.002	-56.0	-8.9	
TFA-1	Lower Toki Lignite-Bearing Formation	-14.79	-15.04			<0.002	-59.0	-9.1	
TFA-1	Lower Toki Lignite-Bearing Formation	-15.04	-15.3			<0.003			
TH-1	Toki Granite	-166.3		<0.02	<0.02	<0.01	-52.0	-8.2	*-16.9*
KNA-6 granite.	Toki Granite	-50.5	-101	<0.05	<0.05	<0.01			*-17.3*

Entries in italics were supplied by T. Iwatsuki. The other entries were taken from Iwatsuki, T., Metcalfe, R., Amano, K., Hama, K., Noda, N., Arthur, R.C. and Sasamoto, H. 2001. Data book on groundwater chemistry in the Tono area. JNC Report JNC TN 7450 2001-03.
Entries in bold italics refer to temperatures inferred from borehole temperature logs

Summary of exchangeable cation data for all cations that were analysed

Borehole	Depth from core top, m			Preliminary Description (Made during sampling or preliminary logging (in the case of 99SI-08))	Description of sub- sample (Made in lab)	Depth Closest Water Conducting Feature Indicated on Log (m)	Numbers of Samples Analysed for exchangeable cations by BGS (as part of Tsukiyoshi Fault project)	Numbers of Samples for which exchangeable cation data obtained by JNC1 (as part of H12 exchangeable cation project)
	Depth Top	Depth Bottom	Mean					
99SI-08								
99SI-08	2.4	2.7	2.55	Slumped carbonaceous sandstone and intraformational conglomerate	None reported	Water-conducting feature not determined	99SI-08/1	Not Analysed by JNC
99SI-08	8.03	8.15	8.09	Brown, silty mudstone overlying fine sandstone (Previously polythene wrapped to prevent drying).	Brown, silty mudstone overlying fine sandstone, outer anulus of core cut away to remove any oxidation effects.	Water-conducting feature not determined	Not Analysed byBGS	99SI-08/JNC1
99SI-08	12.92	13.00	12.96	Brown mudstone with sand layers (Previously polythene wrapped to prevent drying).	Brown mudstone with sand layers, outer anulus of core cut away to remove any oxidation effects.	Water-conducting feature not determined	Not Analysed byBGS	99SI-08/JNC2
99SI-08	13.43	13.57	13.50	Green fault rock (fault breccia) (Previously polythene wrapped to prevent drying).	Green fault rock (fault breccia), outer anulus of core cut away to remove any oxidation effects.	Water-conducting feature not determined	Not Analysed byBGS	99SI-08/JNC3
99SI-08	14.75	14.92	14.84	Fine sandstone from near middle of fault zone interval (Previously polythene wrapped to prevent drying).	Fine sandstone from near middle of fault zone interval, outer anulus of core cut away to remove any oxidation effects.	Water-conducting feature not determined	Not Analysed byBGS	99SI-08/JNC4
99SI-08	15.63	15.83	15.73	Blue-grey (fresh), buff (oxidised) volcaniclastic silty sandstone/tuffaceous sandstone (in fault zone)	None reported	Water-conducting feature not determined	99SI-08/2	Not Analysed by JNC
99SI-08	21.25	21.40	21.33	Brown, disked mudstone. Possibly with bioturbation. Mudstone plastic (Previously polythene wrapped to prevent drying).	Brown, disked mudstone. Possibly with bioturbation. Mudstone plastic, outer anulus of core cut away to remove any oxidation effects.	Water-conducting feature not determined	Not Analysed byBGS	99SI-08/JNC5
99SI-08	22.75	22.94	22.85	Massive, medium carbonaceous sandstone	None reported	Water-conducting feature not determined	99SI-08/3	Not Analysed by JNC
99SI-08	25.13	25.24	25.19	Upper half mudstone: lower half fine sandstone. Mudstone very soft (Previously polythene wrapped to prevent drying).	Upper half mudstone: lower half fine sandstone. Mudstone very soft, outer anulus of core cut away to remove any oxidation effects.	Water-conducting feature not determined	Not Analysed byBGS	99SI-08/JNC6
99SI-08	28.53	28.65	28.59	Very fi ne sandstone/siltstone. Grey. Coarser sand fills in burrows. Fine organic laminae. Bioturbated. Flecks of coaly fragments. (Previously polythene wrapped to prevent drying).	Very fi ne sandstone/siltstone. Grey. Coarser sand fills in burrows. Fine organic laminae. Bioturbated. Flecks of coaly fragments. outer anulus of core cut away to remove any oxidation effects.	Water-conducting feature not determined	Not Analysed byBGS	99SI-08/JNC7
99SI-08	31.07	31.21	31.14	Brown/grey siltstone to fine sandstone. Flecks of organic matter. Bioturbation. rip-up clasts. Current bedding. Interval bounded by drilling breaks (Previously polythene wrapped to prevent drying).	Brown/grey siltstone to fine sandstone. Flecks of organic matter. Bioturbation. rip-up clasts. Current bedding. Interval bounded by drilling breaks. outer anulus of core cut away to remove any oxidation effects.	Water-conducting feature not determined	Not Analysed byBGS	99SI-08/JNC8
99SI-08	33.85	33.94	33.90	Brown/brown hard. compact. very fine sandstone. Lignite grains. Interval bounded by rolled drilling breaks (Previously polythene wrapped to prevent drying).	Brown/brown hard. compact. very fine sandstone. Lignite grains. Interval bounded by rolled drilling breaks. outer anulus of core cut away to remove any oxidation effects.	Water-conducting feature not determined	Not Analysed byBGS	99SI-08/JNC9
99SI-08	46.3	46.6	46.45	Slumped and contorted carbonaceous sandstone with lignite fragments	None reported	Water-conducting feature not determined	99SI-08/4	Not Analysed by JNC
99SI-08	52.40	52.53	52.47	Plastic mudstone (Previously polythene wrapped to prevent drying).	Plastic mudstone. outer anulus of core cut away to remove any oxidation effects.	Water-conducting feature not determined	Not Analysed byBGS	99SI-08/JNC10
99SI-08	59.5	57.7	58.60	Volcaniclastic sandstone/tuffaceous sandstone from below fault	None reported	Water-conducting feature not determined	99SI-08/5	Not Analysed by JNC
99SI-08	62.60	62.72	62.66	Plastic mudstone (Previously polythene wrapped to prevent drying)	Plastic mudstone. outer anulus of core cut away to remove any oxidation effects.	Water-conducting feature not determined	Not Analysed byBGS	99SI-08/JNC11
99SI-08	65.5	65.7	65.60	Volcaniclastic sandstone/tuffaceous sandstone below fault but directly above Toki Formation	None reported	Water-conducting feature not determined	99SI-08/6	Not Analysed by JNC
MIU 2								
MIU2	132.16	132.26	132.21	Rubbled core. with abundant green clay on fracture surfaces. Core very fraemented.	Bulk sample.	135	Not Analysed byBGS	MIU-2/JNC1A
MIU2	132.16	132.26	132.21	Rubbled core. with abundant green clay on fracture surfaces. Core very fraemented.	Green clay-rich sub-sample (but contains wall rock).	135	Not Analysed byBGS	MIU-2/JNC1B

Borehole	Depth from core top, m			Preliminary Description (Made during sampling or preliminary logging (in the case of 99SI-08))	Description of sub-sample (Made in lab)	Depth Closest Water Conducting Feature Indicated on Log (m)	Numbers of Samples Analysed for exchangeable cations by BGS (as part of Tsukiyoshi Fault project)	Numbers of Samples for which exchangeable cation data obtained by JNC1 (as part of H12 exchangeable cation project)
	Depth Top	Depth Bottom	Mean					
MIU2	137.24	137.35	137.30	Granite of fresh appearance cut by many thin (< 1mm) fractures, which are typical of the bulk rock at this locality.	Fresh granite from centre of core. Crystals typically 1 mm to 2 mm across, but occasionally feldspar crystals up to 3 mm across occur. Overall the rock has a pinkish/grey appearance. Biotite is abundant with crystals 1 - 2 mm across.	135	Not Analysed byBGS	MIU-2/JNC2
MIU2	244.73	244.82	244.78	Fractured granite with white clay in fractures.	Bulk sample, consisting of very fractured, sheared, white, clay-rich pegmatite, containing fractures with greenish fault rock. Fractures abundant in zone 1 cm wide. Individual strands range from 0.25 mm to c. 2 mm.	250	Not Analysed byBGS	MIU-2/JNC3A
MIU2	244.73	244.82	244.78	Fractured granite with white clay in fractures.	Clay-rich, white pegmatite with crystals up to 4 mm across. Biotite is absent.	250	Not Analysed byBGS	MIU-2/JNC3B
MIU2	244.73	244.82	244.78	Fractured granite with white clay in fractures.	Sub-sample of vein material containing sheared green fault-rock (rich in ?chloritised biotite?), but with some white wall-rock.	250	Not Analysed byBGS	MIU2/JNC3C
MIU2	248.31	248.39	248.35	Intact granite.	Fresh granite from centre of core. Overall pink/grey appearance. Pink feldspar crystals up to 4 mm across. Abundant biotite crystals up to 2 mm across.	250	Not Analysed byBGS	MIU-2/JNC4
MIU2	887.53	887.7	887.62	Sample of granite with fracture containing possible injection sediment (marked by BGS).	Granite from near centre of core. Picked to be as free as possible from fractures filled or lined with clay, which are abundant at this point. Overall light grey appearance. Biotite crystals are present and up to 2 mm across, but not so abundant as to affect the overall colouration of the rock when seen at arm's length.	900	Not Analysed byBGS	MIU-2/JNC5A
MIU2	887.53	887.7	887.62	Sample of granite with fracture containing possible injection sediment (marked by BGS).	Granite from near centre of core. Picked to contain as many clay-rich fractures as possible. These fractures are abundant at this point. Overall light grey appearance. Biotite crystals are present and up to 2 mm across, but not so abundant as to affect the overall colouration of the rock when seen at arm's length.	900	Not Analysed byBGS	MIU-2/JNC5B
MIU2	887.53	887.7	887.62	Sample of granite with fracture containing possible injection sediment (marked by BGS).	Possible injection sediment.	900	Not Analysed byBGS	MIU-2/JNC5C
MIU2	992.5	992.6	992.55	Granite containing abundant white clay.	Altered granite, rich in unidentified white clay. Overall light grey appearance. Biotite crystals are up to 2 mm across.	990	Not Analysed byBGS	MIU-2/JNC6
MIU2	985.69	985.8	985.75	Granite of fresh appearance.	Granite of fresh appearance from central part of core. Crystals typically around 2 mm across. Overall white in appearance. Pink feldspar is lacking. Biotite present, but not abundant.	990	Not Analysed byBGS	MIU-2/JNC7
MIU3								
MIU3	609.6	609.82	609.71	Fragments of fractured granite.	Green-grey fracture-filling material with some white wall-rock material. Green/grey material is possibly chlorite?	Water-conducting feature not determined	Not Analysed byBGS	MIU-3/JNC1
MIU-3	644.45	644.6	644.53	Granite fault rock: Fault intersection 11, friable sandy breccia and protobreccia.	None reported	Water-conducting feature not determined	MIU-3/13	
MIU-3	661.75	661.88	661.82	Unit 1: fresh medium biotite granite	None reported	Water-conducting feature not determined	MIU-3/5	
MIU-3	699	699.2	699.10	Unit 1: altered medium biotite granite	None reported	Water-conducting feature not determined	MIU-3/6	
MIU-3	704.65	704.8	704.73	Granite fault rock: Main Fault: protomylonite in a matrix of mylonite and ultra-mylonite	None reported	Water-conducting feature not determined	MIU-3/16	
MIU3	707.55	707.62	707.59	Fragments of core of fractured granite with abundant fine (< 1mm wide) anastamosing fractures.	Dark grey/green fault rock with only very small amounts of wall-rock material.	Water-conducting feature not determined	Not Analysed byBGS	MIU-3/JNC2
MIU-3	708	708.3	708.15	Unit 5: altered relatively fine biotite granite	None reported	Water-conducting feature not determined	MIU-3/7	
MIU-3	757.88	758	757.94	Unit 5: fresh relatively fine biotite granite	None reported	Water-conducting feature not determined	MIU-3/23	

Borehole	Depth from core top, m			Preliminary Description (Made during sampling or preliminary logging (in the case of 99SI-08))	Description of sub-sample (Made in lab)	Depth Closest Water Conducting Feature Indicated on Log (m)	Numbers of Samples Analysed for exchangeable cations by BGS (as part of Tsukiyoshi Fault project)	Numbers of Samples for which exchangeable cation data obtained by JNC1 (as part of H12 exchangeable cation project)
	Depth Top	Depth Bottom	Mean					
DH-7								
DH-7	564.10	564.10	564.10	Surface material from weakly altered fracture surface	Surface material from weakly altered fracture surface. Hard. Some granite wall rock.	Water sampled from 560.5 to 567	Not Analysed byBGS	DH-7/JNC1
DH-7	835.7	835.7	835.70	Clay-rich fracture surface	Clay-rich fracture surface. White clay and unidentified greenish/yellow mineral on surface. Slickensided.	Water sampled from 833.5 to 840	Not Analysed byBGS	DH-7/JNC2
DH-7	839.5	839.6	839.55	Material from weakly altered clay-rich fracture surface	Material from weakly altered clay-rich fracture surface. Light green.	Water sampled from 833.5 to 840	Not Analysed byBGS	DH-7/JNC3
DH-7	884.9	885.0	884.95	Material from weakly altered clay-rich fracture surface	Material from weakly altered clay-rich fracture surface. Light green.	Water sampled from 880.0 to 886.5	Not Analysed byBGS	DH-7/JNC4
DH-13								
DH-13	92.70	92.80	92.75	Bulk sample of green (?chloritic), very friable granite, possibly hydrothermally altered	Bulk sample of green (?chloritic), very friable granite, possibly hydrothermally altered.	Water sampled from 157.45 to 164.12	Not Analysed byBGS	DH-13/JNC4
DH-13	157.13	157.23	157.18	Granite of fresh appearance, taken from central part of core	Granite of fresh appearance, taken from central part of core.	Water sampled from 157.45 to 164.12	Not Analysed byBGS	DH-13/JNC1
DH-13	160.32	160.50	160.41	Black vein fracture-filling with some wall rock material attached	Clay (?smectite) scraped from fracture surface dipping at approximately 30° to the core axis. Pale greenish colour.	Water sampled from 157.45 to 164.12	Not Analysed byBGS	DH-13/JNC3

Notes:

1 Data obtained by JNC, using a Japanese contractor

Samples analysed by BGS and data obtained by BGS

N.A. Not Analysed

Summary of exchangeable cation da

Exchangeable cation abundances expressed in mg/kg

Borehole	Depth from core top, m			CEC	Exchangeable cations (mg/kg)					Surface area	Equivalent	Source of Analytical Data	Cation data between shallowest/ deepest fault rock from Tsukiyoshi Fault Zone?	Highest Logged Fault Rock in Tsukiyoshi Fault Zone	Lowest Logged Fault Rock in Tsukiyoshi Fault Zone
	Depth Top	Depth Bottom	Mean	meq/100g	Mg	Na	Ca	K	Total	m2/g	%smectite			m from top of core	m from bottom of core
														11.76	54.1
99SI-08															
99SI-08	2.4	2.7	2.55	24.7	321	425	4853	352	5951	213	27	BGS Report CR/01/17	NO		
99SI-08	8.03	8.15	8.09	35.0	280	390	7900	210	8780	N.A.	N.A.	JNC Contractor's Report. 3/9/01	NO		
99SI-08	12.92	13.00	12.96	25.9	220	400	5800	170	6590	N.A.	N.A.	JNC Contractor's Report. 3/9/01	YES		
99SI-08	13.43	13.57	13.50	53.7	350	800	13000	280	14430	N.A.	N.A.	JNC Contractor's Report. 3/9/01	YES		
99SI-08	14.75	14.92	14.84	51.8	330	700	13000	200	14230	N.A.	N.A.	JNC Contractor's Report. 3/9/01	YES		
99SI-08	15.63	15.83	15.73	55.4	404	988	11567	416	13375	547	68	BGS Report CR/01/17	YES		
99SI-08	21.25	21.40	21.33	34.4	140	610	7300	280	8330	N.A.	N.A.	JNC Contractor's Report. 3/9/01	YES		
99SI-08	22.75	22.94	22.85	27.9	232	727	5803	358	7119	238	30	BGS Report CR/01/17	YES		
99SI-08	25.13	25.24	25.19	23.9	140	480	5000	240	5860	N.A.	N.A.	JNC Contractor's Report. 3/9/01	YES		
99SI-08	28.53	28.65	28.59	24.5	170	520	5000	240	5930	N.A.	N.A.	JNC Contractor's Report. 3/9/01	YES		
99SI-08	31.07	31.21	31.14	26.9	160	540	5400	260	6360	N.A.	N.A.	JNC Contractor's Report. 3/9/01	YES		
99SI-08	33.85	33.94	33.90	28.6	160	690	5800	320	6970	N.A.	N.A.	JNC Contractor's Report. 3/9/01	YES		
99SI-08	46.3	46.6	46.45	27.7	164	784	6158	241	7346	230	29	BGS Report CR/01/17	YES		
99SI-08	52.40	52.53	52.47	71.3	82	1600	16000	690	18372	N.A.	N.A.	JNC Contractor's Report. 3/9/01	YES		
99SI-08	59.5	57.7	58.60	53.6	168	1534	12400	359	14462	554	69	BGS Report CR/01/17	NO		
99SI-08	62.60	62.72	62.66	49.1	67	1400	9800	570	11837	N.A.	N.A.	JNC Contractor's Report. 3/9/01	NO		
99SI-08	65.5	65.7	65.60	29.0	107	1256	7254	320	8937	263	33	BGS Report CR/01/17	NO		
														867.2	914.95
MIU 2															
MIU2	132.16	132.26	132.21	2.1	10	49	3300	52	3411	N.A.	N.A.	JNC Contractor's Report. 3/9/01	NO		
MIU2	132.16	132.26	132.21	3.7	19	80	4200	74	4373	N.A.	N.A.	JNC Contractor's Report. 3/9/01	NO		

Borehole	Depth from core top, m			CEC	Exchangeable cations (mg/kg)					Surface area	Equivalent	Source of Analytical Data	Cation data between shallowest/ deepest fault rock from Tsukiyoshi Fault Zone?	Highest Logged Fault Rock in Tsukiyoshi Fault Zone	Lowest Logged Fault Rock in Tsukiyoshi Fault Zone
	Depth Top	Depth Bottom	Mean	meq/100g	Mg	Na	Ca	K	Total	m2/g	%smectite			m from top of core	m from bottom of core
MIU2	137.24	137.35	137.30	0.8	2	26	160	25	213	N.A.	N.A.	JNC Contractor's Report, 3/9/01	NO		
MIU2	244.73	244.82	244.78	6.4	15	100	1100	110	1325	N.A.	N.A.	JNC Contractor's Report, 3/9/01	NO		
MIU2	244.73	244.82	244.78	0.4	7	30	3200	30	3267	N.A.	N.A.	JNC Contractor's Report, 3/9/01	NO		
MIU2	244.73	244.82	244.78	2.0	1400	54	1400	31	2885	N.A.	N.A.	JNC Contractor's Report, 3/9/01	NO		
MIU2	248.31	248.39	248.35	0.8	3	20	410	32	465	N.A.	N.A.	JNC Contractor's Report, 3/9/01	NO		
MIU2	887.53	887.7	887.62	0.9	2	22	390	31	445	N.A.	N.A.	JNC Contractor's Report, 3/9/01	YES		
MIU2	887.53	887.7	887.62	1.6	2	21	380	31	434	N.A.	N.A.	JNC Contractor's Report, 3/9/01	YES		
MIU2	887.53	887.7	887.62	7.3	6	92	2100	63	2261	N.A.	N.A.	JNC Contractor's Report, 3/9/01	YES		
MIU2	992.5	992.6	992.55	4.1	4	37	1700	30	1771	N.A.	N.A.	JNC Contractor's Report, 3/9/01	NO		
MIU2	985.69	985.8	985.75	0.6	2	13	160	31	206	N.A.	N.A.	JNC Contractor's Report, 3/9/01	NO		
MIU3														522.5	870
MIU3	609.6	609.82	609.71	8.7	3400	180	3400	44	7024	N.A.	N.A.	JNC Contractor's Report, 3/9/01	YES		
MIU-3	644.45	644.6	644.53	3.1	9	99	1766	179	2053	6	1	BGS Report CR/01/17	YES		
MIU-3	661.75	661.88	661.82	3.1	17	118	428	307	871	5	1	BGS Report CR/01/17	YES		
MIU-3	699	699.2	699.10	2.5	39	117	519	236	911	3	1	BGS Report CR/01/17	YES		
MIU-3	704.65	704.8	704.73	15.4	40	202	5962	169	6373	57	7	BGS Report CR/01/17	YES		
MIU3	707.55	707.62	707.59	20.8	5600	420	5600	250	11870	N.A.	N.A.	JNC Contractor's Report, 3/9/01	YES		
MIU-3	708	708.3	708.15	1.3	12	121	412	257	802	0	0	BGS Report CR/01/17	YES		
MIU-3	757.88	758	757.94	1.5	17	98	360	243	718	1	0	BGS Report CR/01/17	YES		

Borehole	Depth from core top, m			CEC	Exchangeable cations (mg/kg)					Surface area	Equivalent	Source of Analytical Data	Cation data between shallowest/ deepest fault rock from Tsukiyoshi Fault Zone?	Highest Logged Fault Rock in Tsukiyoshi Fault Zone	Lowest Logged Fault Rock in Tsukiyoshi Fault Zone
	Depth Top	Depth Bottom	Mean	meq/100g	Mg	Na	Ca	K	Total	m2/g	%smectite			m from top of core	m from bottom of core
DH-7														Not Applicable	Not Applicable
DH-7	564.10	564.10	564.10	0.7	5600	23	5600	36	11259	N.A.	N.A.	JNC Contractor's Report, 3/9/01			
DH-7	835.7	835.7	835.70	1.5	3600	94	3600	140	7434	N.A.	N.A.	JNC Contractor's Report, 3/9/01			
DH-7	839.5	839.6	839.55	1.2	3600	49	3600	31	7280	N.A.	N.A.	JNC Contractor's Report, 3/9/01			
DH-7	884.9	885.0	884.95	2.4	4000	75	4000	45	8120	N.A.	N.A.	JNC Contractor's Report, 3/9/01			
DH-13														Not Applicable	Not Applicable
DH-13	92.70	92.80	92.75	4.7	4300	33	4300	92	8725	N.A.	N.A.	JNC Contractor's Report, 3/9/01			
DH-13	157.13	157.23	157.18	1.7	4	27	1600	38	1669	N.A.	N.A.	JNC Contractor's Report, 3/9/01			
DH-13	160.32	160.50	160.41	1.3	2400	20	2400	23	4843	N.A.	N.A.	JNC Contractor's Report, 3/9/01			

Notes:
1 Data obtained by JNC, using a Japar
Samples analysed by BGS and data c

N.A. Not Analysed

Summary of exchangeable cation da

Borehole	Depth from core top, m			Comments
	Depth Top	Depth Bottom	Mean	
99SI-08				
99SI-08	2.4	2.7	2.55	
99SI-08	8.03	8.15	8.09	
99SI-08	12.92	13.00	12.96	
99SI-08	13.43	13.57	13.50	
99SI-08	14.75	14.92	14.84	
99SI-08	15.63	15.83	15.73	
99SI-08	21.25	21.40	21.33	
99SI-08	22.75	22.94	22.85	
99SI-08	25.13	25.24	25.19	
99SI-08	28.53	28.65	28.59	
99SI-08	31.07	31.21	31.14	
99SI-08	33.85	33.94	33.90	
99SI-08	46.3	46.6	46.45	
99SI-08	52.40	52.53	52.47	
99SI-08	59.5	57.7	58.60	
99SI-08	62.60	62.72	62.66	
99SI-08	65.5	65.7	65.60	
MIU 2				
MIU2	132.16	132.26	132.21	
MIU2	132.16	132.26	132.21	

Borehole	Depth from core top, m			Comments
	Depth Top	Depth Bottom	Mean	
MIU2	137.24	137.35	137.30	Blocks of wood in the core box indicate that the core near this sampling point has been sampled previously for analysis (137.64-137.74 m indicated to have been sampled (though writing on block of wood erroneously states 157.64-157.74 m).
MIU2	244.73	244.82	244.78	Although log indicates water conducting feature at 250 m. the core at this depth is less fragmented that at 244.56 - 245.35. Therefore. sample taken from this latter interval.
MIU2	244.73	244.82	244.78	Although log indicates water conducting feature at 250 m. the core at this depth is less fragmented that at 244.56 - 245.35. Therefore. sample taken from this latter interval.
MIU2	244.73	244.82	244.78	Although log indicates water conducting feature at 250 m. the core at this depth is less fragmented that at 244.56 - 245.35. Therefore. sample taken from this latter interval.
MIU2	248.31	248.39	248.35	
MIU2	887.53	887.7	887.62	Sample taken from immediately adjacent to marker indicating BGS sample MIU2/4 taken previously.
MIU2	887.53	887.7	887.62	Sample taken from immediately adjacent to marker indicating BGS sample MIU2/4 taken previously.
MIU2	887.53	887.7	887.62	Sample taken from immediately adjacent to marker indicating BGS sample MIU2/4 taken previously.
MIU2	992.5	992.6	992.55	At depth of the water conducting feature indicated on the log the core is very broken and has many clay-filled fractures.
MIU2	985.69	985.8	985.75	
MIU3				
MIU3	609.6	609.82	609.71	Same interval as sample MIU-3/12 taken by BGS (fracture sample).
MIU-3	644.45	644.6	644.53	
MIU-3	661.75	661.88	661.82	
MIU-3	699	699.2	699.10	
MIU-3	704.65	704.8	704.73	
MIU3	707.55	707.62	707.59	From down-core end of sample MIU-3/18 sampled by BGS as an example of a fracture between 707.4 and 707.55 m
MIU-3	708	708.3	708.15	
MIU-3	757.88	758	757.94	

Borehole	Depth from core top, m.			Comments
	Depth Top	Depth Bottom	Mean	
DH-7				
DH-7	564.10	564.10	564.10	
DH-7	835.7	835.7	835.70	
DH-7	839.5	839.6	839.55	
DH-7	884.9	885.0	884.95	
DH-13				
DH-13	92.70	92.80	92.75	
DH-13	157.13	157.23	157.18	
DH-13	160.32	160.50	160.41	

Notes:

[Data obtained by JNC, using a Japar
Samples analysed by BGS and data c

N.A. Not Analysed

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Water-rock interaction around a fault: implications for waste disposal

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ABSTRACT: By studying the Tsukiyoshi Fault, central Japan, the Japan Nuclear Cycle Development Institute (JNC) is developing generic approaches to assess the effects of low temperature, post-faulting water-rock interactions on the hydraulic properties of faults. The Tsukiyoshi Fault has a reverse throw of about 30 m and cuts a Cretaceous granite and overlying Miocene sedimentary rocks. In the sedimentary rocks the fault was active for a relatively short interval, probably less than 10 Ma, and last moved several million years ago. Post-faulting spatial and temporal variations in water-rock interactions and groundwater flow paths were possibly coupled. Water movement within the fault zone caused water-rock interactions, including carbonate precipitation and feldspar dissolution, which locally influenced porosity. It may be inappropriate for predictions of future waste migration from a deep repository to assume that inactive faults are necessarily planar and temporally invariant, particularly when considering long-lived wastes such as radioactive wastes.

1 INTRODUCTION

Depending upon their architecture, faults may retard or facilitate groundwater and solute movement underground (Forster & Evans 1991, Caine et al. 1996). Safety assessments for deep waste disposal must take these possibilities into account.

To date, the most sophisticated assessments have been made during research related to radioactive waste disposal. Particularly large and detailed data sets are usually used (e.g. fracture distributions, hydraulic properties etc) and long time periods are considered (often up to about 1 Ma; Savage 1995). However, even these assessments are usually based upon conservative ('worst-case') models employing simplified fault architectures (e.g. faults are planar), maximum hydraulic conductivies and temporally invariant fault properties (e.g. JNC 2000, Nirex 1997). Presently observed properties are usually used to develop these models and are typically applied to the safety assessment's entire time frame. This approach is often thought to be valid because sites are selected to avoid active faults and hence major physical processes responsible for change. However, an implicit assumption is that post-faulting water-rock interactions cause insignificant changes in a fault's properties. While this may be true in many cases, it is desirable to test the assumption on a site-by-site basis. To be able to do this it is important to develop generic approaches for: 1. distinguishing post-faulting water-rock interactions from syn- and pre-faulting water-rock interactions; 2. relating spatial variations in these post-faulting water-rock interactions to variations in rock permeability and porosity. However, there have been few detailed investigations of spatial and temporal relationships between water-rock interactions and the physical properties of faults under conditions relevant to waste management by deep disposal (typically water-saturated conditions at depths up to about 1 km, where temperatures are up to a few tens °C and pressures are up to a few hundred bars). Most previous investigations have focussed on faults with very long, complex histories, typically tens, hundreds or thousands of millions of years (e.g. Äspö, Sweden (Stanfors et al. 1999)). In these cases interpretations are complicated by superimposition of effects from many fault movements. Therefore, it is difficult to demonstrate that presently available investigation techniques can resolve any coupling between temporal changes in both low-temperature water-rock interactions and hydraulic properties.

On-going studies of the Tsukiyoshi Fault in the Tono area of central Japan (Fig. 1), which are being undertaken by JNC, are developing generic approaches for evaluating the significance of water-rock interactions under these relevant conditions. This fault is particularly suitable for study because it had a relatively simple history and it displaces sedimentary rocks that have never been deeply buried. Thus, evidence for low-temperature water-rock interactions can be related to fault structures and porosity

Figure 1. Simplified location map and diagram showing sampling locations. Only boreholes mentioned in the text are labelled. Cores from two boreholes (not shown) located approximately1 km to the east of the mine were also studied.

variations. Here we describe these relationships and evaluate their implications.

2 GEOLOGY AND HYDROCHEMISTRY

Miocene to Pleistocene sedimentary rocks lie on the eroded surface of the late Cretaceous Toki Granite (Fig. 1). The sedimentary rocks are mostly almost horizontally bedded sandstones, siltstones, mudstones and conglomerates. (Yusa et al. 1993). Lignite may be abundant, especially in lower strata.

The Miocene rocks formed between 20 Ma and 15 Ma and compose the Mizunami Group, which comprises three main formations (Fig. 1). The Toki Formation formed mainly in a freshwater lake. In contrast, the Akeyo Formation represents brackish to shallow marine sedimentation, while the overlying Oidawara Formation is a deeper marine deposit.

Pliocene and Pleistocene rocks, composing the Seto Group, unconformably overlie the Mizunami Group. The Seto Group consists of poorly consolidated or unconsolidated fluvial sediments, deposited between around 5 Ma and about 0.7 Ma.

Uranium mineralisation formed about 10 million years ago, just above the base of the Miocene rocks (Ochiai et al. 1989). The deposit is 2–5 m thick, several hundred meters wide and 2-3 km long. In 1972 Tono Mine (Fig. 1) was excavated to explore this deposit. However, the mineralisation is sub-economic and was not worked commercially. Instead, the mine became a research facility.

Among the diagenetic minerals, smectite is associated with clinoptilolite-like zeolite and mixed-layer phases like illite-smectite are absent. This suggests that maximum burial temperatures were low, possibly much less than 150 °C (c.f. Frey & Kisch 1987).

The Tsukiyoshi Fault displaces the Toki Granite and overlying Mizunami Group, including the Tono uranium deposit. However, the Seto Group is not apparently displaced by the fault, indicating that the latest significant fault movement was earlier than about 5 Ma. However, the approximately 15 Ma old Oidawara Formation is cut out. Therefore, the movement history in the sedimentary rocks was probably less than 10 Ma.

Published variations in rock uranium concentrations and the ratios $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ (Nohara et al. 1992) suggest that past water-movement in the fractures within the Toki Lignite Formation may have caused some small-scale uranium transport.

In earlier investigations, groundwaters have been sampled from all the main rock types to about 850 m below ground level (around 500 m below sea level) and are all fresh (total dissolved solid TDS, much less than 1000 mgl^{-1}; Iwatsuki & Yoshida 1999). Groundwater chemistry is possibly controlled by cation exchange with Na- and Ca- smectite and calcite dissolution; these reactions approach equilibrium at depth. With increasing depth, the waters evolve from a Ca-Na-HCO_3 dominated chemistry towards a more Na-HCO_3 composition. Stable oxygen and hydrogen isotopic data indicate a meteoric origin for the water. The isotopic compositions also become slightly lighter as depth increases, suggesting that deeper waters recharged in a cooler climate than the present one. Radiocarbon data indicate that water in the basal Toki Formation recharged around 15 000 years ago (Mizutani et al. 1992).

3 METHODS

The Tsukiyoshi Fault was examined in the mine's walls and in cores from thirteen boreholes (Fig. 1). Most of these boreholes were not drilled to investigate the fault. However, during the present study, three boreholes, 99SI-08, TFA-1 and 98SI-03, were drilled specifically for this purpose and gave particularly high quality rock core from the fault zone in the sedimentary rocks. Borehole 99SI-08 was drilled

at approximately 90° to the fault, while boreholes TFA-1 and 98SI-03 were almost horizontal. 'Core-pack', a flexible polythene core liner, was used to preserve core when drilling 99SI-08. High quality core was also available from two boreholes located about 1 km east of the mine (not shown in Fig. 1). These boreholes intersected the middle of the fault zone in granite, at depths of about 700 m and 900 m.

Specialist sampling and preparation techniques preserved delicate textures in poorly consolidated, and often clay-rich, rocks. Such materials were sampled using 'Kubiena' tins, aluminium boxes with sharpened edges that were pushed into soft rock exposures. Each box was then freed by scraping away surrounding rock and lids were applied to both sides.

Poorly consolidated samples were air-dried and then vacuum-impregnated with epoxy-resin that contained blue dye to highlight porosity. Sections were cut and then polished under paraffin to preserve any water-soluble minerals. Sections to be examined by Back-Scattered Electron Microscopy (BSEM) were coated under vacuum with a 25 nm thick carbon film.

A LEO 435VP, variable pressure, digital scanning electron microscope was used for BSEM-Energy Dispersive X-ray Analyses (EDXA) and conventional Secondary Electron Microscopy (SEM) analyses. Semi-quantitative EDXA analysis aided mineral identification during SEM observations. High-vacuum (< 10^{-4} torr) was used during the BSEM analyses and most SEM analyses. Occasional problems due to high sample moisture and outgassing were overcome using a low vacuum/variable pressure mode (about 3 x 10^{-2} torr).

The bulk and clay mineralogies of fault gouges, fault rocks and wallrocks were determined by X-ray diffraction (XRD). Surface areas of three fault rocks from borehole 98SI-03 were determined by the ethylene glycol monoethyl ether (EGME) method, allowing their 'swelling clay' contents (essentially smectite) to be estimated.

4 RESULTS

The fault is not a single planar feature, but a deformation zone, within which strain is distributed heterogeneously (Fig. 2). The zone's width varies from a few metres to over 100 m. Strain indicators and fault rocks are variably distributed within the zone. Major movement planes are associated with fault gouge, consisting of up to about 50 vol% smectite.

The specialist techniques minimised damage to delicate textural and structural evidence for water-rock interactions, including: 1. replacement of deformed diagenetic smectite by chlorite next to fractures; 2. undeformed fracture-filling clinoptilolite-like zeolite; 3. undeformed fracture-filling pyrite; 4. cross-fibre fracture-filling calcite; 5. calcite replacing matrix smectite; 6. feldspar dissolution adjacent to open fractures. Cross-fibre calcite and dissolution textures in feldspar (Fig. 3) probably post-dated faulting, as such delicate features are unlikely to have survived during fault movements. Volumetrically, calcite is the most important porosity-occluding authigenic mineral in the fault zone and is both fracture-filling and replacive (Fig. 3). Conversely, feldspar dissolution has locally formed porosity (Fig. 3).

The evidence for post-faulting water-rock interactions constitutes a 'chemically damaged zone' within the deformation zone (Fig. 2). Chemically 'damaged' rock is generally associated with physically damaged rock, but the reverse is not always true. Possibly, these relationships reflect spatial variations in water-

Figure. 2 Simplified log of borehole TM-2, comparing indicators of deformation (fracture frequency, fault rock and strain indicator (e.g. grain deformation) distributions, with evidence from calcite distributions for water-rock interactions.

Figure 3. SEM photomicrographs of mineral textures indicating water-rock interactions associated with fracturing in the Lower Toki Formation. A. Clay matrix of sandstone impregnated and replaced by calcite (rc), between clasts (cl). Detrital mica grains have been expanded and exfoliated by calcite (ex). B. Sheared fault gouge and clay matrix, with nucleation of micronodular calcite (nc). C. Finely banded micro-vein (mv) of cross-fibre calcite, at the margin of a quartz clast. D. Fracture surface in mudstone showing plagioclase dissolution.

access caused by variations in porosity and permeability distributions due to the initial faulting. However, the water-rock interactions continued after faulting and clearly influenced porosity and, by inference, permeability.

5 CONCLUSIONS

1 Unlike most faults studied in comparable detail elsewhere, the Tsukiyoshi Fault is reversed, relatively young and probably moved significantly for less than about 10 Ma. The fault allows the effects of faulting in relatively immature sedimentary rocks at low temperatures, to be evaluated.
2 The Tsukiyoshi Fault is not a planar dislocation, but consists of a variable number of prominent movement planes surrounded by damaged zones.
3 Both physically damaged zones and chemically damaged zones were distinguished. The physical 'damage' partly controlled the chemical effects.
4 The chemical 'damage' continued to evolve after faulting and affected the distribution of porosity.
5 Special sampling, preservation and preparation techniques were needed to recognise the mineralogical record of the latest water-rock interactions.
6 It may be inappropriate for safety assessments to assume that fault properties will be temporally invariant, simply because a fault is inactive.

ACKNOWLEGDEMENTS

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For Japan Society of Rock Mechani

地下水水質変化を考慮した水理解析の試み
ースウェーデン　エスポ地下研究施設での例ー

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INTEGRATING GROUNDWATER FLOW AND GEOCHEMISTRY
- AN EXAMPLE OF ÄSPÖ HARD ROCK LABORATORY, SWEDEN -

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In Äspö Hard Rock Laboratory, Sweden, the head change, as well as groundwater chemistry change were monitored during access tunnel construction, which reaches 460m below the sea level. The groundwater chemistries were interpreted with the chemometric analysis and the seven groundwater components are identified. Models are firstly calibrated to the head change and then further calibrated to groundwater chemistry change. Mixing ratio of the seven components was used to calibrate the models against groundwater chemistry. The flow model successfully modeled the groundwater chemistry change after calibrating the transport aperture, which affects the pore velocity. It is concluded that the groundwater chemistry is useful data to assess the reliability of the groundwater flow model and further add information on transport aperture, which is crucial to mass transport.

スウェーデン　エスポ島地下研究施設においてはアクセストンネル掘削時における周辺の水頭変化に加え、水質の変化が観測されている。水質に関しては、主成分分析の結果7種類の地下水が区分された。本稿においては、従来のアクセストンネル掘削時における水頭変化に加え、観測点における7種類の地下水の混合比の予測を追加することにより水理モデルの検証および信頼性の検討を行なった。その結果、地下水の混合比は、水頭変化を再現する水理地質構造モデルに加え実流速に関する情報（亀裂開口幅）を追加することにより再現できることが分かった。これらのことから、地下水化学データの利用は、水理モデルの検証に利用できるばかりでなく実流速に関するキャリブレーションに利用可能であることが分かった。

1．はじめに

近年、水理モデルを構築あるいは検証する上での地球化学データの利用の重要性が認識されてきている。利用可能な地球化学データとしては、地下水化学、地下水年代、鉱物結晶形などがある。高レベル放射性廃棄物の地層処分においては、モデルの信頼性の確保が重要な課題であり、水理モデルの妥当性を水理データ以外のデータを用いて検証するための努力がなされている。水理と地下水化学の統合については、世界的にも手法が開発段階にあり、近年スウェーデン南部のエスポ地下研究施設において、過去に実施された坑道掘削に伴う地下研究施設周辺の水位低下の予測解析[1)]に加え、坑道等における湧水の水質変化に着目し、水理と地下水化学の統合に関する検討が行なわれた。この検討は、エスポ地下研究施設水理・物質移行モデリングタスクフォースにおいて6ヶ国9機関が参加して行なわれた。本論文は、サイクル機構が同タスクフォースで行なった検討結果を取りまとめたものである。

2．サイトおよび実験の概要

エスポ地下研究施設は、図-1に示すようにスウェーデン南部のエスポ島に位置し、3600mの斜坑で地

図－1　エスポ地下研究施設の位置とモデル化領域

下460mに達している。地質は先カンブリア紀の主としてスモランド花崗岩とエスポ閃緑岩から構成される。坑道掘削は、1990年10月に開始され、1994年9月に終了した。坑道内には堰が各所に設置され、区間毎の流量が測定された。また、エスポ島およびその周辺に掘削された63孔のボーリング孔で水頭が測定された。地下水水質データは、ボーリングと坑道の98箇所で測定された。水質に関しては、Na, K, Ca, Mg, HCO_3, Cl, SO_4, ^2H, ^3H, ^{18}O等が測定された。

3．モデル化の方針とモデル化

(1) モデル化の基本方針

タスクフォースにおいては、モデルキャリブレーションと予測の2段階で解析を行なうこととなり、坑道切羽2900mまでのデータを用いたキャリブレーションと2900－3600mまでのデータに対する予測解析を行なうこととなった。サイクル機構は、水質データの有効性を示す上で、水理データだけに対するキャリブレーションを行なったモデルと水質データを加えたキャリブレーションを行なったモデルの違いを見るため、2900－3600mの予測を両方のモデルで行なうこととした。

(2) モデル化領域と地質構造モデル

モデル化領域は、図-1に示すようにアクセス坑道の螺旋状部を中心とし、エスポ島全体を含む2kmx2kmx深さ1kmとした。

主要な地質構造として、図-2に示した22枚の断層をモデル化した。また、健岩部については実測値から得た確率密度関数を基に統計的に亀裂を発生させた。使用した主なパラメータを表-1に示す。

図-2　モデル化した主要な構造

(3) 境界条件と初期条件

a) 水理境界

表-1　水理地質構造モデルのパラメータ

Fracture Set	Deterministic Fracture Zones	Background Fracture Properties
Name	Fracture Zone Fractures	Background fractures
Location	22 Planar Homogeneous Zones (Rhén et al., 1997[2])	Baecher/Bart Model
Size	Surface Traces Mean = 1420 m	LogNormal (μ = 13.7 m, σ = 12.7 m)
Orientation	3 Point Solution	Bootstrap SKB, 1994 Fractures Mapped in Tunnels
Transmissivity	Rhén et al., 1997	LogNormal ($\mu = 9 \times 10^{-7}$ m^2/s, $\sigma = 5 \times 10^{-6}$ m^2/s)
Storativity	0.001 $T^{1/2}$	0.001 $T^{1/2}$
Intensity	Rhén et al., 1997	P_{32} = 0.020214 (m^2/m^3) (22704 fractures)
Transport Aperture	2 $T^{0.5}$	2 $T^{0.5}$

図-3　境界条件

初期水頭については、図-3に示すように、底面は不透水境界、側方境界はSvensson(1999)[3]の広域水理モデルから得られる水頭を与えた固定水頭境界、上部境界については陸上部は浸透量を与えた固定流量境界、バルト海については水頭を0とする固定水頭境界とした。なお、バルト海については海底堆積物の影響を考慮するため厚さ1mのスキンを設定した。

坑道内側境界は、各堰で測定された湧水量をグループ節点流量として与えた。

b) 地下水化学

この解析においては、起源の異なる地下水を特定し、坑道への地下水流入に伴いどのように地下水が混合したかをモデル化する必要がある。このためには、混合と岩石ー水反応を区別する必要がある。このため、地下水組成のデータ全てを対象とした主成分分析[4,5]を行なうこととした。ここでは、図-4に示すように実測された地下水組成をもたらす端成分の組成とその混合割合を計算した。計算の結果、7つの端成分が特定された。得られた端成分を表-2に示す。

図-4　端成分と混合割合の計算

表-2　端成分

Chemical Component	Na	K	Ca	Mg	HCO3	Cl	SO4	O18	D	Tr	Bal
1	8508.6	5.1	17235.0	0.0	47.1	44001.5	800.3	-11.8	-75.7	14.6	-1.1
2	2066.3	0.0	1379.1	169.1	225.4	6163.5	0.0	-8.8	-68.5	0.0	-1.4
3	456.9	5.5	258.4	16.7	0.0	1207.9	79.8	-12.4	-94.2	0.0	-2.1
4	0.0	1256.2	0.0	2020.1	505.6	0.0	0.0	0.0	0.0	492.0	92.0
5	0.0	0.0	0.0	0.0	22039.5	0.0	0.0	0.0	0.0	0.0	-100.0
6	0.0	0.0	0.0	0.0	298.8	0.0	0.0	0.0	0.0	391.5	-100.0
7	2021.3	17.8	205.4	8.0	0.0	3230.3	1284.4	-14.3	-107.9	0.0	-8.6

図-5　端成分の深度分布

端成分1は鹹水。端成分2はバルト海水ないし塩分濃度の高いリトリナ海水、端成分3は氷河水、端成分5, 6は現在の岩石ー水反応に微生物の影響が加わったもの、端成分7は堆積物中の空隙水、端成分4はK, Mgに富む岩石ー水反応による水、と解釈された。各端成分の深度分布を図-5に示す。

(4) 性能指標

モデル化の結果を判断する性能指標として、タスクフォースでは以下の指標が使われた。

水理モデルに関しては、各測定箇所における水頭の実測値と予測値の差の平均を次の式で計算した。

$$dh = \frac{\sum_{i=1}^{n} (h_i^m - h_i^c)}{n} \qquad (1a)$$

$$dh(abs) = \frac{\sum_{i=1}^{n} \left| h_i^m - h_i^c \right|}{n} \qquad (1b)$$

$$Dh = \sqrt{\frac{\sum_{i=1}^{n} (h_i^m - h_i^c - dh)^2}{n-1}} \qquad (1c)$$

ここに、

n: ボーリング孔の水頭測定区間数

h:ボーリング孔のパッカー区間での水頭

m:水頭の測定値

c :水頭の計算値

また、地下水組成の混合比の性能指標としては、次の式で各測定箇所での端成分の混合比の実測値と計算値の差の平均値を計算した。

$$dg(abs) = \frac{\sum_{i=1}^{n} \left| g_i^m - g_i^c \right|}{n} \qquad (1d)$$

ここに、g_iはi番目の地下水の端成分の%値。

4. 水理モデルのキャリブレーションと混合割合の予測

水理モデルに関しては、上記性能指標を尺度に表-3に示すキャリブレーションを行なった。主な内容としては、以下の通りである。

- エレベーター立坑掘削時の急激なステップ状水頭低下を再現するための立坑を通過する亀裂の追加
- ボーリング孔内の透水亀裂を表現するconditioned fractureの追加と水理応答のない同fractureの削除
- バルト海底の低透水性のスキンの除去

上記のキャリブレーションの結果、図-6に示すように水頭の予測値と実測値の差が改善された。図-7に水頭の時間変化の一例を示す。

表-3 水理キャリブレーション

モデル	キャリブレーション内容	dh
H-1	22 本の破砕帯のみモデル化 バルト海直下 10m の透水量係数 1/100 に低減	4.94
H-2	エレベータ立坑を通過する 2 枚の透水性断層追加	5.30
H-3	H-1 モデルにバックグラウンド亀裂 22704 個追加	4.20
H-4	H-2 モデルにバックグラウンド亀裂 22704 個追加	2.74
H-5	H-3 モデルに間隙水圧測定区間に実測された透水性亀裂（透水量係数：$10^{-6}m^2/s$）を 161 個追加	9.45
H-6	H-4 モデルに間隙水圧測定区間に実測された透水性亀裂（透水量係数：$10^{-6}m^2/s$）を 161 個追加	10.18
H-7	H-6 モデルの間隙水圧測定区間の透水性亀裂を 69 個に減らすと同時に透水量係数を $10^{-8}m^2/s$ に低減	10.05
H-8	水位低下を減少させるためバルト海直下 10m の透水量係数低減を廃止	5.13

水理キャリブレーションの最終モデルであるH-8モデルを用いて地下水端成分の混合割合を計算すると、図-8, 9に示すように良好に混合割合を予測した区間と誤差の大きい区間とが認められた。

図-6 水理および地下水化学キャリブレーションによるdhおよびdgの変化

図-7 KAS08孔MA81区間の水頭変化

図-8 KA3005A孔における端成分の実測と予測の比較

図-9 KAS07孔における端成分の実測と予測の比較

5. 地下水組成に対するキャリブレーション

水頭変化は圧力の伝播現象であるのに対して、地下水組成の変化は物質移行プロセス、ここではトンネル掘削後の加速された流速場での現象なので拡散現象等の緩慢なプロセスの影響は少なく、主として実流速を反映していると考えられる。図-9に見られるような実測と予測の違いについては、予測の方が実流速が速いため変化が早く起きていると推定され

た。この状況は亀裂の貯留係数の違いと物質移行開口幅の違いに起因する可能性がある。このため、亀裂の貯留係数および物質移行開口幅$a_T=\alpha T^{1/2}$を過去のトレーサー試験に基き$\alpha=2$に当初設定したが、表-3に示すように変更した。

表-3　物質移行開口幅の補正

透水性断層	モデル	
	C-1	C-2
	貯留係数の補正係数	αの補正係数
EW-1N	1	1
EW-1S	3	3
EW-3 (z=500-200)	1	1
EW-3 (z<200)	3.2	3.2
EW-7	1	1
NE-1	1	1
NE-2	3.3	3.4
NE-3	1	1
NE-4N	3.5	2.5
NE-4S	1	1
NW-1	1	1
NNW-1	1	1
NNW-2	1.5	2
NNW-3	1	1
NNW-4	1	1
NNW-5	1	1
NNW-6	1	1
NNW-7	1	1
NNW-8	1.7	1
SFZ11	1	1
SFZ14a	1	1
SFZ14b	1	1

貯留係数の変更は、図-6に示すように地下水組成の混合比の誤差（*dg*）は改善されたものの水頭の誤差(*dh*)の増加をもたらした。一方、物質移行開口幅を補正したことにより、*dg*が*dh*の誤差をもたらすことなく低減され、より信頼性の高い結果と判断された。

図-10にモデルC-2の結果の一例を示す。

図-10 KAS07孔における端成分の実測と予測の比較

6．まとめ

従来の水理モデルは、水頭変化あるいは流量といったパラメータで検証され、途中の移行経路の妥当性に関する検討が困難であった。しかし、今回のように地下水組成データを使用することにより、移行経路の情報が追加され、水理モデルの検証および信頼性向上に有効と考えられる。さらに、地下水組成の変化は、物質移行現象であり、本来移流に加えてマトリクス拡散や収着性の溶質である場合には収着も関わってくる。今回のような、坑道掘削後の坑道全体が揚水試験と見なせる速い流速場においては移流が卓越するため、実流速の推定、すなわち亀裂性媒体では物質移行開口幅、多孔質媒体においては空隙率の推定・検証に有効と考えられる。

今後は、我が国の実際の地下水問題への適用性が課題となる。また、今回使用していない鉱物変化、放射性同位体等の手法の適用が今後の課題と考えられる。

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【研究報告】

炭酸塩鉱物の同位体組成に基づくpH条件の長期安定性の解析手法

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Study on pH Conditions in Deep Underground by Using Isotopic Analysis of Carbonate Minerals

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岐阜県東濃地域の土岐花崗岩を対象として、割れ目充填鉱物（主に方解石）の化学組成・同位体組成に基づき、地下深部の地球化学的状態の長期的変遷についての予察的検討を行った。その結果、化学組成・同位体組成から、方解石の起源として、① 熱水起源、② 海水起源、③ 天水起源が考えられた。海成の方解石の存在は、その領域が方解石沈澱後、千数百万年間にわたって方解石の溶けることのない弱アルカリ性のpH条件にあった可能性を示しており、方解石の同位体組成を解析することによりpH環境の長期的変遷について解析する手法を示すことができた。

This study was undertaken to develop a method for evaluating geochemical environments in deep granitic basement rocks. The method involves analyzing fracture-filling minerals to determine their isotopic compositions. A preliminary isotopic investigation ($\delta^{13}C$, $\delta^{18}O$, ^{14}C activity) of the groundwater and fracture-filling calcite in granite at the Tono research site, central Japan, was conducted. The isotopic compositions were used, together with geological evidence for the history of the Tono area, to infer the origins of the waters from which the calcite precipitated. These waters were:① hydrothermal solutions. ② relatively 'old' fresh water, ③ seawater, and ④ present groundwater. The investigation methods were very valuable for evaluating the temporal variations of geochemical conditions deep underground. The isotopic evidence for seawater is so far the most direct evidence that seawater penetrated into the granite in this area in the past.

キーワード
炭酸塩鉱物、同位体組成、pH条件、長期安定性、花崗岩、^{14}C
Calcite, Carbon Isotope Composition, pH Condition, Geohistry, Granite, ^{14}C

1．はじめに

東濃地科学センターでは地層科学研究の一環として、深部地下環境の長期的変遷にかかわる研究を行っている。この研究においては、地下水の流動状態や地球化学的状態がどう変化してきたかという情報が不可欠である。岐阜県東濃地域（図１）においては、これまでにウラン鉱床が胚胎している堆積岩を対象に、古水理地質学的研究のフレームワークの提案と、そのための地質学・水理学・地球化学的データの編集が行われている（Yusa et al., 1993[1]）。一方、本地域の基盤をなす花崗岩については、地質学・水理学・地球化学的な調査研究が実施されており、特に、地球化学的研究分野においては、これまでに原位置における地下水の水質や物理化学パラメータを基に、地下深部のpHや酸化還元電位（以下、Eh）、それに寄与する主要な化学反応（水−鉱物反応）が明らかになってきている[2]。しかしながら、調査により明らかになったpHやEhなどの地球化学的状態の長期的変遷についての考察は、いまだなされていない。

地下深部の地球化学的状態は、主に地下水と地下水の流動経路沿いにある岩石中の鉱物との反応により形成される。そのため流動経路沿いの鉱物の溶解や沈殿といった地球化学的プロセスを調べ

図１　調査地域の地質と試錐孔の配置

ることによって、地下深部の地下水と岩石との相互作用による地球化学的状態を解析することが可能となる。特に、流動経路沿いに沈殿している炭酸塩鉱物は、地下水のpH条件を反映する重要な鉱物の一つであり、例えば、炭酸塩鉱物の化学組成や同位体組成から、それを沈殿させた水の種類（海水、淡水など）について推測することができる[3)-6)]。

東濃地域は、これまでの地質調査の結果、過去のある期間、湖底下又は海底下にあったことが明らかになっており、土岐花崗岩の風化表層部に連結した割れ目にも湖水や海水が浸透していた時期があったものと推測される（図２）。したがって、花崗岩の割れ目中に沈殿している炭酸塩鉱物の化学組成や同位体組成を調査することによって、湖水や海水がどの程度地下深部まで侵入していたのか、その貯留期間などについても情報を得ることが可能である。

また、炭酸塩鉱物は、一般に地下水が炭酸塩鉱物に対して飽和平衡状態になりやすい弱アルカリ性のpH条件において、安定に存在できると考えられる。そのため、炭酸塩鉱物の沈殿した年代を特定できれば、炭酸塩鉱物が溶解しない弱アルカリ性のpH条件が保持されてきた期間について情報を得ることができると考えられる。

本報告は、東濃地域の土岐花崗岩を対象に行った、割れ目充てん鉱物の化学組成・同位体組成に基づく地球化学的状態（特にpH条件）の長期的変遷に関する予察的研究について述べたものである。この研究は、地下深部の地球化学環境の長期的安定性を示すために必要な古水理地質学的研究の一部をなすものであり、割れ目充てん鉱物の化学組成・同位体組成データを用いた研究手法の開発を目的とする。

２．調査地域の概要

岐阜県東濃地域では、第三紀の堆積岩である瑞浪層群〔下から土岐夾炭累層（上部層・下部層）、明世累層、生俵累層〕と瀬戸層群が、基盤である土岐花崗岩を不整合に覆っている（図２）。土岐夾炭累層（上部層）、明世累層、生俵累層は浅い海で堆積した海成層であることが分っている。これらの地層は、シルトや砂岩、泥岩の互層から成り、貝化石を豊富に含んでいる。土岐夾炭累層（下部層）は、湖で堆積した湖成層と考えられており、下部に風化した土岐花崗岩の礫を含んでいる[7)]。

時代	年代(Ma)	地層		堆積環境	岩相
鮮新世	0.7-5	瀬戸層群		湖成	礫岩、砂泥互層
中新世	15-16	瑞浪層群	生俵累層	海成	凝灰質泥岩 シルト
			明世累層		凝灰質砂岩 シルト質砂岩
			土岐夾炭累層 上部層		凝灰質砂岩 礫岩
	18-22		土岐夾炭累層 下部層	湖成	砂泥互層 リグナイト 礫岩
白亜紀	72.3	土岐花崗岩			黒雲母花崗岩

図２　東濃地域の地史と堆積環境

土岐花崗岩は、主に中・粗粒の黒雲母花崗岩及び角閃石一黒雲母斑岩から構成されており、石英斑岩やアプライト脈の貫入が所々に存在する。また、花崗岩の地表から深部（深度約1,000m）まで、割れ目が観察されている。これらの割れ目は、その規模や表面の岩相などにより緑泥石を多く含む緑色変質を伴う割れ目帯と、カオリナイトを多く含む白色変質を伴う割れ目帯に分類されている[8]。

花崗岩中の地下水の起源は、これまでの水素・酸素同位体比の調査結果から天水起源と考えられている。深度1,000m付近までの地下水の総溶存成分濃度は150mg/ℓ程度である。水質は表層付近で中性であり、Na^+・Ca^{2+}・HCO_3^-に富む水質から、深度とともに弱アルカリ性のNa^+・HCO_3^-に富む水質に変化する。このような水質は、主に長石類の溶解反応とそれに続く地下水一粘土鉱物間のイオン交換反応により形成されたものと考えられている[8]。

3．サンプリング及び分析手順

東濃地域で行われている地下水流動研究用に掘削された深度500～1,000mの試錐孔（図１）の試錐コアを利用し、花崗岩の割れ目表面に沈殿している炭酸塩鉱物を採取した。これらの試錐孔では、パッカーシステムを使用した採水方法[8]により、深度1,000mまでの地下水試料を採取し、化学分析、同位体分析を行うと同時に、原位置の物理化学パラメータ（温度・電気伝導度・pH・Eh・溶存酸素濃度）の測定が行われている[2]。

本研究では、得られた炭酸塩鉱物試料について、SEM-EDS（走査型電子顕微鏡一エネルギー分散型X線分析装置）、EPMA（電子プローブマイクロアナライザー）による鉱物の結晶形や表面構造の観察、化学組成分析を行うとともに、質量分析計・タンデム型加速器質量分析計により同位体組成〔炭素同位体比（$\delta^{13}C$）、酸素同位体比（$\delta^{18}O$）、放射性炭素濃度（^{14}C）〕分析を行っており、それらの結果に基づき、総合的に炭酸塩鉱物の起源について解析している。本報告では、これまでにデータの得られている炭酸塩鉱物〔主に方解石（$CaCO_3$）〕の化学組成と同位体組成に関する研究結果について述べることとする。

方解石は真空ライン中においてリン酸と反応させ炭酸ガスを回収し、質量分析計により、その炭素・酸素同位体比（$^{13}C/^{12}C$・$^{18}O/^{16}O$）の測定を行った[9]。測定結果については各々δ値（$\delta^{13}C$・$\delta^{18}O$）で表す。なおδ値の定義は以下の通り。

・$\delta^{13}C=[(^{13}C/^{12}C)_{試料}/(^{13}C/^{12}C)_{国際標準試料}-1]\times10^3$ ‰

・$\delta^{18}O=[(^{18}O/^{16}O)_{試料}/(^{18}O/^{16}O)_{国際標準試料}-1]\times10^3$ ‰

$\delta^{13}C$の国際標準試料：PDB（アメリカPeedee層から得られた矢石化石）

$\delta^{18}O$の国際標準試料：SMOW（標準平均海水）

測定精度は$\delta^{13}C$、$\delta^{18}O$に対して±0.2‰である。

また、生成した炭酸ガスの一部を還元、グラファイト化し、タンデム型加速器質量分析計[10]により^{14}C濃度を測定した。

4．結果

化学組成、同位体組成の分析はSEM-EDS分析により鉱物の表面構造・化学組成から割れ目表面に沈殿していると確認された方解石について行った。これらの方解石は、割れ目表面をフィルム状に覆うように沈殿しており、六方晶、C軸方向に長大化した自形結晶や層状に割れ目に張り付いた他形の沈殿も観察される。これらの様々な沈殿状態は起源となった水の化学組成や温度・圧力環境等を反映していると予想され、地下深部の地球化学的状態を知るために極めて重要な情報をもたらすと考えられる。

4.1　方解石の炭素同位体組成

地下水中の溶存無機炭素及び方解石の炭素・酸素同位体組成を表１に示す。溶存無機炭素の炭素同位体比は表層水で－20～－16‰、地下水で－18～－14‰の範囲にある。方解石の炭素同位体比は約－29～＋３‰にばらついている。これらの方解石を沈殿させた溶存無機炭素の同位体比は、方解石と溶存無機炭素間の同位体分別係数[11]から、表１のように求められる。また、一部の方解石について最大4.5pMC（%Modern Carbon：世界的核実験が始まる前の大気中の^{14}C濃度を100としたパーセンテージ）の^{14}Cが検出されている。

4.2　方解石の化学組成

割れ目表面に沈殿している方解石の化学組成は、その起源となった水の化学組成を反映している。特にCaと同様の価数（２価）あるいはイオン半径を持つ元素がCaの代わりに結晶中に含まれていることが予想される。方解石の化学組成に

表1　地下水中の溶存無機炭酸、割れ目中の方解石と方解石を沈殿させた水の同位体組成

地点	標高 (m)	地下水 $\delta^{13}C$ (‰-PDB)	地下水 ^{14}C (pMC)	方解石 $\delta^{13}C$ (‰-PDB)	方解石 $\delta^{18}O$ (‰-SMOW)	方解石 ^{14}C (pMC)	方解石を沈殿させた水 $\delta^{13}C$* (‰-PDB)
表層水 (n=6)		-18.1±1.9	1.6				
堆積岩中の貝化石 (n=5)				0.3±1.7	28.6±1.3		-1.6±1.7
DH-3	-147			-14.4	22.3		-16.2
DH-3	-307			-14.7	20.8		-16.5
DH-5	41			-17.6	22.6	0.7	-19.4
DH-5	31			-17.6	8.0	0.6	-19.4
DH-5	16			-17.6	14.9	0.8	-19.4
DH-5	-20	-17.5	45.5				
DH-5	-53			-18.2	21.6	0.5	-20.1
DH-5	-165			-26.0	21.0		-27.8
DH-6	-6			-28.6	20.8		-30.4
DH-6	-158			-25.1	23.3	0.6	-26.9
DH-6	-263			-2.2	14.0		-4.0
DH-6	-305			-12.2	19.2	0.4	-14.0
DH-6	-330			-9.2	18.4	0.6	-11.0
DH-6	-461			-20.7	23.8	<0.25	-22.5
DH-6	-481			-15.8	23.6	0.3	-17.6
DH-6	-483			-11.1	18.1	0.4	-12.9
DH-6	-488			-16.0	22.8		-17.9
DH-6	-518			-10.2	21.7		-12.1
DH-6	-540			-16.2	22.7		-18.0
DH-7	-19			-16.5	22.8	<0.25	-18.3
DH-7	-28			-18.6	25.3	0.7	-20.4
DH-7	-131			-9.6	5.9		-11.4
DH-7	-183			-19.2	19.0	1.9	-21.0
DH-7	-224			-10.9	22.3	1.1	-12.7
DH-7	-246			-8.5	7.2		-10.3
DH-7	-297			-12.0	-2.0		-13.8
DH-7	-398			-9.5	14.9	1.8	-11.3
DH-7	-401			-14.5	18.8	1.3	-16.3
DH-7	-496			-7.6	1.6		-9.4
DH-7	-509			-13.5	23.3		-15.4
DH-7	-557			-12.7	25.1		-14.6
DH-7	-615			-14.2	24.5		-16.0
DH-8	67			-17.3	15.8	1.4	-19.1
DH-8	-265			-10.9	20.8	<0.25	-12.7
DH-8	-375	-17.8	36.7				
DH-8	-431			-13.1	14.6	1.0	-14.9
DH-8	-602	-14.5	18.8				
DH-8	-708	-16.9	29.9				
DH-9	92			-16.7	23.1	4.5	-18.5
DH-9	91			-11.1	18.8	0.8	-12.9
DH-9	84			0.1	22.4	<0.25	-1.8
DH-9	52			-11.3	18.6		-13.1
DH-9	-11			-6.8	6.2		-8.6
DH-9	-44			0.3	22.6		-1.5
DH-9	-111			-7.9	18.0		-9.7
DH-9	-196			-3.9	16.7		-5.7
DH-9	-277			-2.3	21.5		-4.1
DH-9	-290			1.2	20.5		-0.6
DH-9	-293			-2.7	21.1		-4.5
DH-9	-295			0.1	22.3		-1.7
DH-9	-361			-1.3	22.3		-3.2
DH-9	-369			-6.2	7.1		-8.0
DH-9	-404			2.4	23.2		0.6
DH-9	-414			-10.5	4.2		-12.4
DH-9	-421			-11.9	20.0		-13.8
DH-9	-429			-10.5	20.8		-12.3
DH-9	-463			-6.7	13.6		-8.6
DH-9	-491			0.7	22.2		-1.1
DH-9	-508			-2.7	20.5		-4.5
DH-9	-517			0.8	21.4		-1.1
DH-9	-559			-6.5	21.2		-8.3
DH-11	-24			-7.7	25.1		-9.5
DH-11	-52			-9.4	-2.5		-11.2
DH-11	-185			-15.7	9.0		-17.5
DH-11	-308			-11.9	19.3		-13.7
DH-11	-319			-13.8	23.4		-15.6
DH-11	-331			-11.9	18.9		-13.7
DH-11	-380			-11.8	21.3		-13.6
DH-11	-386			-11.8	25.7		-13.6
DH-11	-393			-11.9	19.3		-13.7
DH-11	-403			-2.4	21.7		-4.3
DH-11	-409			-5.0	20.2		-6.8
DH-11	-427			-10.7	20.0		-12.6
DH-11	-435			-6.7	20.7		-8.5
DH-11	-497			-4.8	20.1		-6.6

* 方解石－水間の同位体分別係数 α=1.00185 at 20℃ (Emrich et al., 1970)
空欄はデータなし。

図３　方解石中の鉄、マンガン濃度と炭素同位体比の相関（DH-９号孔）

起源となった溶液の違いによる特徴がないかどうか明らかにするために、幅広い炭素同位体比を示すDH-９号孔の試料を対象にEPMAによる組成分析を行った。その結果、炭素同位体比が０‰に近づくほど、Mn、Fe含有量が高くなる傾向が見られた（図３）。

５．考察

東濃地域の地史を考慮すると、割れ目中に沈殿している方解石の起源として、

① 花崗岩の貫入活動に伴う熱水
② 湖成層の土岐夾炭累層下部層及び瀬戸層群が堆積した時代の湖水
③ 海成層の明世累層、生俵累層が堆積した時代の海水
④ その後の天水起源の地下水

等が考えられる。

図４　沈澱水温と方解石のδ18O値の相関

沈澱水温は、方解石の酸素同位体比と現在の地下水又は海水の酸素同位体比から得られる分別係数αにより計算した。$1000\alpha = 2.78 \times (10^6 \times T^{-2}) - 3.39$ (O'Neal, 1969)

５．１　酸素同位体比に基づく方解石の沈殿温度の推測

方解石が溶液から沈殿する時の方解石ー溶液間の酸素同位体分別係数は、温度の関数で表され、O'Neil et al.(1969)[12]によって次のように求められている。

$$1000 \ln \alpha = 2.78 (10^6 T^{-2}) - 3.39$$

α：分別係数
T：温度（K）

方解石が淡水あるいは海水から沈殿したとして、各々の水の酸素同位体比を淡水：－8.3‰（現在の地下水の値）、海水：０‰と仮定すると、方解石の酸素同位体比から、その沈殿水温を図４のように求められる。酸素同位体比が－２～10‰の方解石は約20‰周辺の値を示すものに比べ、数十℃～数百℃以上高い温度条件下で沈殿したと計算される。

一方、熱水を伴う水ー岩石反応により方解石が沈殿した場合、その酸素同位体比は岩石の値に近づくことが示されている[13]。一般的な花崗岩の酸素同位体比は約－４～13‰であり[14]、酸素同位体比が－２～10‰の方解石が熱水から沈殿したという仮説と矛盾しない。また、沈殿温度のばらつきは、複数回の熱水の貫入あるいは場所ごとの沈殿温度の違いを反映していると推測される。

５．２　炭素同位体比、^{14}C濃度に基づく過去５万年内に沈殿した方解石の同定

酸素同位体比が－２～10‰の方解石試料を除いた各試錐孔の方解石の炭素同位体比は、約－29

図５　各試錐孔における方解石の炭素同位体組成

～＋３‰にばらついている（図５）。このうちDH-５、７～９号孔の標高０m付近の方解石は、炭素同位体比が－20‰付近の溶存無機炭素から沈殿したと計算される（図５）。この値は現在の表層水の溶存無機炭素の炭素同位体比とよく一致する。これらの方解石は最大4.5pMCの^{14}Cを含んでいる（表１）。表層水が地下深部へ浸透していく過程においては、長石などのケイ酸塩鉱物の溶解反応により地下水中にCaイオンが供給される。また、ケイ酸塩鉱物の溶解反応によりpHが上昇し、炭酸水素イオン、炭酸イオンに富むようになる。そのため、地下水はある深度から方解石に対して飽和状態になる[15]。起源となった水の炭素同位体比が表層水や地下水の溶存無機炭素と同様の値を示し、かつ^{14}Cを含んでいる方解石は、表層水や地下水がより深部へ浸透していく過程で、方解石に対して飽和状態になった深度で沈殿しているものと考えられる[16),17]。また、沈殿した時期は、^{14}Cの検出限界濃度（<0.25pMC）とその半減期（約5,730年）から考えて、少なくとも過去５万年以内と推測される。このような方解石は、DH-６～８号孔で標高０m以深においても観察され、高透水性割れ目に沿って、方解石に対して不飽和な水がより深部まで浸透しているものと推察される。

５.３　炭素同位体比・化学組成に基づく海成の方解石の同定

DH-９、11号孔の深部では、地下水の溶存無機炭素の炭素同位体比と方解石の炭素同位体比が大きく異なり、現在の地下水と方解石が同位体平衡にないことから、これらの方解石は現在の地下水と異なった炭素同位体比（－14～＋１‰）を持つ溶存無機炭酸から沈殿したと考えられる。Shikazono and Utada (1997)[18]では、花崗岩を覆う堆積岩（海成層と湖成層）の方解石の同位体比について、

海成層の方解石：δ^{13}C＝－11～＋３‰
　　δ^{18}O＝＋20～＋28‰
湖成層の方解石：δ^{13}C＝－19～－６‰
　　δ^{18}O＝＋18～＋24‰

と求め、方解石中の炭素が堆積岩中の有機物や貝化石からもたらされたとしている。DH-９、11号孔の方解石の炭素同位体比は、湖成層あるいは海成層の方解石と同様の値を示し、これらの方解石が堆積岩層が堆積したのと同時期に、湖水あるいは海水から沈殿した可能性を示唆する。この場合、方解石の化学組成や同位体組成は、その時代の湖水や海水の組成を反映していることが考えられる。

湖水起源の方解石については、その時代の湖水中の溶存無機炭素の炭素同位体比が現在の表層水又は湖水と同様に、数‰～十数‰であった可能性があるため、湖成層の堆積と同時期に沈殿した方解石を判別することはできない。一方、海水起源の方解石の同位体比については、各時代の海水の炭素同位体比が比較的よく求められている[19]。海成層が堆積した時代（16-15Ma）の貝化石の炭素同位体比は、約０～２‰前後である。土岐花崗岩

を覆う海成層（明世累層）においても、貝化石の炭素同位体比は、0.3±1.7‰という値を示している（表１）。炭素同位体比が０‰付近の値を示す炭素の起源としては、

① 海成層中の貝化石が溶解して、花崗岩深部まで運ばれている場合
② 海成層が堆積した時代に花崗岩中に浸透した海水から沈殿した場合

が考えられる。貝化石が溶解して、花崗岩深部まで運ばれている場合は、地下水の炭素同位体比が貝化石（０‰付近）と地下水（20‰付近）の中間的な値になり、それから沈殿する方解石は十数‰の値になると思われる。そのため、炭素同位体比が０‰付近の値を示す方解石は海水から沈殿したと推測される。

化学組成の分析結果を見ると、このような炭素同位体比が０‰付近の方解石は、十数‰の炭素同位体比を示す方解石に比べMn、Feの含有量が高いという特徴がある。溶液中のMn、Feの化学種は、酸化還元状態によりその価数が変化し、還元的条件おいて２価の状態で存在する。北野(1979)[20]は、塩分濃度が高い沿岸部においては陸水から供給された重金属懸濁物が分解、堆積し、汽水中から取り除かれることを示している。また、沿岸堆積物中において、還元的な間隙水中で方解石が生成する過程でMnが取り込まれて$MnCO_3$として沈殿することも示している。

以上のことから、炭素同位体比が０‰付近の方解石は十数‰の値を示すものに比べ、塩分濃度が高く還元的な環境で沈殿したと推測される。このような環境は沿岸の海底で普遍的に見られる環境であり、炭素同位体比が０‰付近の方解石が海水から沈殿したという仮説と矛盾しない。このような海成の方解石の存在は、その領域が方解石沈殿後、千数百万年間にわたって方解石の溶けることのない弱アルカリ性のpH条件にあった可能性を示す。

図５に示される方解石の炭素同位体比の深度分布は、試錐孔毎に異なっており、DH-３、５～８号孔では、標高－600m付近まで現在の表層水、地下水と同じ炭素同位体比を持つ地下水から沈殿した方解石が観察される。一方、DH-９、11号孔の深部では、海水起源と考えられる方解石が観察されている。

このような起源の異なる方解石の分布状態は、炭酸塩鉱物の沈殿した年代や割れ目密度、地下水の流動状態など様々な要因による弱アルカリ性のpH条件の長期的安定性の違いを反映している可能性がある。言い換えれば、このような情報から地下水の流動状態がどのように変化してきたかという古水理地質学的な情報も得られる可能性がある。

６．おわりに

岐阜県東濃地域において花崗岩の割れ目中の方解石の炭素・酸素同位体組成からその起源を推定し、この地域の地史と統合的に解析することによりpH環境の長期的変遷や表層環境の地下深部への影響について解析する手法を示すことができた。東濃地域の基盤花崗岩においては、現世の地下水から方解石が沈殿している割れ目がある一方で、方解石の沈殿後、千数百万年間にわたって方解石の溶けることのない化学的条件が維持されている領域がある。このような情報は、地下水の流動状態がどのように変化してきたかという古水理地質学的な研究を行う上で非常に重要である。また、本研究で用いた手法は、東濃地域と同様に地史が明らかになっており、同位体的に特徴のある海水起源の方解石の沈殿があると予想される調査地において、同位体研究により地球化学的状態あるいは水理学的状態の変遷を示すことができるため、地下深部の水理地球化学的状態の長期的変遷を考察する上で、非常に有効な手法となると考えられる。

今後、方解石の沈殿状態や結晶形態の観察データに基づき、方解石を沈殿させた水の化学組成や温度・圧力環境等を推察し、手法の信頼性を向上させていくとともに、弱アルカリ性のpH条件が長期間維持されるための、主要な要因を明らかにしていく予定である。

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The role of the Tsukiyoshi Fault as a control on nuclide migration in the Tono uranium deposit, central Japan

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Abstract

To date, relatively little use has been made of natural analogue studies to build an understanding of long-term processes that will control the hydraulic behaviour of faults around a High Level Radioactive Waste (HLW) disposal system. Typically, Performance Assessment (PA) for such systems assumes that the properties of faults are temporally invariant. Often, it is also assumed that the properties of any particular fault will be spatially invariant. In most cases, PA incorporates conceptual models for faults that are based largely upon investigations of normal faults. These PA models may be inappropriate for geologically recent reverse faults in a convergent plate margin setting, such as that of Japan. For all these reasons, the Japan Nuclear Cycle Development Institute (JNC) is conducting a natural analogue study of a reverse fault, the Tsukiyoshi Fault, which cuts the Tono uranium deposit of central Japan. The initial results of this investigation are presented in this paper. These results suggest that a description of the fault as a single planar fracture is inaccurate. Instead, it is more appropriate to describe the fault as a relatively complex zone of fracturing, extending for several metres around a central zone of fault rocks and fault gouge, up to several tens of centimetres wide. Furthermore, there has been a complex history of fluid movement through the fault zone. There is also evidence that the hydraulic properties of the hanging wall and footwall are different and may have varied over time. However, uranium-series isotopic data suggest that uranium has been retained in the fault's gouge for at least one million years. It is postulated that water/rock interactions have created suitable chemical conditions in the fault gouge to immobilise the uranium even though past fluid movement has occurred through the fault zone.

Introduction

Performance Assessments (PA) for potential deep geological repositories for High Level Radioactive Waste (HLW) must take into account the influence of faults on mass transport through the geosphere. It is necessary to ensure that the conceptual and numerical models underpinning PA incorporate appropriate representations of faults, based upon a sound understanding of the relevant mass transport processes and flow pathways. However, typically, PA assumes that faults have temporally invariant properties. It is often also assumed that these properties are spatially invariant in any particular fault. It is important to test these assumptions, particularly in active tectonic settings where relatively recent faults are widespread. In particular, it is desirable to evaluate whether such faults behave in the same way as the faults that occur in relatively stable tectonic settings, that have been considered by most PA to date.

In Japan, any future underground disposal of HLW will take place close to a convergent plate margin. Thus, it is likely that a PA for any future HLW repository in Japan will need to consider mass transport through geologically recent reverse faults. However, there is relatively little information upon which to base representations of the long-term behaviour of such faults in the PA. This deficiency arises because globally, most research related to HLW disposal has focussed upon stable tectonic shield settings and/or extensional sedimentary basin settings.

To help fill this gap in knowledge, the Japan Nuclear Cycle Development Institute (JNC) is conducting research on a reverse fault, the Tsukiyoshi Fault. This fault cuts a uranium deposit at the natural analogue site of Tono Mine, in Gifu Prefecture, central Honshu, Japan (Figure 1). Here, we outline the general approach to the investigations of this fault and present the initial findings.

Figure 1 Geology and in-situ experimental area at Tono mine

Geological Setting

In central Japan, a series of small Neogene to Quaternary basins are developed on pre-Tertiary granitic basement rocks. The Tono Mine is located almost entirely within Miocene to Pleistocene sedimentary rocks that fill one of these basins (Figure 1). These sedimentary rocks were deposited between 20 Ma and 0.7 Ma and the lowermost strata lie directly on the eroded surface of the late Cretaceous Toki Granite (Yusa et al. 1993). The deepest of the sedimentary rocks contain the Tono uranium deposit, which was formed approximately 10 million years ago (Ochiai et al., 1989; Kobayashi, 1989). The uranium mineralisation lies immediately above the unconformity, in a zone that is 2–5 m thick, with an area of several hundred meters wide and 2-3 km long.

In the vicinity of the mine, the Tsukiyoshi Fault has an approximately east-west orientation, a southerly dip of between 60° and 70°, and a reverse displacement of about 30 m. The fault displaces the Toki Granite and overlying Miocene strata of the Mizunami Group (deposited between 20 Ma and 15 Ma; Itoigawa, 1974), including the Tono uranium deposit.

However, the fault does not displace the Pliocene to Pleistocene Seto Group, which overlies the Mizunami Group unconformably (Figure 1). Previous investigations have identified the fault as a dominantly planar feature, which usually contains a green clay gouge of variable width, but which is up to around 20 cm wide.

From bottom to top, the Mizunami Group consists of three formations: the Toki Formation (divided into the Lower Toki Formation and the Upper Toki Formation), the Akeyo Formation and the Oidawara Formation. The Toki Formation is considered to consist mainly of fresh water lacustrine deposits (Yusa et al., 1993), although fluvial sediments may also be present (Yoshida et al. 1994). In contrast, the Akeyo Formation is considered to represent brackish to shallow marine sedimentation, while the overlying Oidawara Formation is thought to be a deeper water marine deposit (Yusa et al., 1993).

Methods

The Tsukiyoshi Fault was examined in exposures in the walls of Tono mine and in two horizontal, parallel, fully-cored boreholes, 98SI-03 and TFA-1, that were drilled from a mine gallery (Figure 1). These boreholes were drilled 0.5 m apart, for distances of 18 m and 30 m respectively. They intersected the fault at a distance of 14.6 m from the gallery wall. The core from Borehole 98SI-03 was logged systematically and then sampled for more detailed petrographic analysis. In addition, the fault clay of the Tsukiyoshi Fault was sampled from accessible exposures in the mine galleries. A single sample was also taken from near the base of Borehole TFA-1.

It was particularly challenging to collect and prepare poorly consolidated samples of fault rocks and gouge, for microscopic investigations. Such samples were collected from both the core and the exposures in the mine walls, by means of 'Kubiena' tins (Figure 2). These tins are aluminium boxes with sharpened edges and lids on opposite sides. The boxes were pushed into the soft clay-rich fault rocks and rock material was then scraped from around each box until it was freed from the core or mine wall. The boxes were then capped and sealed.

Figure 2 A Photograph illustrating an exposure of the Tsukiyoshi Fault in the walls of an adit in the Tono mine.

The samples were air-dried and then vacuum-impregnated with epoxy-resin to stabilise the friable materials during sectioning. A blue dye was added to the epoxy-resin to highlight the porosity during optical microscope observation. Sections were cut and polished under paraffin in order to preserve any water-soluble minerals (e.g. gypsum or anhydrite) that might be present. Those sections to be examined using backscattered scanning electron microscopy (BSEM) were coated under vacuum with a thin film of approximately 25 nm thick, to provide them with an electrically-conductive surface.

The sections were examined initially by optical microscopy. They were then investigated in more detail by back-scattered scanning electron microscopy (BSEM), to provide high-resolution mineralogical and spatial information on mineral relationships and rock microfabric. Simultaneously, semi-quantitative microchemical information was obtained by energy-dispersive X-ray microanalysis (EDXA). BSEM-EDXA and SEM analyses were performed using a variable pressure digital scanning electron microscope (SEM). Semi-quantitative EDXA analysis during the SEM investigations aided mineral identification. SEM-EDXA analyses were largely performed under high-vacuum mode (i.e. $<10^{-4}$ torr). However, some samples were examined by low vacuum/variable pressure SEM (i.e. chamber vacuum of approximately 3×10^{-2} torr) to overcome problems with high sample moisture content and sample outgassing (due to high smectite contents).

The bulk and clay mineralogy of samples of fault gouge, fault rock and representive samples of different sandstone, siltstone and mudstone lithologies were determined by X-ray diffraction (XRD).

Pore fluids were extracted from samples of the fault gouge by means of a squeezing procedure. These fluids were analysed for a range of major, minor and trace elements by inductively coupled plasma mass spectroscopy (ICPMS) and ion chromatography (IC).

As part of the regional hydrogeological studies, the impact of the Tsukiyoshi fault on groundwater flow in the Tertiary sediments has also been studied. During the construction of Number 2 Shaft (Figure 1) the resulting drawdown effect on the piezometric head in the surrounding rock mass was studied, by observing groundwater levels and hydraulic heads in 14 nearby boreholes (Koide et al., 1996).

Initial Observations and Discussion

An exposure of the fault in the mine tunnel is illustrated in Figure 2. This figure shows the complex zone of clay gouge and brecciation associated with the fault and some major associated fractures in the hanging wall. The width of the fault zone varies markedly, even over distances parallel to the fault, of a few tens of centimetres.

The main features of the mineral paragenesis in the zone of fracturing associated with the Tsukiyoshi Fault are summarised in Table 1 and a simplified log of the core from Borehole 98SI-03 is presented in Figure 3. This figure shows the relationship between the frequency of fracturing in the core and the prominent plane of movement, identified as the 'Tsukiyoshi Fault'

in previous studies. It can be seen that the frequency of fracturing becomes greater as this prominent fracture plane is approached. A damaged zone that is at least 7 m wide occurs around this fracture plane.

Table 1 Fracturing and diagenetic history

Stage of Mineralisation	Characteristics
Sediment Deposition	Deposition of immature organic-rich sediments containing abundant granite-derived clasts and volvanic-derived material
Early Diagenesis (i)	· Precipitation of authigenic KAOLINITE (Hanging wall ONLY - higher level) · Kaolinite "books" form in open porosity · interlayer replacement and exfoliation of detrital micas · Precipitation of authigenic PYRITE Fl framboidal in matrix
Early Diagenesis (ii)	· Replacement of volcanic detritus and glass by SMECTITE + ZEOLITE (Clinoptilolite) · Secondary TiO2 (?anatase) alteration product of Ti-Fe oxides and ferromagnesian minerals
Compaction	· Deformation of micas · PYRITE + CALCITE associated with mica deformation bands · Alteration of micas to SMECTITE · Deformation of plastic SMECTITE-replaced clasts · Loss of matrix porosity
Reverse Faulting	Formation of CLAY GOUGE and CRUSH BRECCIA
Normal Faulting	Deformation of clay beds - formation of clay smears
Calcite veining	· CROSS FIBRE CALCITE VEINING - Cross-cutting fault gouge and crush bbreccias Fl Overpressuring - crack-seal growth · DIALATIONAL CALCITE VEINING Fl Hanging wall only
Late fracture dilation	· Dilation of slickensided fractures (locally cross-cut calcite veins) · Late stage SMECTITE + CALCITE in open fractures Fl 'Fresh water' l CALCITE morphology

Chlorite and smectite occur in the fault gouge, while calcite veining occurs in both the gouge and in fractures within the damaged zone. The rocks surrounding the fault gouge are rich in smectite, K-feldspar and quartz fragments. Some albite fragments are found in a smectite matrix. Detailed textural features of one sample of fault gouge in the core from Borehole 98SI-03, are illustrated in Figure 4. This figure shows that smectite in the fault gouge has evidently been deformed during movements of the fault, indicating more than one phase of movement. A further important feature of this illustration is the occurrence of small calcite crystallites that compose the majority of the calcite 'vein' cutting this sample. Isolated calcite spherulites can be seen in the deformed smectite. These crystallites evidently nucleated within the smectite matrix and post-date smectite deformation.

Figure 3 A simplified geological log illustrating visual observations made on the core from Borehole 98SI-03.

Fine-grained calcite was also found to coat the surfaces of fine fractures within the fracture-damaged zone around the Tsukiyoshi Fault in borehole 98SI-03. This calcite appears to be paragenetically late and where there has been sufficient pore space for euhedral crystal growth, it typically forms fine equant crystals. Some vein calcite also shows a cross-fibre texture, as illustrated in Figure 4. The relationship of this calcite to the euhedral, equant calcite is unclear, but the cross-fibres are indicative of its formation by a 'crack-seal' mechanism (Barker, 1990). The calcite from the Tsukiyoshi Fault zone appears either to be manganese- and iron-free or else to be only very weakly ferromanganoan.

Figure 4. Scanning Electron Micrograph showing evidence for temporal variations inthe characteristics of the Tsukiyoshi Fault.

The observations show that the Tsukiyoshi Fault is not simply a two-dimensional planar feature, but instead is a three-dimensional zone with characteristics that vary from place to place (c.f. Figure 2 and 3). The hydraulic data for the present groundwater system suggest that this zone presently restricts groundwater flow across it. Notably, boreholes on opposite sides of the fault showed differing hydraulic responses during the sinking of the Number 2 shaft (Figure 5).

However, there has clearly been some flow of meteoric water through the sedimentary rock sequence in the recent geological past. No component of residual marine water has been found in the Tono area, even though sedimentological and palaeontological data indicate that such water was once present here. Instead, previous investigations of stable oxygen and hydrogen isotopes have demonstrated that all the groundwaters sampled in the Tono area had a meteoric origin (Mizutani et al., 1992). Radioacarbon data suggest that the groundwaters in the base the Mizunami Group were recharged earliest, at approximately 15000 years before the present (Mizutani et al. 1992). Thus, any older waters that were present have been flushed from the sedimentary rocks of the Tono area.

The available data are consistent with the Tsukiyoshi Fault playing a role in such flushing. In studies of other deep groundwater systems, the calcite crystal morphology has been shown to correlate closely with groundwater composition (Milodowski et al., 1998). Crystals with c-axis flattened and equant crystal forms have been found to coexist with fresh groundwaters, whereas forms with elongated c-axes occur with saline groundwater (Milodowski et al., 1998). If this relationship holds generally, then the presence of relatively late, equant calcite crystals within the fracture zone associated with the Tsukiyoshi Fault, may also indicate the passage of fresh groundwater through this fault zone in the past. This hypothesis is supported by the chemistry of

Figure 5 Variations in piezometric head versus time, during the sinking of Number 2 Shaft, for two points in each of two boreholes, TH-5 and TH-2. The former borehole is located to the north of the Tsukiyoshi Fault, whereas the latter is located to the south of this fault. For a given depth, different head variations versus time were observed in each borehole.

the calcite. The very low to zero concentrations of Fe and Mn in the calcite imply that the water from which it precipitated had low concentrations of Fe(II) and Mn(II). Possibly, these low concentrations could have resulted from the water being very fresh and/or being too oxidising for Mn2+ and Fe2+ to exist in solution. In either case, an implication is that the fault may have conducted meteoric waters. However, while it can be stated that such circulation occurred relatively recently in the history of the fault and clearly post-dates any fault movement, it has yet to be established whether or not this circulation is on-going. If such circulation does occur at present, it is not necessarily inconsistent with the hydraulic evidence for the fault acting as a barrier; the fault may be hydraulically anisotropic, allowing flow along it, but not across it. Certainly, the petrographic and mineralogical observations made in the present study are consistent with different parts of the fault zone behaving in different ways. For example, dilational calcite veining occurs only in the hanging wall, implying that fluid circulation occurred here, but not elsewhere.

The porewater extracted from the fault gouge in core from Borehole TFA-1 is fresh and is broadly similar in composition to flowing groundwaters extracted from other parts of the sedimentary sequence.
This finding is also consistent with the possibility that the fault zone has conducted fresh water. However, the timing of such water flow and the relationship between the pore water and the present groundwater circulation is unclear.

The hydraulic characteristics of the Tsukiyoshi Fault at the location of the core examined have clearly changed over time. For example, within relativley small areas of the fault, some calcite formed by a crack-seal mechanism, whereas other calcite filled open porosity. The small veins of calcite and the evidence for parts of the rock matrix being replaced by calcite are evidence that mass transport occurred in the fault gouge which is now a barrier to groundwater movement. However, the extent to which such mass transport occurred in the past is presently unknown. The most recent movement of the fault had a normal sense, although the normal displacement was smaller than the earlier reverse displacement. The mineralogical evidence for the circulation of fresh-waters post-dates this last movement and may reflect a change in the hydraulic properties of the fault zone caused by the changing sense of displacement.

In spite of this evidence for groundwater movement in and around the Tsukiyoshi Fault Zone, there is no evidence for significant movement of uranium since the formation of the Tono ore deposit around 10 million years ago (Yusa et al. 1993). Uranium-series isotopes imply that uranium has been almost immobile in the gouge of the Tsukiyoshi Fault for at least the last million years (Shinjo et al. 1997). A possible explanation for this is that water/rock interactions have buffered the chemistry of the waters in such a way as to prevent uranium being dissolved significantly in circulating waters. It has been suggested by Iwatsuki et al. (1995), that reactions involving organic matter in the Toki Lignite Formation have effectively caused reducing conditions to be maintained (Shikazono and Utada, 1997)

Conclusions

The present study has demonstrated that the Tsukiyoshi Fault is not simply a single planar fracture. Instead,, it is associated with a zone of fracturing that is up to at least 7 m in width. There has clearly been a complex history of fluid movement through this fault zone. Some evidence suggests that the hanging wall and foot wall of the fault zone had differing hydraulic properties for at least part of the history of the fault zone. The mineralogical data suggest that some of these hydraulic properties may have changed over time. There has been mass transport along the fault zone, but this has caused insignificant mobilisation of uranium.

On-going research aims to characterising further the spatial variations in the characteristics of the fault and the temporal variations in its hydraulic properties. The goal is to evaluate the degree to which spatial and temporal variations in properties are significant over scales of space and time that are relevant to PA.

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Mineralogical and petrological evidence for the hydrogeological characteristics of the Tsukiyoshi Fault, Japan

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Abstract

Generic approaches for determining the spatial and temporal variability of a fault's hydrogeological properties are being developed by studying the reversed Tsukiyoshi Fault at Tono, central Japan. This fault is associated with zones of deformation/damage that are sometimes wider than the fault's displacement. The hydraulic characteristics probably vary laterally over metres to tens of metres and the hanging wall and foot wall have different hydraulic properties. It is also possible that some of these properties may have changed over time, due to physical processes and/or to water/rock interactions, even at relatively low temperatures and pressures (to a few tens of degrees centigrade and hundreds of bars). It is suggested that mineralogical and structural data can be used to estimate the most transmissive conditions within a fault in the past. These estimates can then be used to select conservative ('worst-case') fault parameters for assessing the future safety of underground waste repositories. Such information can also be used to design a repository to avoid faults with permeable crush zones. The study demonstrates the value of integrating detailed mineralogical and petrological studies into a borehole drilling programme for characterizing the hydraulic properties of faults.

Keywords: fractures, geochemsistry, hydrogeological controls, waste management

Faults may affect the migration of water and solutes, including pollutants, deep underground. Groundwater advection and solute migration will be influenced by hydraulic properties that depend on fault architecture (Forster & Evans 1991; Caine *et al.* 1996). Solute partitioning between groundwater and rock will depend on water/rock interactions within the fault (Kharaka *et al.* 1999). Therefore, to predict water and solute migration, the present physical and chemical characteristics of faults must be determined and future changes in these characteristics predicted.

However, poor understanding of some fault types may hinder planning data acquisition to investigate a fault's full range of hydraulic variability. Notably, there are relatively few detailed studies of reversed faults. Typically, investigations have also focussed on fault characteristics that developed at relatively high temperatures and pressures (often several hundred degrees centigrade and several kilobars), usually over a long period (often tens of millions of years). Activities like waste management by deep disposal or storage, or groundwater resource management, consider rocks to depths of one or two kilometres. In contrast to most studies, therefore, the temperatures and pressures over relevant past and future time scales (often *c.* 1 Ma for radioactive waste disposal) are relatively low (to a few tens of degrees centigrade and hundreds of bars). Arguably the most detailed fault studies under these conditions are those connected with radioactive waste disposal (e.g. Savage 1995). However, these investigations have mostly focussed on faults with very long, complex histories, often of tens, hundreds or thousands of millions of years (e.g. Äspö, Sweden (Stanfors *et al.* 1999) or Whiteshell, Canada (Davidson *et al.* 1994)). In these cases interpretations are typically complicated by superimposition of effects from many fault movements. An exception is Yucca Mountain, Nevada, where faulting occurred within the last 15 Ma (USDOE 1988). However, the tectonic setting is extensional and the results are of uncertain applicability to reversed faults.

These limitations are being addressed by a study of the reversed Tsukiyoshi Fault at Tono in central Japan, by the Japan Nuclear Cycle Development Institute (JNC; Figure 1). Results from this investigation are presented here, together with some generic implications for conceptual models of spatial and temporal variability in this type of fault, and for future data acquisition.

General approach

Information acquired during studies spanning more than four decades was assembled. The Tsukiyoshi Fault's orientation, displacement, and movement history were interpreted using geological data from surface mapping, boreholes and mine workings. Hydraulic tests and groundwater and rock chemical data were also related spatially to the fault. However, these earlier studies had many different purposes, mostly not targeted on the fault. As a result, there were many

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Fig. 1. Simplified geological map of the Tono area, showing the location of the Tono mine (detailed in Fig. 2).

uncertainties in the interpretations. Therefore, new data were collected by:

(i) re-examining borehole cores collected during previous investigations; and
(ii) drilling new boreholes specifically to study the fault. The new information was used to evaluate how future fault studies could reach a similar or improved degree of understanding with less investigation.

Geology and hydrogeology of the Tono Area

In the study area, Miocene to Pleistocene sedimentary rocks lie within a small Neogene basin developed on the eroded late Cretaceous Toki Granite (Fig. 1). The sedimentary rocks consist of almost horizontally bedded sandstones, siltsones, mudstones and local conglomerates (Yusa *et al.* 1993). Organic matter may be abundant, especially in lower strata, which contain lignite.

The Miocene rocks were deposited between 20 Ma and 15 Ma and form the Mizunami Group (Itoigawa 1974). From bottom to top, this group consists of three formations separated by unconformities: the Toki Formation, the Akeyo Formation and the Oidawara Formation (Yusa & Yamakawa 1992; Yusa *et al.* 1993; Yusa & Sakuma 1994; Shikazono & Utada 1997). The Toki Formation is mainly a freshwater lacustrine deposit, although fluvial sediments also occur. In contrast, the Akeyo Formation represents brackish to shallow marine sedimentation, while the overlying Oidawara Formation is a deeper water marine deposit.

Pliocene and Pleistocene rocks, composing the Seto Group, unconformably overlie the Mizunami Group. The Seto Group consists of poorly consolidated or unconsolidated clay, silts and conglomerates containing rhyolite and chert clasts. They were deposited within a fluviatile environment from around 5 Ma to about 0.7 Ma.

Uranium mineralization formed about 10 Ma, just above the unconformity with the granite (Ochiai *et al.* 1989; Kobayashi 1989). The deposit is 2–5 m thick and covers an area several hundred metres wide and 2-3 km long (Fig. 1). Tono Mine was excavated in this deposit in 1972, initially for exploration (Fig. 2). However, the mineralization is sub-economic and was never worked commercially. Instead, the mine became a research facility, initially of the Power Reactor and Nuclear Fuel Development Corporation (PNC) and, since 1998, of JNC.

The Tsukiyoshi Fault displaces the Toki Granite and overlying Mizunami Group, including the Tono uranium deposit. However, the fault does not displace the Seto Group (Fig. 2). Thus, the latest fault movement must have been earlier than 5 Ma. Since the Oidawara Formation is cut out by the fault and has an age of around 15 Ma, the movement history in the sedimentary rocks was less than *c.* 10 Ma. Previously, the Tsukiyoshi Fault was interpreted as being planar with an approximately east-north-east/west-south-west orientation, a southerly dip of 60° to 70°, and a reverse displacement of about 30 m (Fig. 2).

Hydrogeological observations made in boreholes up to *c.* 1000 m deep suggest that near Tono Mine, groundwater flow is topographically controlled (Koide *et al.* 1996; JNC 2000). As a consequence of topographical gradients, water from up to a few hundred metres deep in the vicinity of the mine is thought to be flowing from higher ground in the north, NW and SW, in the general direction of the Toki River towards the SE (Fig. 1). Water at the level of the main mine drift is thought to have been recharged about 1.75 km to the NW of the mine, where the surface elevation is around 300 m above sea level. There are significant contrasts between

Fig. 2. A simplified diagram showing the geology of Tono Mine and locations where the Tsukiyoshi Fault was examined. Inset is a simplified plan showing the main mine tunnels and borehole locations. The orientation of the fault is based on earlier studies. Boreholes 98SI-03 and TFA-1 are almost horizontal while 99SI-08 was inclined northwards at 55° to the horizontal. Boreholes KNA-3 and KNA-6 were inclined northwards at 45°.

Table 1. *Summary of hydraulic properties of lithologies affected by the Tsukiyoshi Fault (adapted from JNC 2000.*

Hydrogeological Unit	Porosity	Hydraulic Conductivity (ms^{-1})
Surface soil and Seto Group	0.4	1.0×10^{-7}
Oidawara Formation	0.3	5.0×10^{-8} to 5.0×10^{-10}
Akeyo Formation	0.3	1.0×10^{-8} to 5.0×10^{-10}
Toki Formation	0.3	1.0×10^{-8} to 5.0×10^{-9}
Basal conglomerate and weathered granite	0.3	1.0×10^{-7}
Granite	0.1	1.0×10^{-9}

the hydraulic properties of different rock formations (Table 1).

The hydrogeological significance of the Tsukiyoshi Fault was deduced from hydrogeological measurements made during the sinking of No. 2 Shaft (Fig. 2) in 1990 and 1991. Piezometric head records for 14 surrounding boreholes, within an area of 1 km^2 centred on the shaft imply groundwater flow across the Tsukiyoshi Fault is retarded, but that the hanging-wall is sufficiently permeable to allow significant groundwater movement (Yamane *et al.* 1996; Figure 3).

Previously published variations in the uranium concentrations, $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ (Fig. 4; Nohara *et al.* 1992) also suggest that within the Toki Lignite Formation there has been small-scale uranium transport in fractures.

Groundwaters have been sampled from all the main rock formations of the area (Fig. 2), to *c.* 850 m below the surface (*c.* 500 m below sea level). These waters are all fresh (total dissolved solid content, TDS $\ll$ 1000 mgl^{-1}), implying relatively short groundwater residence time and/or relatively little water/rock interaction (Iwatsuki *et al.* 1995; Iwatsuki & Yoshida 1999). Variations in groundwater chemistry appear to be controlled by cation exchange with Na- and Ca- smectite and dissolution of calcite; these reactions approach equilibrium at depth. The waters therefore evolve from a Ca-Na-HCO_3 dominated chemistry at shallower depths, towards a

Fig. 3. Simplified diagrams showing groundwater head variations near the Tsukiyoshi Fault. During shaft sinking, little additional drawdown occurred in the deeper monitoring interval in TH-2, where heads remained lower than those in the other intervals, possibly due to the nearby mine tunnel. In contrast, at a similar depth, but below the fault zone's top, in the deeper monitoring interval in TH-5, heads changed in a similar way to those in the shallower monitoring intervals. These observations are consistent with the fault being a barrier to flow across it.

more Na-HCO_3 composition at greater depths (Iwatsuki *et al.* 1995; Iwatsuki & Yoshida 1999). Stable oxygen and hydrogen isotopic data indicate a meteoric origin for the waters. Isotopic compositions become slightly lighter with increasing depth, consistent with the deeper waters being recharged in a cooler climate than the present one. Radiocarbon data indicate that water at the base of the Toki Formation recharged around 15 000 years ago (Mizutani *et al.* 1992).

Fig. 4. Simplified log of borehole KNA-3 (see Fig. 2 for location), showing variations in uranium concentrations, $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ and the relationship of these variations to fractures. The deviations corresponding to fractures suggest some past mobility of uranium.

There remained several limitations to the interpretations of the Tsukiyoshi Fault based upon these previously acquired data, notably:

- The fault's geometry was uncertain and the distribution of associated deformation unknown.
- The fault's precise role in influencing groundwater flow was unclear. Hydraulic evidence suggested that a single fault plane is a barrier to groundwater flow across it, but the variable hydraulic conductivities of different rock formations (Table 1) suggest that alternatively the fault may break the continuity of the strata.
- There was an unknown spatial relationship between the fault and the small-scale uranium migration suggested by variable U-concentrations and U-series isotope ratios in some rocks.
- The importance of water/rock interactions for controlling the permeability distribution in and around the fault could not be evaluated, because no mineralogical data existed for the fault.
- There was no evidence for the past history of the fault zone.

Methods

The Tsukiyoshi Fault was examined in the walls of Tono mine and in cores from ten boreholes (Fig. 2): 99SI-08; TFA-1; 98SI-03; 98FE-01; KNA-6; TM-2; MIU-2;

Fig. 5. (a) Photograph illustrating an exposure of the Tsukiyoshi Fault in the walls of an adit at the base of No. 2 Shaft, illustrating the use of Kubiena tins for sampling (b) illustration of clay smears indicating normal fault movement.

TH-1; TH-2; and TH-3. These boreholes are separated at scales ranging from only 50 cm (98SI-03 and TFA-1) up to 1 km (TM-2 and MIU-2). The first three were drilled specifically to study the fault and rock core from the fault zone was of high quality in these boreholes.

After initial logging and sampling of all cores and mine exposures, cores from 98SI-03 and TFA-1 were sampled for the most detailed petrographic analysis. These boreholes commenced in the fault's foot wall and were drilled at 5° below the horizontal, for 18 m and 30 m respectively (Fig. 2). Both intersected the most prominent plane of displacement at a distance of 14.6 m from the tunnel wall. These boreholes were chosen for detailed investigations because they were almost bedding-parallel. Therefore, fault-related porosity variations could be distinguished from lithology-related variations, more easily than in boreholes at a high angle to the bedding.

The samples were all poorly consolidated and in places were clay-rich, particularly near the main fault plane. The most poorly consolidated material was sampled using 'Kubiena' tins, which are aluminium boxes with sharpened edges that were pushed into the soft clay-rich fault rocks (Fig. 5). Each box was then freed from the core or mine wall by scraping away surrounding material. Lids were then applied to both sides of the box.

Poorly consolidated materials were air-dried and then vacuum-impregnated with epoxy-resin. The resin contained a blue dye to highlight porosity. Sections were then cut and polished under paraffin to preserve any water-soluble minerals. Sections to be examined using Back-Scattered Electron Microscopy (BSEM) were coated under vacuum with a carbon film, *c.* 25 nm thick.

A LEO 435VP, variable pressure, digital scanning electron microscope was used for BSEM-Energy Dispersive X-ray Analyses (EDXA) and conventional Secondary Electron Microscopy (SEM) analyses. Semi-quantitative EDXA analysis aided mineral identification during SEM observations. The instrument was fitted with an Oxford Instruments ISIS 300 digital EDXA system, a KE-Developments four-element solid-state back-scattered electron detector and an Evert-Thornley scintillation-type electron detector. High-vacuum ($< 10^{-4}$ torr) was used during the BSEM analyses and most SEM analyses. Occasional problems due to high sample moisture and out-gassing were overcome using a low vacuum/variable pressure mode (*c.* 3×10^{-2} torr).

The bulk and clay mineralogy of fault gouge, fault rock and representative wallrock samples were determined by X-ray diffraction (XRD), using a Phillips PW1700 series diffractometer operating at 45 kV and 40 mA and Co-Kα radiation. The ethylene glycol monoethyl ether (EGME) method was used to determine surface areas of three fault rocks from the Tsukiyoshi Fault in borehole 98SI-03. This method allowed each sample's 'swelling clay' contents (essentially smectite) to be estimated.

New Observations

In contrast to previous studies, the new observations indicate that the Tsukiyoshi Fault is not a single structural discontinuity, but a zone of faulting (cf. Figs. 5–7). The geometry and detailed structure of this zone vary spatially and it is now apparent that fault intervals range from only a few centimetres to more than 60 m (Fig. 6). The uppermost fault-rock development becomes shallower from west to east in boreholes TH-1, TH-2 and TH-3, being at 108 m, 120 m and 128 m above sea level respectively (Fig. 6). This variation is the opposite of that interpreted for the single major plane of fault movement from the earlier data. En-echelon discontinuities within the fault zone, with abrupt changes in elevation between different fault strands may explain the discrepancy. However, variations in the fault zone's dip or sharp changes in the fault zone's orientation are alternative explanations.

The new study confirmed that geometrically the fault is reversed, with a displacement of about 30 m.

Fig. 6. Simplified diagrams showing variations in the width of the Tsukiyoshi Fault in different boreholes within the study area and the variable fault rock distributions in the fault zone.

However, fabrics indicating some late normal fault movement were also found, for example in the gallery at the base of Shaft 2 (Figs. 2 & 5b).

Detailed spatial and temporal variations in the properties of the Tsukiyoshi Fault were apparent in borehole 98SI-03 (Fig. 7 & Table 2). Fracturing with mineralogical evidence for past fluid flow (fracture-filling minerals, fracture wallrock alteration or mineral dissolution textures on fracture surfaces) post-dated the latest faulting (Table 2). In this borehole, the single fault plane named previously as the 'Tsukiyoshi Fault' occurs at 14.5 m and is associated with a damaged zone characterized by the highest fracturing frequency (Fig. 7). However, the new logging reveals a more complex zone of faulting at least 6 m wide. In this zone two prominent fault strands are reflected in a bimodal fracture frequency, with most of the minor fracturing occurring between these strands. The fractures in the hanging wall of the fault strand at 14.5 m often show dilatational fabrics and are mineralized. In contrast, dilatational fabrics are absent from the foot wall fractures, which are largely unmineralized shear planes or microfaults, with thin clay smears and gouges produced by wallrock deformation.

The bulk- and clay- mineralogy of samples from in and around the Tsukiyoshi Fault are summarized in Table 3. All samples contain smectite, which is the most abundant mineral in finer grained lithologies. Sharp XRD peaks show the smectite to be highly crystalline

Fig. 7. A simplified geological log illustrating visual observations on core from borehole 98SI-03. The distributions of calcite veins and open fracture porosity in the hanging wall are consistent with the hanging wall being relatively permeable at the present and in the past.

Table 2. *Summary of fracturing and diagenetic history in borehole 98SI-03. This sequence is similar to that seen in other boreholes.*

Event	Where seen[1]	Mineralogical/Petrological Feature	Mineral Occurrence
Early diagenesis - pre-significant compaction	FW HW FW+HW FW+HW	Kaolinite (Stratigraphically high) Pyrite (Stratigraphically low) Smectite + Zeolite (Clinoptilolite) TiO_2 (?anatase)	Matrix porosity + replaces mica Matrix porosity Replaces volcanic detritus Replaces Ti-Fe oxides, Fe/Mg minerals
Burial/ Compaction	FW+HW FW+HW	Pyrite + calcite Smectite	Matrix porosity Replaces mica
Reverse Faulting	FW+HW FW+HW	Clay gouge and crush breccia Granulation seams	Main zone of fault movement Main zone of fault movement
Normal Movement	FW+HW HW	None None	
Secondary chlorite formation	HW	Mg-rich chlorite	Replaces smectite rocks near fractures
Late zeolite mineralization	HW	Zeolite	Fracture porosity
Late sulphide mineralization	HW HW	Pyrite and zeolite Pyrite	Fracture porosity Replaces early diagenetic pyrite
Main calcite mineralization	HW	Calcite	Fracture porosity + replaces smectite
Late fracture dilation	HW HW	Calcite[2] + smectite Feldspar dissolution	Fracture porosity Adjacent to fractures

1. Relative to location of main plane of movement: FW = Foot wall; HW = Hanging wall
2. Calcite has a morphology similar to that of calcite that coexists with fresh water at other localities (e.g. Sellafield, U.K.; Milodowski *et al.* 1998).

near the fault. A major to minor Na-Ca zeolite-like phase was also observed in all samples under BSEM-EDXA, but was recognized by XRD only above the hanging wall. The zeolite contains variable Na and Ca, but XRD suggests that some at least is clinoptilolite.

Sand and gravel-sized, shard-like fragments of highly smectitized and zeolitized, fine-grained volcanic rock or glass are common (Fig. 8a). Many altered volcanic clasts still contain vestigial igneous fabrics. More rarely, shards are preserved as partly altered Na-K-Ca silicate glass (Fig. 8a). Sorting is typically very poor, with sand grains and lithic clasts being supported by a silt-matrix or a smectite-rich pseudomatrix (of diagenetic rather than sedimentological origin), having little or no visible natural porosity (Fig. 8a). Some sandstones display a better-sorted, grain-supported fabric, but still lack significant matrix porosity (Fig. 8b).

Illite, chlorite and kaolinite are minor to trace clay constituents (Table 3). Illite occurs in all samples, but the other clay minerals are variably distributed across the main fault strand (14.5-14.67 m). Kaolinite is observed only below the main fault strand. In contrast, though one generation of chlorite replaces detrital biotite flakes throughout borehole 98SI-03, a second generation occurs only in the matrix in the hanging wall. This latter chlorite replaces smectite adjacent to fractures in the fault's damaged zone. Chloritization is also evident in the fault gouge and probably post-dated gouge development. However, deformed smectite also occurs in the fault gouge, indicating more than one phase of fault movement (Fig. 9).

Within relatively small areas of the fault zone, three sorts of calcite can be distinguished on textural grounds:

(i) calcite showing a cross-fibre texture that evidently formed by a 'crack-seal' mechanism (Barker 1990; Figure 9a);
(ii) calcite replacing pre-existing clay minerals (Fig. 9b); and
(iii) calcite forming euhedral, equant crystals that line open porosity (Fig. 10).

The first two types are closely associated within the central fault zone, but the third type occurs in the hanging wall only. However, the relationship of the calcite in the central fault zone to the euhedral, equant calcite is unclear. The calcite from the Tsukiyoshi Fault zone appears either to be Mn- and Fe-free or else to be only very weakly ferromanganoan.

Table 3. *Summary of mineralogical information obtained by XRD for the rocks in the vicinity of the Tsukiyoshi Fault in borehole 98SI-03.*

Sample Location	Distance along borehole (m)	Description and sampling details	Bulk Sample XRD Results			Fine Clay Fraction XRD Results and Surface Area Determinations (Expressed as Equivalent wt% Smectite)			
			Major Phases	Minor Phases	Trace Phases	Major Phases	Minor Phases	Trace Phases	Equivalent Smectite %+
Foot wall	3.19-3.29	Silty sandstone (sample taken from base of core stick, away from fracture surface)	Smectite	Quartz, anorthite, mica	Kaolinite	Smectite	Kaolinite†		Nd
Foot wall	14.43-14.55	Friable, gravely sandstone	Quartz	Albite, orthoclase	Smectite, mica	Smectite	Illite	Kaolinite	Nd
Fault gouge	14.60-14.65	Green clay gouge from centre of fault zone	Smectite	Calcite, quartz, chlorite, orthoclase, albite	Mica	Smectite	Chlorite, illite		39
Fault gouge	14.55-14.90	Sandy breccia/gouge from footwall of fault	Smectite	Quartz, albite, orthoclase	Mica, ?amphibole	Smectite*	Chlorite	Illite	37
Hanging wall	14.67-14.74	Hanging wall rock matrix. Dark brown lignitic mudstone (sample taken from base of core stick, away from the fracture surface)	Smectite	Anorthite, clinoptilolite (matched to JCPDS reference pattern 25-1349), quartz	?Mica	Smectite*		Chlorite, clinoptilolite	49
Hanging wall	15.03-15.19	Muddy siltstone. Sample taken from unveined section of core stick	Smectite	Anorthite, clinoptilolite, quartz		Smectite*		Illite, clinoptilolite	Nd
Hanging wall	16.61-16.70	Poorly sorted sandstone. Sample taken from lower half of sample supplied	Quartz	Albite, orthoclase, smectite	Clinoptilolite, mica, amphibole	Smectite	Chlorite	Clinoptilolite	Nd

*High degree of crystallinity, sharp peaks.
†Very poor crystallinity, broad peaks.
+From EGME. Nd = Not determined

Fig. 8. (a) Back-scattered Scanning Electron Micrograph (BSEM) of a litharenite. Shard-like, altered volcanic glass (g) occurs in a pseudomatrix formed by compaction and deformation of volcanic fragments now altered to smectite and zeolite. Dark cracks are an artefact of shrinkage during sample preparation. (b) BSEM photomicrograph of grain-supported litharenite showing angular detrital quartz (q), plagioclase (p), orthoclase (o), mica (m) and quartz-feldspar lithic grains in a smectite and zeolite matrix (black). Competent quartz and feldspar grains are fractured and micas are deformed by burial compaction. Both (a) and (b) show samples from the foot wall.

Fig. 9. (a) BSEM photomicrograph of a calcite vein from the main fault strand. Cross-fibre calcite (CiC) grades into replacive calcite. Wallrock smectite is deformed, indicating that it formed prior to the last fault movement. (b) BSEM photomicrograph showing micronodular calcite nucleated within and replacing/cementing a smectite-rich matrix of fault gouge.

Also in Borehole 98SI-03, textures within wallrocks of open fractures in the fault's hanging wall indicate that plagioclase dissolution formed framework grain porosity (Fig.11).

Discussion

Hydrogeological evolution

Conditions of faulting Rocks unaffected by faulting contain well-crystalline smectite, with no illite-smectite or chlorite-smectite interstratification. This implies that ambient temperatures at the time of faulting did not exceeded those of the upper limit of diagenetic zone alteration (around 150°C based on white mica crystallinity; Kisch 1991). While faulting itself may have caused locally higher temperatures to occur, there is no mineralogical evidence for this; the chlorite replacing smectite in the fault zone could have formed at similar temperatures to the smectite (cf. Velde 1985).

The depths of faulting are more difficult to constrain, because erosion has removed an unknown rock thickness during several periods. The sedimentary rocks are currently up to *c.*300 m thick and in the last 0.7 Ma, up to *c.* 350 m of strata may have been eroded during uplift amounting to about 500 m (Yusa *et al.* 1993). Thus, since the fault's last movement, the sedimentary sequence's base has been at a maximum depth of at least *c.* 650 m. The low inferred temperature of faulting implies maximum burial depths of only a few kilometres, though in the absence of information about past geothermal gradients any estimate is very uncertain.

Fig. 10. Paragenetically late, equant, euhedral late-stage calcite crystals precipitated on the surface of a microporous fracture with polished and slickensided surfaces, in lignitic mudstone from the hanging wall of the Tsukiyoshi Fault.

Fig. 11. SEM photomicrograph of a slickensided fracture cutting lignitic silty mudstone, showing plagioclase with dissolution textures exposed on the fracture surface. The dissolution has formed framework grain porosity in the wallrock.

History of groundwater flow and water/rock interactions

Mineralogical evidence for the earliest water/rock interactions is not restricted to the fault and probably records pre-faulting diagenesis, which included:

- chloritization of biotite crystals throughout the core (this may have been pre-depositional).
- post-depositional formation of smectite, by hydration of volcanic detritus (this smectite is deformed near the fault; Figure 9a);
- kaolinite formation;
- pyrite formation.

However, in borehole 98SI-03 the early diagenetic kaolinite occurs only on the downthrow side while early diagenetic pyrite occurs only on the upthrow side. Possibly, this distribution reflects pre-faulting variations in the chemistry of circulating formation waters. The kaolinite could have been formed by reactions involving relatively oxidizing, low-pH meteoric waters while the pyrite could have formed in the presence of more reducing waters, higher-pH waters. Similar mechanisms for kaolinite formation have been proposed in studies of other localities (Strong & Milodowski 1987; Metcalfe *et al.* 1994). The chemistry of the waters may have been partly depth-related and/or reflect lithological variability, more reducing conditions predominating in more organic-rich and/or deeper lithologies (Fig. 12a). In either case, the fault clearly juxtaposed the kaolinite-bearing rocks against deeper pyrite-bearing rocks (Fig. 12b).

In contrast the mineral occurrences that are localized within the fault zone suggest past water movement through the zone:

- secondary chlorite adjacent to fractures in the hanging wall and in the fault gouge;
- fracture-filling calcite in the hanging wall and calcite replacing fracture wallrocks and fault gouge;
- clinoptilolite in fractures within the hanging wall;
- pyrite in fractures within the hanging wall;
- smectite on surfaces of open fractures in the hanging wall;
- feldspar dissolution on the surfaces of open fractures in the hanging wall.

The gradation of cross-fibre, fracture-filling calcite into nodular replacive calcite (Fig. 9a), suggests that both these types formed at about the same time. The undeformed nature of the fibrous calcite suggests that it probably formed after the last fault movement.

Formation of chlorite from Ca-smectite may have produced the replacive calcite, by liberating Ca to the pore-fluid, which possibly contained bicarbonate generated by low-temperature organic matter diagenesis. This mechanism is similar to weathering reactions in rocks containing both silicate minerals and organic matter (Berner 1995). Alternatively, the bicarbonate could have been derived near to the surface, if the fault conducted water downwards.

In a detailed study of groundwaters at Sellafield, UK, the morphologies of open void-lining calcite crystals correlate with groundwater composition (Milodowski *et al.* 1998). There, crystals with c-axis flattened and equant crystal forms coexist with fresh groundwaters, whereas forms with elongated c-axes coexist with saline groundwater. If this relationship holds generally, the relatively late, equant calcite crystals within the fracture zone associated with the Tsukiyoshi Fault, may indicate the passage of fresh groundwater through this fault zone in the past. The very low to zero Fe and Mn concentrations in this calcite are also consistent with it precipitating from fresh water and/or oxidizing water with low Fe(II) and Mn(II) concentrations. Some open porosity persists, raising the possibility that this calcite may still be forming.

These mineralogical observations, coupled with the heterogeneous spatial distribution of relatively high- and

Fig. 12. Schematic diagrams illustrating a revised conceptual model. (a) Oxidizing meteoric water circulates relatively rapidly at shallower levels, because the rocks still retain significant porosity having not yet been fully compacted by burial. Kaolinite forms under these conditions. Deeper, where circulation is less vigorous, kaolinite is not formed, but pyrite develops, owing to more reducing conditions. (b) Rocks bearing early diagenetic kaolinite and pyrite are displaced against one another. A relatively permeable damaged zone develops in the fault's hanging wall. The main plane of movement and the foot wall damaged zone are relatively impermeable. (c) Some generic implications for data acquisition are illustrated. Borehole 1 is designed with no knowledge of mineral distributions or micro-structures. Consequently, the borehole does not penetrate the fault's damaged zone and both hydraulic test intervals are sited within this zone, near the weathered top of the granite and the unconformity. Borehole 2's design uses knowledge of mineral distributions and micro-structures. The hydraulic tests can be located on both sides of the fault, so as to test rock within and outside the damaged zone. The borehole penetrates the fault away from major rock formation boundaries and at a high angle, thereby respectively simplifying interpretation of the test results and minimising the borehole's length.

low-porosity zones (e.g. fault rocks; Figure 6), imply that the fault zone may presently influence groundwater movement over scales ranging from a few metres to at least several tens of metres. The largest spatial range of the fault's effect is in the granite, where the fault zone is widest (Fig. 6).

Studies elsewhere (Smellie & Laaksoharju 1992; Milodowski et al., 1998) suggest that feldspar dissolution and clay mineral precipitation may cause groundwater pH to increase along flow-paths, leading ultimately to calcite precipitation. A similar process may have operated, or may be operating, within the Tsukiyoshi Fault's hanging wall, where plagioclase dissolution has occurred in open porosity (Fig. 11). This phenomenon would also be consistent with observed groundwater pH changes. In the Lower Toki Formation, the groundwater's pH is *c.* 9, but surface waters have a pH of *c.* 6 (Iwatsuki & Yoshida 1999), there being insignificant pH buffering by calcite, which is rare to absent in the near-surface weathered zone.

According to the new observations some fractures for which uranium concentrations and U-series isotope radioactivity ratios were reported previously (Nohara *et al.* 1992; Figure 4), probably lie within the Tsukiyoshi Fault's damaged zone. Thus, the elevated uranium concentrations, and variable $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ radioactivity ratios in wallrocks of fractures in borehole KNA-3 (Fig. 4) suggest some uranium transport by movement of groundwaters in the fault's hanging wall and/or diffusion. This interpretation follows because, in the absence of uranium and/or thorium transport, radioactivity ratios for $^{234}U/^{238}U$ and $^{230}Th/^{234}U$, would attain equilibrium values of unity, owing to the decay series:

The equilibrium ratio of unity arises because the measured radioactivity due to a particular isotope in a

A $^{238}U - \alpha - {}^{234}Th - \beta - {}^{234}Pa - \beta - {}^{234}U - \alpha - {}^{230}Th$

given sample depends on both the amount of the isotope that is present and its half-life. Isotopes with short half-lives will be less abundant than parent isotopes with longer half-lives. However, at equilibrium, the radioactivity of a given molar quantity of short half-life isotope will be higher than that of the same quantity of longer half-life parent.

Isotope movement in groundwaters can cause a rock's $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ radioactivity ratios to vary from 1 in various ways (reviewed in Metcalfe *et al.* 1998). Important processes include greater solubility of U than Th under oxidizing conditions, and recoil-induced preferential leaching of ^{234}Th under more reducing conditions. Oxidizing water that has previously leached uranium may also subsequently precipitate uranium if it encounters more reducing conditions, causing the rock's uranium-series isotopic ratios to vary. A combination of these processes may explain the isotopic variations seen in KNA-3. However, the sample with the lowest $^{230}Th/^{234}U$ of 0.87 possibly gained *c.*15% of its ^{234}U within the last few hundred thousand years, otherwise the ratio would have returned to unity by radioactive decay (Nohara *et al.* 1992).

The samples are probably up to several tens of metres from the main plane of fault movement, consistent with the fault influencing groundwater flow over this spatial scale. However, the overall distance over which uranium moved cannot be deduced from a single core. Remote from the fault zone, $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ are both 1.0 when averaged over 1 m^3 blocks of rock (Nohara *et al.* 1992; Ochiai et al., 1989; Yusa *et al.* 1993). Thus, distant from the fault, any uranium mobilization was over less than one metre.

The new information allows previously sampled groundwaters to be related spatially to the Tsukiyoshi Fault with greater confidence than previously. When this is done, no relationship can be deduced between the chemistry of the waters and the proximity of the fault. Thus, from the water chemistry, it cannot be deduced whether the fault controlled circulation of present groundwaters. However, a combination of stable oxygen and hydrogen isotopic data and radiocarbon data indicate that groundwaters flowed through the sedimentary rocks in general, within the last 15 000 years (Mizutani *et al.* 1992).

Evolution of hydraulic properties In 98SI-03, the past evolution of porosity (Table 2) indicates that the Tsukiyoshi Fault's hydraulic characteristics changed, during fault movements and afterwards. The distribution of secondary chlorite suggests that past water movement occurred along the fault and through the hanging wall, which was more permeable than the foot wall. However, the fault gouge's lack of open porosity suggests that the fault zone's centre is now less permeable than previously.

The cross-fibre textures of calcite suggest the fault gouge's permeability varied intermittently, possibly due to cyclical over-pressuring, hydraulic fracturing and stress release (Barker 1990). These changes post-dated the latest shear along the fault because the cross-fibres are undisturbed. The association between secondary calcite and secondary chlorite implies that changes in hydraulic properties, accompanying the cyclical pressure variations, may also have influenced secondary chlorite formation within the fault gouge.

In contrast, the occurrence of late calcite in open pore space in the hanging wall, and the paucity of open pore space in the foot wall, suggest that the fault's hanging wall may presently have a higher permeability than the foot wall. However, the hydraulic data indicate that presently the fault restricts groundwater flow between the foot wall and the hanging wall (Fig. 3).

If this latest calcite is currently forming, the consequent porosity occlusion may be decreasing the hanging wall's hydraulic conductivity. However, any continuation of plagioclase dissolution would have the opposite effect. The possible coupling between these processes makes the overall spatial scale and direction of the change unclear.

Present permeability variations inferred from the new mineralogical observations are consistent with previously observed groundwater heads (Fig. 3) reflecting a barrier function of the fault itself, rather than the fault breaking the hydraulic continuity of the surrounding rocks.

Generic implications for data acquisition

The new study has dramatically changed the conceptual model of the Tsukiyoshi Fault (cf. Figs. 2 & 12). Understanding has been greatly improved by detailed mineralogical, petrological data and structural geological data, acquired to complement the data available originally from hydraulic testing and geological studies. The boreholes drilled to investigate the hydraulic properties of the fault, in the absence of this detailed information, did not penetrate the fault zone fully. Consequently, the locations of hydraulic tests relative to the fault zone were often unclear. For example, previously, the hydraulic test at 154.5 maSL in borehole TH-5 (Fig. 3) was thought to lie in the foot wall of the fault. However, the latest data from boreholes near to TH-5 suggest that this test may lie within the fault zone, albeit on the foot wall side of the main fault strand (though this hypothesis could not be checked because suitable core did not exist from TH-5).

Some generic lessons can be drawn for future data acquisition. Continuous fracture logging of rock core during borehole drilling would enable the extent of the damaged zone associated with a fault to be determined. It would then be possible to ensure that the borehole penetrates the fault zone fully and any hydraulic tests

could be sited appropriately (Fig. 12c). This approach requires flexibility in borehole design, notably in specifying the length. Provision for penetrating a deformation zone at least as wide as the fault's throw is prudent. The borehole length needed to penetrate a fault fully would also be minimized by drilling at a high angle to the fault (Fig. 12c).

Interpretations of previous data were also complicated by most of the previous boreholes (TM-2, 98FE-01, KNA-6, TH-1, TH-2 and TH-3) intersecting the fault near to the unconformity between the sedimentary rocks and the granite (Fig. 2). In these boreholes, it is difficult to interpret the relative hydraulic significance of stratigraphically controlled lithological changes and fault-related deformation. In contrast, boreholes 99SI-08; TFA-1; 98SI-03 and MIU-2 intersected the fault away from formation boundaries. Therefore, in these boreholes, structurally controlled porosity variations could be used much more confidently to infer permeability variations. A generic lesson is that to characterize a fault's hydraulic properties, it is usually desirable that a borehole should intersect the fault away from formation boundaries (Fig. 12c).

To characterize the hydrogeological properties fully, it will be necessary to plan tests within both the hanging wall damaged zone and the foot wall damaged zone. The variability of fault-rock frequency, even between boreholes that are closer than 20 m apart (Fig. 6) means that different water-bearing 'compartments' with dimensions on the scale of metres to tens of metres, may exist within the fault zone. Hydraulic tests would need to be sited carefully with respect to these compartments, if the full range of hydraulic properties is to be characterized adequately.

Generic implications for underground radioactive waste disposal

Performance Assessments, (PA) for any potential underground radioactive waste repository generally involve risk calculations for a relatively small number of 'scenarios' that represent plausible future states of the repository/geosphere system (Savage 1995). Scenarios should consider realistic combinations of natural features and processes.

Previously, groundwater flow models used in PA have tended to represent faults as planar, time-invariant features with higher hydraulic conductivities than the surrounding rock mass (e.g. JNC 2000). The present work highlights that such a representation may be unrealistic.

It is appropriate to take into account the hydraulically effective widths in PA. Ensuring that the planar representation of a fault in a groundwater flow model has the same hydraulic properties as the actual fault zone that it represents can achieve this goal. However, while the present hydraulically significant width of a fault could be established from hydraulic testing, the current study has identified chemical and physical processes that may plausibly change the transmissivity of a fault zone over time. In the Tsukiyoshi Fault's case, the absolute timing of these changes is unknown, but many of the changes must have taken less than 10 Ma. The possibility that they could have occurred over time scales comparable with PA, typically *c.*1 Ma, cannot be ruled out.

Repository structures should also avoid permeable zones of faults that could act as significant nuclide transfer paths (e.g. JNC 2000). The present study implies that repository designs should account for possible temporal variations in the widths and locations of these potential pathways.

It is suggested that realistically conservative scenarios should incorporate the highest transmissivities that can be inferred for a fault zone in the past, taking into account structural and mineralogical data. Similarly, this information can be used to deduce maximum distances over which transmissive fracture pathways will extend normal to the fault.

Conclusions

Unlike most faults that have been studied at comparable levels of detail elsewhere, the Tsukiyoshi Fault is reversed, relatively young, had a history of movement of < 10 Ma in the sedimentary rocks and, at the stratigraphical levels studied, was probably never deeply buried. Thus, it provides an opportunity to study faulting and associated water/rock interactions in relatively immature sedimentary rocks at temperatures of less than around 150 °C (and possibly much lower temperatures).

The study demonstrates that detailed mineralogical studies can indicate a complex history of water movement around a fault that cannot be deduced by other means. Previously, surface mapping and logging of planes of major displacement in rock core from boreholes resulted in the Tsukiyoshi Fault being interpreted as a simple planar feature. However, detailed, integrated studies of fracture distributions, mineral parageneses and mineral chemistry show that this fault's structure is much more complex, comprising a zone of fracturing containing several fault strands. The new observations suggest that the fault itself acts as a barrier to flow across it, rather than behaving simply as a feature that disrupts the hydraulic continuity of the faulted rocks. However, the fault zone has conducted water parallel to it in the past and may do so at the present. The fault rocks appear to have compartmentalized this flow, by dividing relatively high- and low- permeability zones.

Since knowledge of water movement history in faults is relevant to evaluating the performance of any future radioactive waste repository, mineralogical studies of

the type described here should be an integrated part of any investigation programme. The study highlights that, to adequately characterize a fault by hydraulic testing, it is highly desirable to undertake detailed structural, mineralogical and petrological studies, to establish the limits of the damaged zone surrounding the fault. This information can be used to guide the selection of suitable hydraulic test or monitoring intervals in boreholes, so that the full interval of rock affected by the fault is characterized. It is desirable that characterization should use boreholes designed to penetrate the fault zone fully and to avoid intersecting it near to rock formation boundaries. Where practicable, boreholes should be drilled at a high angle to a fault zone, thereby minimizing the length of borehole drilling required to penetrate the zone.

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Isotopic and morphological features of fracture calcite from granitic rocks of the Tono area, Japan: a promising palaeohydrogeological tool

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Abstract

This study aimed to develop a methodology for assessing the hydrochemical evolution of a groundwater system, using fracture-filling and fracture-lining calcite. Fracture calcite in deep (to ca. 1000 m) granitic rocks of the Tono area, central Japan, was investigated by optical and electron microscopy, and chemical and isotopic analysis. Coupled with geological evidence, these new data imply 3 main origins for the waters that precipitated calcite: (1) relatively high-temperature hydrothermal solutions, precipitating calcite distinguished by $\delta^{18}O_{SMOW}$ from −3 to ca. 10‰, and with $\delta^{13}C_{PDB}$ from ca. −18 to −7‰; (2) seawater, probably partly of Miocene age, which precipitated calcite distinguished by $\delta^{13}C_{PDB}$ of ca. 0‰ and $\delta^{18}O_{SMOW}$ > ca. 20‰; (c) fresh water, with a variable $\delta^{13}C_{PDB}$ composition, but which precipitated calcite distinguished by $\delta^{13}C_{PDB}$ that was significantly < 0‰ and as low as ca. −29‰ and $\delta^{18}O_{SMOW}$ > ca. 17‰. Data for ^{14}C suggest that at least some of the fresh-water calcite formed within the last 50 ka. The present day hydrogeological regime in the Tono area is also dominated by fresh groundwater. However, the marine calcite of probable Miocene age found at depth has shown no evidence for dissolution and many different calcite crystal forms have been preserved. Studies of other groundwater systems have correlated similar crystallographic variations with variations in the salinity of coexisting groundwaters. When this correlation is applied to the Tono observations, the calcite crystal forms imply a similar range of groundwater salinity to that inferred from the isotopic data. Thus, the present study suggests that even in presently low-salinity groundwater systems, calcite morphological variations may record the changing salinity of coexisting groundwaters. It is suggested that calcite morphological data, coupled with isotopic data, could provide a powerful palaeohydrogeological tool in such circumstances. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Palaeohydrogeology is the reconstruction of past groundwater compositions and groundwater flow rates and flow directions, using a combination of geological evidence, chemical and isotopic compositions of groundwaters, mineralogical data, and hydraulic measurements (Chapman and McEwen, 1993). Evaluating the chemical and hydrogeological stability of low-temperature (<ca. 50 °C) groundwater systems is one important aspect of palaeohydrogeological studies. Applications of such evaluations lie in such diverse fields as water resource development and the safe management of radioactive waste by deep disposal. Particularly in the latter case, information about the stability of deep groundwater systems is valuable for developing conceptual models, and for testing predictive models, for future changes deep underground.

To some extent, the history of past groundwater movement can be deduced from the present chemical characteristics of sampled groundwaters (e.g. ^{3}H, ^{14}C, ^{36}Cl activities etc: see review in Metcalfe et al., 1998). However, this type of data is of limited value for evaluating the past chemical conditions of the groundwaters. Many geochemical parameters in the past, such as pH and mineral saturation states, cannot usually be constrained directly by this approach. In extreme cases,

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when it is desired to constrain past chemical conditions at greater times than the residence time of the groundwater, it may be entirely inappropriate to use chemical data from sampled groundwaters.

For these reasons, interpretations of the stability of deep groundwater systems are increasingly being based upon mineralogical information. Chemical and isotopic data from carbonate minerals have been found to be particularly useful, because these minerals occur commonly in low-temperature groundwater systems. Carbonate minerals may form at low temperatures in response to many processes, including mixing between chemically distinct groundwaters and temperature increases along flow paths. These processes may cause chemical and isotopic variations in the groundwaters, which may be recorded by the crystals of carbonate minerals that precipitate.

Such records were used to assess the hydrochemical stability of saline groundwaters and brines in a deep crystalline shield setting in Sweden over timescales of 10 to 100 ka years (Wikberg, 1997; Wallin and Peterman, 1999). This work showed that some calcite at Äspö and Laxemar was precipitated under different hydrogeological conditions to those prevailing at the present. In contrast, data from calcite in deep groundwaters from a basin margin setting at Sellafield in NW England, were related to the present hydrogeological system (Metcalfe et al., 1998; Milodowski et al., 1998). Calcite data were used to constrain the distances over which saline groundwaters have moved, over timescales of thousands to tens of thousands of years. In yet another type of application Marshall et al. (1993) deduced the past source of water, precipitation processes and rock–water interactions in a presently unsaturated rock mass at Yucca Mountain, USA, by using secondary calcite in volcanic rock.

However, these previous investigations have focussed either on the unsaturated zone or upon groundwater systems presently characterised by saline waters or brines. Therefore, it remains uncertain as to what extent data from carbonate minerals are applicable for tracing the past movements of groundwaters in presently fresh, water-saturated groundwater systems. In particular, from previous investigations, it is unclear under what circumstances carbonate minerals might preserve evidence for 'old' saline waters when more recent flushing by fresh waters has occurred.

An opportunity to address these uncertainties arose during on-going research being undertaken by the Japan Nuclear Cycle Development Institute (JNC) in the Tono area of central Japan (Fig. 1). This research is aimed at developing generic methods to determine hydrochemical conditions and long-term changes deep underground. These generic methods may eventually be used to characterise any possible future deep geological isolation site for radioactive waste, at a location that has yet to be determined, elsewhere in Japan.

The Tono area is particularly suitable for developing mineralogical methods for studying fresh groundwater systems because, compared to many deep groundwater systems investigated elsewhere in the world, its hydrochemical evolution has been relatively simple. Interpretations of deep groundwater chemistry from mineralogical data elsewhere may be complicated by the past or present occurrence of many sources of saline water and brine (e.g. evaporites, basinal diagenetic waters, brines from continental shield rocks etc). However, there is no evidence for such sources of salinity in the Tono area, as is typical for Japan. Instead, geological evidence (see below) implies that marine and/or brackish waters may have descended into the fracture network in a basement granite, and then been flushed by fresh water. Here, the authors report a study that aimed to establish whether the calcite generated within the fractures in the granite records these episodes of saline/brackish water infiltration and subsequent flushing by fresh water. An evaluation was made of the value of isotopic and morphological data from the calcite for constraining the timing and chemical conditions of precipitation.

2. Background

2.1. Geological setting

In the study area, Pliocene to Pleistocene rocks of the Seto Group (5 to 0.7 Ma) unconformably overlie Miocene sedimentary rocks of the Mizunami Group (27 to 14.85 Ma). These latter rocks in turn unconformably overlie a basement of Cretaceous granitic rocks, the Toki Granite (72.3 Ma; Shibata and Ishihara, 1979; Fig. 2). The middle and upper parts of the Mizunami Group, the Akeyo Formation and Oidawara Formation respectively (16.3 to 14.85 Ma), are composed of shallow marine siltstone–sandstone alternations. In contrast, the lower part of the Mizunami Group, the Toki lignite-bearing formation (27 to 20 Ma) consists of lignite-bearing fluvial deposits (Shikazono and Nakata, 1999). The deepest of the sedimentary rocks contain a U deposit, the Tono U deposit, which was formed approximately 10 Ma ago (Kobayashi, 1989; Ochiai et al., 1989). The U mineralisation lies immediately above the unconformity with the granite, in a zone that is 2–5 m thick, covering an area that is several hundred m wide and 2–3 km long.

The basement granitic rocks consist of medium- to coarse-grained biotite granite and medium-grained hornblende–biotite porphyry, and are partly intruded by quartz porphyry and aplite dikes (Sakamaki, 1985). The fracture system within the granitic rocks can be classified into moderately fractured zones and intensely fractured zones, using the frequency and characteristics of fracturing as a criteria (Iwatsuki and Yoshida, 1999a).

Fig. 1. Location map showing the general geological features of the study area and the locations of the borehole studied.

Both these types of zone have RQD of 0% (RQD = rock quality designation, the sum of the lengths of core that have both circular cross sections and lengths of > 10 cm, expressed as a percentage of each metre of core). However, the types of fracture fillings and associated alteration distinguish between these different zones. Within the moderately fractured zones, fracture fillings consist mainly of chlorite and montmorillonite. Several moderately fractured zones are also associated with a pegmatitic texture, but there is little alteration of the rock matrix. However, the intensely fractured zones are associated with a strongly altered rock matrix, showing alteration to clay minerals such as kaolinite. Within these intensely fractured zones, major fractures are seen in core to have wall rocks damaged by smaller fractures. The occurrence of this type of zone is probably related to the faulting that has affected this area, such as the formation of the Tsukiyoshi fault, (Fig. 1; Iwatsuki and Yoshida, 1999a). This fault was probably active from between 10 and 15 Ma ago until around 5 Ma ago (Hama et al., in press; Yamakawa, 1991).

2.2. Chemical and hydraulic conditions of present groundwater

Hydrogeological investigations in boreholes up to ca. 1000 m deep suggest that in the study area, groundwater flow is controlled by topography (Koide et al. 1996; JNC, 2000). Theoretical groundwater flow models suggest that generally, groundwater flows from high ground in the N and NE of the study area, towards the valley of the Toki River in the SW (Fig. 1). Water at a depth of around 1000 m in the centre of the area around DH-9 and DH-11 is thought to have been recharged in high ground about 2.5 km towards the NE near DH-3, where the topography is between 300 m above sea level (masl) and 400 masl. Discharge is thought to occur into the valley of the Toki River (Fig. 1), at an elevation of around 150 masl. However, superimposed on this deeper flow system are shallower flow systems in which groundwater flow is controlled by the local topography.

Groundwaters have been sampled from all the main rock formations of the area (Fig. 2) to a depth of ca. 980 m below the ground surface [ca. 710 m below sea level (mbsl)]. The chemistry of these waters has been described in several previous studies, notably Iwatsuki et al. (1995), Iwatsuki and Yoshida (1999b) and JNC (2000). These have revealed that all the groundwaters are all fresh (total dissolved solid content, TDS << 1000 mgl^{-1}) and have δD and $\delta^{18}O$ values indicating a meteoric origin. Groundwater solutes are dominated by Na^+, Ca^{2+} and HCO_3^- near the surface, and by Na^+ and HCO_3^- at greater depth. The Na^+ concentrations of the groundwaters increase with depth and there is a

Fig. 2. Schematic geological column of the Tono area (modified after Itoigawa, 1974).

corresponding decrease in Ca^{2+}, Mg^{2+} concentrations at a depth of 200 m below ground level (greater than sea level). Below this depth, the increase in Na^{+} concentrations is nearly equivalent to the decrease in combined Ca^{2+} and Mg^{2+} concentrations, suggesting that a Na–(Ca^{2+}, Mg^{2+}) ion exchange reaction occurs between clay minerals such as montmorillonite and groundwaters. However, in the granitic rocks the chemical evolution of groundwater is mainly controlled by the water/rock interactions involving plagioclase and calcite (Iwatsuki and Yoshida, 1999b). The saturation indices show that calcite would dissolve in the groundwater at depths shallower than ca. 250 m below ground level (ca. 100 mbsl), while the deeper groundwater is nearly in equilibrium with calcite (Iwatsuki et al., 2000).

The recharge timing is inferred from both ^{3}H and ^{14}C concentrations of the groundwaters. Data from several fractures indicate that surface waters have penetrated to depths up to about 210 m below the surface (around 150 masl) within the last 40 a. At greater depths, up to about 880 m (ca. 550 mbsl), mixtures of relatively recently recharged water and relatively 'old' groundwater, which is devoid of ^{3}H, are observed in several fractures. The estimated ^{14}C age of the relatively 'old' groundwater ranges from 6.5 to 14 Ka (Iwatsuki et al., 2000).

2.3. *Palaeohydrogeological framework*

Previous workers (Seo et al., 1989; Yusa et al., 1993) presented a palaeohydrogeological interpretation of the Tono area, based on both hydrogeological and hydrochemical data for the sedimentary rocks in the vicinity of the Tono U deposits. Additionally, the genesis and long-term stability of the U deposits have been studied, using isotopic data from coexisting calcite and pyrite (Shikazono and Utada, 1997, Shikazono and Nakata, 1999). The chemical processes, redox conditions and groundwater evolution in the Toki granite have been investigated by in-situ measurements of physico-chemical parameters, such as pH and Eh, and by determining the chemical compositions of groundwater samples (JNC, 2000). However, these investigations have not enabled past changes in hydrochemical conditions to be deduced clearly.

Yusa et al. (1993) interpreted the geological evidence in terms of the palaeohydrogeology of the area. They summarised variations in the depositional environments of the sedimentary rocks and related these to the uplift and subsidence history of the area. There were episodes of sediment deposition from freshwater (Toki Formation and Seto Group), brackish and marine water (Oidawara Formation and Akeyo Formation), that were separated by periods of erosion. The elevation of the Tono area was interpreted to have increased by around 500 m during the last 0.7 Ma, accompanied by between 200 and 350 m of erosion (Yoshikawa, 1974).

These earlier interpretations raise the possibility that in the Miocene, marine and/or brackish waters may have descended from the sedimentary rocks into the fracture network in the underlying granite (Fig. 2), and then been flushed by fresh water. This flushing is expected to have occurred during the uplift and erosion preceding the deposition of the Seto Group and during the uplift and erosion during the last 0.7 Ma, and possibly also at other times. However, prior to the present study there was no direct evidence for this flushing in the granite.

3. Sampling and analytical methods

In general, studies of mineral precipitates in fresh groundwater systems, particularly relatively young ones, tend to be hindered by crystal sizes being relatively small. In the present study, calcite crystals were often only a few tens of μm across. This means that separation and/or analysis of crystals with a single morphological type, or belonging to a single generation, was difficult or impossible. Additionally, attempts to constrain groundwater chemistry using fluid inclusions were unsuccessful. Therefore, the approach that was adopted was to collect a large number of samples, to separate different generations of calcite as far as possible, and than to examine the scatter of isotopic compositions. In this way, it was aimed to identify limiting calcite compositions. These could then be interpreted against the background of the hydrochemical evolution of the area inferred from geological and palaeontological evidence.

Groundwaters and carbonate minerals were sampled from 7 boreholes penetrating basement granitic rocks (Fig. 1 maximum depth of 1000 m). Groundwater samples were collected by using a double packer system with a batch style bottle while maintaining in-situ water pressure and chemical condition.

Dissolved inorganic C (DIC), principally as HCO_3^- and CO_3^{2-} ions, was precipitated from groundwater as $SrCO_3$ by adding $SrCl_2$ and NaOH to water samples in the field. Fracture-filling and fracture-lining carbonate minerals were selected under a binocular microscope.

The mineralogical composition and purity of the samples were established by an X-ray powder diffraction meter (RIGAKU-RINT 1100). A scanning electron microscope equipped with an energy-dispersive X-ray System (SEM–EDS; Jeol-JSM 5400LV) and an electron probe micro analyzer (EPMA; JXA 8600) were used to determine the crystal morphologies and the chemical compositions of the mineral samples.

The $SrCO_3$ samples precipitated from groundwater and small amounts of each powdered carbonate mineral sample were converted to CO_2 gas by reacting with 100% phosphoric acid in a vacuum line. Carbon and O isotope ratios were determined by isotope ratio mass

spectrometry. The results are reported using the conventional δ-notation, with respect to the PDB standard for $^{13}C/^{12}C$ and the SMOW standard for $^{18}O/^{16}O$. When calculating the isotopic compositions of oxygen, the following relation between $\delta^{18}O$ reported against PDB and SMOW, was used:

$$\delta^{18}O_{SMOW} = 1.03086\ \delta^{18}O_{PDB} + 30.86\ (‰)$$

(International Atomic Energy Agency, 1983).

A part of each CO_2 gas sample was reduced to graphite by reacting with H_2 (Kitagawa et al., 1993). Radioactive C concentrations in the resulting graphite samples were measured by tandem accelerator mass spectrometer (NEC 15SDH-2) (Xu et al., 2000). The precisions are ±0.2‰ for $\delta^{18}O$ and $\delta^{13}C$, and ±0.5% pMC (pMC: percent modern C) for ^{14}C concentrations.

4. Results and discussion

4.1. Origins and timing of calcite precipitation

4.1.1. Hydrothermal calcite precipitation

The X-ray powder diffraction and EPMA analyses indicated that the carbonate minerals on the fracture surfaces are mainly calcite, enabling calcite-water isotopic fractionation relationships to be used in the interpretation.

The isotopic analyses are tabulated in Table 1 and summarised in Fig. 3. Two main fields can be distinguished in the fig. The scatter of points within and between these two fields can be explained by a combination of mixing between groundwaters and DIC from different sources, prior to calcite precipitation, and by the possibility that samples included calcite with different origins. Most of the calcite plots within a relatively narrow range of O isotope compositions, with $\delta^{18}O_{SMOW}$ around +20±5‰, but within a relatively wide range of C isotopic compositions, from −29 to +3‰. This calcite is considered further in the next section. However, some calcite plots towards relatively ^{18}O-depleted compositions, having $\delta^{18}O_{SMOW}$ from −3 to ca. +10‰, and within a relatively narrow range of carbon isotopic compositions, with $\delta^{13}C_{PDB}$ between ca. −18‰ and ca. −7‰.

The isotopic composition of calcite is a function of the isotopic composition of the water and the dissolved inorganic C in the water, and the temperature. The fractionation of O isotopes, especially, shows a greater temperature-dependence. If isotopic equilibrium is assumed between the calcite and the water, the following function linking calcite–water isotopic fractionation factors and temperature can be used (O' Neil et al., 1969):

$$1000 \ln \alpha = 2.78\ (10^6\ T^{-2}) - 3.39$$

where α = the O isotope fractionation factor between calcite and water; T = water temperature (K).

As discussed previously, apart from an early, relatively high-temperature hydrothermal vein assemblage, which includes epidote, chlorite, quartz and K-feldspar, the only water types for which there is any evidence in the area are seawater, brackish water and fresh water. As is typical for Japan, obvious sources for water more saline than seawater, such as evaporite deposits, are absent from the Tono area. Therefore, Fig. 4 is drawn for present groundwater ($\delta^{18}O_{PDB}$ = 8.3‰) and seawater ($\delta^{18}O_{PDB}$ = 0‰). For any water composition, there is an inverse relationship between temperature and the isotopic composition of the calcite that is formed. The calcite plotting within the relatively low $\delta^{18}O_{SMOW}$ field (Fig. 3) probably formed either at a relatively high temperature from seawater and/or at lower temperature from water that was relatively depleted in ^{18}O.

The $\delta^{18}O_{SMOW}$ value of the water that precipitated the calcite is unknown. However, meteoric precipitation in the absence of significant water/rock interactions produces groundwaters that are most depleted in ^{18}O. While meteoric waters may have a wide range of isotopic compositions, most of those in this area have $\delta^{18}O_{SMOW}$ values greater than around −10‰ (e.g. Waseda and Nakai, 1983). For illustrative purposes, this can be taken as a reasonable minimum value for the waters that precipitated the Tono calcite. This approach implies that the calcites plotting within the relatively low $\delta^{18}O_{SMOW}$ field formed at temperatures higher than around 75 °C; the lowest $\delta^{18}O_{SMOW}$ value, −2.5‰, would require a temperature of more than 230 °C. Even if the groundwaters had $\delta^{18}O_{SMOW}$ compositions as low as −20‰, which might have arisen only in the unlikely case that recharge occurred under very cold climatic conditions (cf. Gat, 1988), a temperature of around 90 °C would be needed to explain the lightest $\delta^{18}O_{SMOW}$ value measured. This is considerably in excess of the temperatures presently encountered in the boreholes (around 30 °C at the depths of 500 to 1000 m below ground level). Thus, calcite analyses with $\delta^{18}O_{SMOW}$ from ca. −3 to ca. +10‰ are most easily explained by formation from relatively high temperature, meteoric hydrothermal fluids. This possibility is supported by the fact that most of this calcite comes from fractured zones that are associated with chloritization suggesting hydrothermal alteration (Iwatsuki and Yoshida, 1999a).

4.1.2. Relatively new calcite precipitation from the fresh water

It can be appreciated from Fig. 4 that the calcites plotting within the relatively high $\delta^{18}O_{SMOW}$ field, with $\delta^{18}O_{SMOW}$ values around +20‰, could have precipitated at relatively low temperatures, less than ca. 50 °C. This inferred low-temperature calcite has a very wide range of $\delta^{13}C_{PDB}$, from −29‰ to +3‰. The C

Table 1
Isotopic compositions and morphologies of calcite on the fracture surface

	Depth (m)	Sea level (m)	Ground water $\delta^{13}C$ (‰ PDB)	Ground water ^{14}C (pMC)	Calcite $\delta^{13}C$ (‰ PDB)	Calcite $\delta^{18}O$ (‰ SMOW)	Calcite ^{14}C (pMC)	Solution from which calcite precipitated $\delta^{13}C$[a] (‰ PDB)	$\Delta^{18}O$[b] (‰ smow)	Temp.[c] (°C)	Temp.[d] (°C)	Calcite morphology
Soil zone ($n=6$)			−18.1 ±1.9	102.4 ±1.6								
Shell fossils in the Tertiary sedimentary rocks ($n=5$)					0.3±1.7	28.6±1.3	No data	−1.6±1.7	−0.8±1.3	−9.1±4.1	23.7±5.9	No observation
DH−3	503	−147			−14.4	22.3	Not enough sample	−16.2	−6.9	14	58	No observation
DH−3	663	−307			−14.7	20.8	Not enough sample	−16.5	−8.4	20	68	No observation
DH−5	269	41			−17.6	22.6	0.7	−19.4	−6.6	13	55	No observation
DH−5	279	31			−17.6	8.0	0.6	−19.4	−20.8	103	222	No observation
DH−5	295	16			−17.6	14.9	0.8	−19.4	−14.1	51	118	No observation
DH−5	330	−20	−17.5	45.5	–	–	–	–	–	–	–	–
DH−5	363	−53			−18.2	21.6	0.5	−20.1	−7.6	17	62	No observation
DH−5	476	−165			−26.0	21.0	Not enough sample	−27.8	−8.2	20	66	No observation
DH−6	325	−6			−28.6	20.8	0.3	−30.4	−8.3	20	67	Rhombohedral form
DH−6	478	−158			−25.1	23.3	0.6	−26.9	−5.9	10	51	No observation
DH−6	582	−263			−2.2	14.0	0.5	−4.0	−15.0	56	128	Indistinct structure
DH−6	625	−305			−12.2	19.2	0.4	−14.0	−9.9	28	80	No observation
DH−6	649	−330			−9.2	18.4	0.6	−11.0	−10.7	32	86	No observation
DH−6	780	−461			−20.7	23.8	<0.2	−22.5	−5.4	8	48	No observation
DH−6	800	−481			−15.8	23.6	0.3	−17.6	−5.6	8	49	Polyhedra form
DH−6	803	−483			−11.1	18.1	0.4	−12.9	−11.0	33	88	No observation
DH−6	808	−488			−16.0	22.8	<0.2	−17.9	−6.4	12	54	No observation
DH−6	838	−518			−10.2	21.7	<0.2	−12.1	−7.5	16	61	No observation
DH−6	859	−540			−16.2	22.7	Not enough sample	−18.0	−6.5	12	55	No observation
DH−7	359	−19			−16.5	22.8	<0.2	−18.3	−6.5	12	55	Indistinct structure
DH−7	364	−24			−16.9	n.d.	0.3	−18.7	N.d.	n.d.	n.d.	No observation
DH−7	368	−28			−18.6	25.3	0.7	−20.4	−3.9	2	40	No observation
DH−7	471	−131			−9.6	5.9	0.9	−11.4	−22.8	124	273	No observation
DH−7	523	−183			−19.2	19.0	1.9	−21.0	−10.1	29	81	Mica−like form
DH−7	564	−224			−10.9	22.3	1.1	−12.7	−6.9	14	58	No observation
DH−7	586	−246			−8.5	7.2	0.4	−10.3	−21.6	111	241	Hexagonal form
DH−7	637	−297			−12.0	−2.0	0.9	−13.8	−30.5	261	1123	Indistinct structure
DH−7	738	−398			−9.5	14.9	1.8	−11.3	−14.1	51	118	Rhombohedral form
DH−7	741	−401			−14.5	18.8	1.3	−16.3	−10.3	29	82	Indistinct structure
DH−7	836	−496			−7.6	1.6	Not enough sample	−9.4	−27.0	184	476	Indistinct structure
DH−7	849	−509			−13.5	23.3	Not enough sample	−15.4	−6.0	10	52	No observation
DH−7	897	−557			−12.7	25.1	1.6	−14.6	−4.2	3	41	No observation

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Table 1 (*continued*)

	Depth (m)	Sea level (m)	Ground water		Calcite			Solution from which calcite precipitated				Calcite morphology
			$\delta^{13}C$ (‰ PDB)	^{14}C (pMC)	$\delta^{13}C$ (‰ PDB)	$\delta^{18}O$ (‰ SMOW)	^{14}C (pMC)	$\delta^{13}C^{a}$ (‰ PDB)	$\Delta^{18}O^{b}$ (‰ smow)	Temp.^{c} (°C)	Temp.^{d} (°C)	
DH−7	955	−615			−14.2	24.5	Not enough sample	−16.0	−4.7	5	44	Complex polyhedra form
DH−8	203	67			−17.3	15.8	1.4	−19.1	−13.2	45	108	Rhombohedral form
DH−8	535	−265			−10.9	20.8	<0.2	−12.7	−8.3	20	67	No observation
DH−8	645	−375	−17.8	36.7	–	–	–	–	–	–	–	–
DH−8	701	−431			−13.1	14.6	1.0	−14.9	−14.4	53	122	No observation
DH−8	872	−602	−14.5	18.8	–	–	–	–	–	–	–	–
DH−8	978	−708	−16.9	29.9	–	–	–	–	–	–	–	–
DH−9	184	92			−16.7	23.1	4.5	−18.5	−6.1	11	53	No observation
DH−9	185	91			−11.1	18.8	0.8	−12.9	−10.3	30	82	No observation
DH−9	191	84			0.1	22.4	<0.2	−1.8	−6.8	13	57	Indistinct structure
DH−9	224	52			−11.3	18.6	2.6	−13.1	−10.5	31	84	Indistinct structure
DH−9	287	−11			−6.8	6.2	<0.2	−8.6	−22.5	121	266	No observation
DH−9	320	−44			0.3	22.6	Not enough sample	−1.5	−6.6	13	56	Elongate rhomb form
DH−9	387	−111			−7.9	18.0	0.7	−9.7	−11.1	34	89	Polyhedra form
DH−9	472	−196			−3.9	16.7	Not enough sample	−5.7	−12.3	40	100	Indistinct structure
DH−9	537	−262			−3.8	21.1	<0.2	−5.7	−8.1	19	66	Polyhedra form
DH−9	553	−277			−2.3	21.5	Not enough sample	−4.1	−7.7	17	63	No observation
DH−9	565	−290			1.2	20.5	1.6	−0.6	−8.6	22	69	Indistinct structure
DH−9	569	−293			−2.7	21.1	<0.2	−4.5	−8.1	19	66	Indistinct structure
DH−9	570	−295			0.1	22.3	Not enough sample	−1.7	−6.9	14	57	Elemental and elongate rhombohedral, hexagonal, mica−like form
DH−9	637	−361			−1.3	22.3	<0.2	−3.2	−6.9	14	58	Indistinct structure
DH−9	645	−369			−6.2	7.1	Not enough sample	−8.0	−21.7	112	242	Polyhedra form
DH−9	679	−404			2.4	23.2	Not enough sample	0.6	−6.0	10	52	Indistinct structure
DH−9	689	−414			−10.5	4.2	Not enough sample	−12.4	−24.5	145	334	Rhombohedral form
DH−9	696	−421			−11.9	20.0	Not enough sample	−13.8	−9.2	24	74	Indistinct structure
DH−9	704	−429			−10.5	20.8	Not enough sample	−12.3	−8.3	20	67	Rhombohedral form
DH−9	738	−463			−6.7	13.6	1.8	−8.6	−15.3	59	132	Polyhedra form
DH−9	767	−491			0.7	22.2	<0.2	−1.1	−7.0	14	58	Elongate rhomb form
DH−9	783	−508			−2.7	20.5	<0.2	−4.5	−8.6	21	69	No observation
DH−9	793	−517			0.8	21.4	Not enough sample	−1.1	−7.7	18	63	indistinct structure
DH−9	834	−559			−6.5	21.2	Not enough sample	−8.3	−7.9	18	65	hexagonal, mica−like form
DH−11	329	−24			−7.7	25.1	<0.2	−9.5	−4.2	3	41	indistinct structure
DH−11	357	−52			−9.4	−2.5	Not enough sample	−11.2	−31.0	277	1528	indistinct structure
DH−11	490	−185			−15.7	9.0	0.5	−17.5	−19.8	93	201	indistinct structure
DH−11	614	−308			−11.9	19.3	Not enough sample	−13.7	−9.8	27	78	polyhedra form

(*continued on next page*)

Table 1 (*continued*)

	Depth (m)	Sea level (m)	Ground water $\delta^{13}C$ (‰ PDB)	Ground water ^{14}C (pMC)	Calcite $\delta^{13}C$ (‰ PDB)	Calcite $\delta^{18}O$ (‰ SMOW)	Calcite ^{14}C (pMC)	Solution from which calcite precipitated: $\delta^{13}C^{a}$ (‰ PDB)	$\Delta^{18}O^{b}$ (‰ smow)	Temp.[c] (°C)	Temp.[d] (°C)	Calcite morphology
DH-11	624	−319			−13.8	23.4	0.3	−15.6	−5.9	10	51	indistinct structure
DH-11	636	−331			−11.9	18.9	<0.2	−13.7	−10.2	29	82	indistinct structure
DH-11	686	−380			−11.8	21.3	Not enough sample	−13.6	−7.9	18	64	indistinct structure
DH-11	690	−385			−11.8	25.7	<0.2	−13.6	−3.6	1	38	indistinct structure
DH-11	699	−393			−11.9	19.3	<0.2	−13.7	−9.8	27	78	polyhedra form
DH-11	708	−403			−2.4	21.7	<0.2	−4.3	−7.5	16	61	polyhedra form
DH-11	714	−409			−5.0	20.2	0.4	−6.8	−8.9	23	72	indistinct structure
DH-11	733	−427			−10.7	20.0	<0.2	−12.6	−9.2	24	73	indistinct structure
DH-11	740	−435			−6.7	20.7	<0.2	−8.5	−8.5	21	68	polyhedra form
DH-11	803	−497			−4.8	20.1	0.4	−6.6	−9.0	23	72	indistinct structure

[a] Calculated using $\alpha = 1.00185$ at 20 °C (Emrich et al., 1970).
[b] Calculated using $\alpha = 1.0294$ at 20 °C (O' Neil, 1969).
[c] Calculated using α which was estimated assuming $\delta^{18}O$ of groundwater (−8.3‰).
[d] Calculated using α which was estimated assuming $\delta^{18}O$ of seawater (0‰).

isotopic composition of the calcite is an indicator of the source of the C. The theoretical $\delta^{13}C$ values of DIC from which the calcite precipitated were calculated using the isotopic fractionation factor between DIC and calcite (Emrich et al., 1970):

$$\alpha = (^{13}C/^{12}C)_{\text{calcite}} / (^{13}C/^{12}C)_{\text{bicarbonate}}$$

$$\alpha = 1.00185 \ (20\ ^{\circ}C)$$

Apart from in the shallowest parts of DH-6, and in the deeper parts of DH-5, DH-9 and DH-11, the $\delta^{13}C_{PDB}$ values calculated for DIC agree well with those of present surface water or groundwater (Fig. 5). The ^{14}C measurements of calcite were limited, but several samples of fracture calcite contain ^{14}C, up to 4.5 pMC (Table 1). The radiocarbon results cannot be used to deduce the absolute timing of calcite formation, because this process may involve mixing between ^{14}C and non-radioactive C derived from earlier generations of 'old' calcite. However, the detection of ^{14}C in a sample means that at least a component of the calcite must have formed within the last 50 ka years. ^{14}C-bearing calcite with similar $\delta^{13}C_{PDB}$ values to present surface water or groundwater can be surmised to be relatively new precipitates from the fresh water.

4.1.3. *Calcite precipitation from marine water or a mixture of marine and fresh water*

The water that precipitated calcite in the deeper parts of DH-9 and DH-11 is calculated to have contained DIC with $\delta^{13}C_{PDB}$ between −14‰ and +1‰, that is DIC with $\delta^{13}C_{PDB}$ considerably higher than that of DIC from present groundwater (Fig. 5). These relatively heavy C isotopic values are most readily explained by the calcite precipitating either from water containing C of marine origin, or from water containing a mixture of C of marine and fresh water origin. This possibility is supported by results from previous work on the overlying sedimentary rocks by Shikazono and Utada (1997). They classified calcite from the Mizunami Group into: (1) calcite in the marine parts of the formation ($\delta^{13}C_{PDB} = -11$‰ to +3‰, $\delta^{18}O = +20$‰ to +28‰); and (2) calcite precipitated from DIC originating from a combination of organic matter oxidation and from dissolution of marine carbonates in the lacustrine parts of the formation ($\delta^{13}C_{PDB} = -19$‰ to −6‰, $\delta^{18}O = +18$‰ to +24‰). The isotopic compositions of carbonate from the marine sedimentary rocks thus cover a very similar range to that of the calcite in the granite, in the deeper parts of DH-9 and DH-11.

Two alternative mechanisms are suggested for the transport of a component of C with a marine origin into the Toki granite. Possibly, infiltrating groundwaters dissolved shell fossils in the marine sedimentary formation, entered the granitic rocks and then precipitated the DIC as calcite on the fracture surfaces. In this case,

Fig. 3. Plot illustrating variations in the compositions of stable O and C isotopes in the fracture calcite studied. The compositions of marine, fossil, calcite from the sedimentary rocks and calcite that theoretically would equilibrate with present surface water are shown for comparison. The fields indicate the possible end-members for the groundwaters in the study area: seawater, fresh water and hydrothermal water. Present temperatures at the depths from 500 to 1000 m are about 30 °C. The calcite with the $\delta^{18}O_{SMOW}$ values greater than +17‰ could have precipitated at relatively low temperature (<30 °C).

there was possibly also mixing between C derived from the shell fossils with the $\delta^{13}C_{PDB}$ around 0‰ and organic matter with the $\delta^{13}C_{PDB}$ around −25‰ in the sedimentary rocks. This process might have occurred at any time following the deposition of the sedimentary rocks. Alternatively, calcite may have precipitated directly from seawater that infiltrated into fractures in the granitic rocks, possibly during the Miocene. The heavier $\delta^{13}C_{PDB}$ compositions, around 0‰, are most easily explained by a direct precipitation from the DIC in marine water. The morphology of the calcite crystals provides independent evidence that this second process occurred (see below).

It is noteworthy that in borehole DH-9, calcite bearing ^{14}C, but with an apparent marine $\delta^{13}C_{PDB}$ composition occurs at a depth of 565 m (290 mbsl) while in DH-11, ^{14}C-bearing calcite having an apparent mixed marine/freshwater signature $\delta^{13}C_{PDB}$ composition occurs at depths of 714 m and 803 m below the surface (409 and 497 mbsl respectively). However, these values do not necessarily imply that calcite has been precipitated from marine water during the last 50 ka years. It is more likely that these values reflect the analysis of multiple generations of calcite and/or recycling of 'old' marine C from earlier calcite, during calcite precipitation from fresh water that also contained a component

Fig. 4. Relative formation temperatures of calcite plotted as a function of the calcite's stable O isotopic composition. Two illustrative isotopic compositions are assumed for the water precipitating the calcite: $\delta^{18}O_{SMOW} = 0‰$ (seawater); and $\delta^{18}O_{SMOW} = -8.3‰$ (present groundwater). Temperatures were calculated using the relationship of O' Neil et al. (1969) given in the text.

of ^{14}C. The lack of textural evidence for calcite dissolution (cf. fresh crystals in Fig. 6) implies that any recycling of C from older calcite involved calcite dissolution higher in the flow system, closer to the recharge zone.

The upper parts of DH-6 and deeper parts of DH-5 contain calcite with the lightest observed C-isotope compositions, consistent with a relatively large component of C derived from organic sources. The lightest compositions cannot be explained by simple equilibrium between inorganic carbon species. There are rare reports of similarly light carbon isotopic compositions of carbonate minerals in other low-temperature settings (e.g. Wigley et al., 1978; Wallin and Peterman, 1999). These light compositions are usually explained by the presence of C having an organic origin. A similar explanation for the lightest C-isotope compositions of Tono calcite is considered reasonable, though the precise mechanism by which organic C was recycled into the calcite is uncertain.

4.2. Morphology of calcite crystals

Among the calcite crystals sampled in the present study, several different morphologies were observed (Table 1, Fig. 6). Distinct crystal morphologies could not be seen in all the samples selected for stable isotopic work, owing to the small size of the crystals and the fact that it was usually necessary to analyse a mixture of more than one kind of crystal. However, the existence of a range of calcite crystal forms is significant because it suggests that a range of waters with several different compositions may have precipitated the calcite.

Previous workers (Folk, 1974; Given and Wilkinson, 1985; Gonzalez et al., 1992, Metcalfe et al., 1998, Milodowski et al., 1998; Bath et al., 2000) have identified relationships between calcite morphologies and the conditions of calcite precipitation. Notably, the morphology of a calcite crystal appears to be a function of the degree of calcite super-saturation in the water and/or crystal growth kinetics. These factors in turn reflect the chemical conditions of the water, such as pH, and Mg^{2+} and Na^{+} concentration, the rate of supply of carbonate constituents and the crystallization rate, which is partly a function of temperature. According to Folk (1974), the overall effect of these factors is that fresh-water calcite occurs as elemental rhombs or mica-like forms. However, within hypersaline to normal marine environments, sideward growth of calcite crystals is selectively inhibited so that elongate rhombohedral crystal forms develop. In a mixture between seawater and fresh water, calcite crystals may show complex polyhedral forms. The relationship between calcite crystal forms and water salinity suggested by Folk (1974) is illustrated in Fig. 7.

More recently, Metcalfe et al. (1998) and Milodowski et al. (1998) found a clear correlation between calcite morphology and the salinity of present deep groundwaters at Sellafield in NW England (Fig. 8). Here calcite

Fig. 5. $\delta^{13}C_{PDB}$ values of surface water, groundwater, calcite and water in equilibrium with calcite (excluding values from calcite considered to have a hydrothermal origin).

with elongated *c*-axis morphology occurred in zones occupied by saline water, whereas calcite with flattened *c*-axis morphology occurred in zones occupied by fresh water.

Application of these relationships between water salinity and calcite morphology to the observations at the Tono area, imply that the fracture calcite in the Toki granite precipitated from water with salinity ranging from fresh water to sea water equivalent salinity. This range is similar to that deduced independently from the stable isotopic data. There are insufficient data with which to establish confidently whether or not there is a correlation between morphological forms of calcite crystals and their isotopic compositions. However, both occurrences of elongate rhomb forms, which indicate relatively high groundwater salinity, coincide with $^{13}C_{PDB}$ compositions close to 0‰, consistent with a marine origin. These are important observations, because they suggest that the calcite actually precipitated from marine water, rather than from fresh water that had simply inherited marine C isotopic compositions, for example during interactions with carbonate in marine sedimentary rocks.

elemental rhombohedral calcite (DH-6/-6 m S.L.)

hexagonal, mica-like calcite (DH-9/-559 m S.L.)

polyhedral calcite (DH-9/-262 m S.L.)

elongate rhombohedral calcite (DH-9/-295 m S.L.: upper layer of fracture fillings)

elemental rhombohedral calcite (DH-9/-295 m S.L.: lower layer of fracture fillings)

Fig. 6. The morphologies of calcite crystals observed on fracture surfaces. In DH-9, at a depth of 570 m (295 mbsl), elongate rhombohedral calcite covers the elemental rhombs and mica-like forms. These relationships may record a hydrogeochemical change from fresh water to seawater during the marine deposition.

Fig. 7. A relationship between crystal morphology of calcite and salinity (modified from Folk, 1974).

Fig. 8. Correlation between calcite morphology and present deep groundwater salinity in borehole 10A at Sellafield, NW England (modified from Metcalfe et al., 1998 and Milodowski et al., 1998). The elongate crystals, coinciding with saline water are similar in shape to the elongate rhomb calcite observed in the present study.

Furthermore, there is evidence that the morphological relationships of calcite have the potential to record variations in groundwater compositions. Several calcite morphologies, including elemental rhombohedral forms, mica-like forms and elongate rhombohedral forms are detected in the same fracture at a depth of 570 m below the surface (295 mbsl) in borehole DH-9 (Fig. 6). At this point, elongate rhombohedral calcite covers the elemental rhombohedral, mica-like calcite. If the correlation between morphology and salinity is correct, then an

implication is that at this point the calcite records an early flushing of fresh water by seawater during the marine sedimentation (16.3–14.85 Ma).

4.3. Implications for the stability of the groundwater system

Flushing of the groundwater system by fresh water probably occurred more than once. Such a process is expected to have coincided with periods of uplift, most recently during the last 700 ka. However, in the eastern boreholes, DH-9 and DH-11, the inferred ages of relatively low-temperature calcite in the fracture system may range from the Miocene to the last few tens of thousands of years, and conceivably even to the present. Furthermore, there is no textural evidence for calcite dissolution in any of the samples (Fig. 6). Thus, rather than being removed by flushing events, morphological and isotopic variations in the calcite may actually provide a record of flushing events in this eastern area. An implication is that buffering of groundwater compositions by water/rock reactions has caused the waters that are presently shallower than 150 to 200 m below ground level in this area to remain saturated with respect to calcite. This aspect of groundwater chemical stability has enabled calcite morphologies reflecting earlier groundwater compositions to be preserved.

This assertion is also consistent with theoretical considerations. Water/rock interactions accompanying flushing may have caused preservation of earlier calcite generations, at least in downstream parts of flow paths. For example, fresh groundwater is currently flowing through the rocks of the study area. However, at depths greater than 200 m or so, these waters are saturated with calcite (e.g. Iwatsuki and Yoshida, 1999b). If such water flows to greater depths, temperature gradients and water/rock interactions such as silicate hydrolysis, might be expected to cause further calcite precipitation, rather than calcite dissolution. Thus, upstream in a flow path, near a recharge zone, it is expected that calcite would dissolve. However, at larger distances downstream from the recharge zone, 'old' calcite might be preserved and overgrown by more recent calcite. This process might explain why ^{14}C-bearing calcite, indicating a relatively recent age, has apparent marine stable C isotopic signatures in boreholes DH-9 and DH-11.

5. Conclusion

Geological and palaeontological evidence suggests that in the Tono area there have been only 3 main types of water: early relatively high-temperature, hydrothermal waters; and later, low-temperature marine water and fresh water. The hydrochemical evolution of the area has not been complicated by sources of salinity such as evaporites or deep sedimentary basins. Therefore, investigations in the Tono area are particularly valuable for establishing the applicability of mineralogical evidence to interpret the history of flushing by fresh water.

The isotopic compositions and morphologies of fracture calcites in the deep granitic rocks of the Tono area record a spatial and temporal change of hydrochemical conditions. These new findings are consistent with 3 main origins of the fracture calcites:

- relatively high-temperature hydrothermal solutions, precipitating calcites distinguished by $\delta^{18}O_{SMOW}$ from −3 to ca. 10‰, and with $\delta^{13}C_{PDB}$ from ca. −18 to −7‰;
- seawater, probably partly of Miocene age, which precipitated calcite distinguished by $\delta^{13}C_{PDB}$ of ca. 0‰ and $\delta^{18}O_{SMOW}$ > ca. 20‰;
- fresh water, with a variable $\delta^{13}C_{PDB}$ composition but which precipitated calcite distinguished by $\delta^{13}C_{PDB}$ that was significantly <0‰ and as low as ca. −29‰ and $\delta^{18}O_{SMOW}$ > ca. 17‰.

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The hydrochemical conditions have probably remained saturated with calcite for several million years in areas where the calcite of inferred marine origin exists. Such areas occur at relatively large distances from the recharge zones in the present, regional groundwater flow system. To maintain weakly alkaline, calcite-saturated conditions, it is suggested that pH-buffering reactions, such as calcite dissolution or silicate hydrolysis, occur upstream from the localities where there is calcite of inferred marine origin.

The isotopic data from the granite provide the first evidence that marine water penetrated into the deep groundwater system in the past. This is an important result because inland in Japan, ~~all~~ the present low-temperature (<50 °C), deep (to several hundred metres) groundwaters investigated previously are ~~universally~~ predom. fresh (total dissolved solids less than several hundred mg/l). The present work is the first time that evidence for the past existence of low-temperature saline waters, at depths of several hundred metres, has been reported far ~~away~~ from present coastal areas of Japan.

The range of past groundwater salinity interpreted from the isotopic data for the calcite is consistent with geotherm. or the range of salinity inferred from the variations in crystal morphologies. Thus, the present study suggests that even in presently low-salinity groundwater systems, isotopic and morphological variations of calcite record hydrogeological change and preserve the evidence of past groundwater chemistry and seawater infiltration.

The isotopic and morphological data from calcite in this deep, fresh groundwater system are consistent with previous inferences about hydrochemical evolution, based upon geological and palaeontological evidence.

Thus, the present study demonstrates the potential for developing the methodology as a palaeohydrogeological tool.

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The Redox Environment of Deep Groundwaters Associated with the Tono Uranium Deposit, Japan

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ABSTRACT

An unconformity underlying the Tono uranium deposit in central Japan represents the approximate location of a redox front separating relatively oxidizing groundwaters (Eh ≈ 0 mV) in the weathered, fractured Toki granite (TG) from strongly reducing pore fluids (Eh ≈ -360 mV) in sedimentary rocks of the overlying Lower Toki Lignite-bearing Formation (TL). Uranium has been effectively immobilized in the TL during the past 10 million years. Stable and reversible redox potentials measured *in-situ* in boreholes penetrating the sedimentary rocks and granite appear to be controlled by the Fe(III)-oxyhydroxide — Fe^{2+} redox couple. A simplified analytical model of front migration suggests that chemical buffering by pyrite alone would limit the propagation velocity of the front into the TL to less than 8×10^{-6} m yr^{-1}. The model is constrained by Darcy fluxes derived from groundwater flow models and relative ^{14}C groundwater ages, average modal abundances of pyrite in the TL, and the analytical detection limit for dissolved oxygen in TG groundwaters (2 ppm). Model results also suggest that the redox buffering capacity of the TL would be exhausted within 10 million years if an upper bound $O_2(aq)$ concentration in TG groundwaters fixed by equilibrium with atmospheric $O_2(g)$ (8.5 ppm) is assumed. Immobilization of uranium in the TL is thus attributable to oxidation-reduction reactions that minimize $O_2(aq)$ concentrations primarily in the TG, and secondarily in the TL.

INTRODUCTION

The Tono uranium deposit in Gifu Prefecture, central Japan provides evidence that a mechanically stable, chemically reducing environment can be maintained for long periods of time at depths within a few hundred meters of the surface. Uranium has been effectively immobilized in the deposit during the past 10 million years despite the present, and probably past, inflow of groundwater that is sufficiently oxidizing initially to mobilize the uranium. The findings suggest that geological disposal concepts for high-level nuclear waste elsewhere can be justified in requiring that chemically reducing conditions persist over similar time periods.

The hydrogeological and geochemical processes involved in isolating uranium within the Tono deposit are currently under investigation by the Tono Natural Analogue Project. The present paper summarizes results of this project dealing specifically with the spatial and temporal stability of a redox front that appears to have played a decisive role in the genesis and long-term preservation of the ore body. These results include analyses of groundwater samples, which are summarized in Table I. Complete analyses, including descriptions of groundwater sampling and analytical techniques, are given in reference [1]. The geology and hydrogeology of the area is summarized in Fig. 1, and described in detail in references [2] - [4].

Table I. Analytical data characterizing the redox status of groundwaters of the Tono area*.

Bhl	Frm	depth (mbgl)	uncnf (m)	pH	Eh (mV)	ΣFe (ppm)	Fe^{2+} (ppm)	SO_4^{2-} (ppm)	HS^- (ppm)	Eh_c (mV)
TH-1	TL	-138[1]	27[2]	9.5	n.m.	<0.02	<0.02	12.2	0.9	-368[5]
TH-2	TU	-75[1]	96[2]	8.2	n.m.	<0.02	<0.02	1.1	0.2	-285[5]
TH-3	TU	-86[1]	74[2]	8.4	n.m.	<0.02	<0.02	1.3	30.1	-312[5]
TH-3	TL	-124[1]	36[2]	8.8	n.m.	<0.02	<0.02	17.1	25.7	-331[5]
TH-4	A	-61[1]	114[2]	7.6	n.m.	<0.02	<0.02	5.4	25.7	-253[5]
TH-6	O	-68[1]	95[2]	7.8	n.m.	0.09	<0.02	12.2	0.4	-251[5]
TH-6	A	-104[1]	59[2]	8.8	n.m.	0.06	0.03	35.0	16.5	-327[5]
										-33[6]
TH-6	TU	-132[1]	31[2]	8.7	n.m.	0.04	<0.02	51.0	37.4	-323[5]
TH-6	TL	-153[1]	10[2]	9.0	n.m.	<0.02	<0.02	41.0	15.1	-341[5]
TH-8	TL	-121[1]	18[2]	7.9	n.m.	<0.02	<0.02	3.6	0.2	-261[5]
DH-11[4]	O	-134	131	9.0	-323	0.21	0.05	4.2	<0.1	-43[6]
DH-13	TU	-10	30	7.5	-19	0.18	0.14	18.4	<0.1	162[6]
DH-12	TL	-161	9	9.7	-42	<0.05	<0.05	<0.4	n.m.	
MIU-4	TL	-74	3	9.4	-88	<0.05	<0.05	4.9	n.m.	
KNA-6	TL	-160	10[3]	9.6	-360	0.005	<0.02	0.7	0.09	
KNA-6	TG	-180	-10[3]	8.3	0	0.008	<0.02	0.2	<0.01	
DH-4[4]	TG	-187	n.a.	6.8	49	9.3	9.3	0.1	n.m.	
DH-5[4]	TG	-327	n.a.	7.8	-16	0.41	0.24	7.8	n.m.	125[6]
DH-6	TG	-737	n.a.	8.9	-303	0.18	0.2	5.5	n.m.	
DH-7	TG	-564	n.a.	10.1	-398	8.9	8.5	4.6	n.m.	-339[6]
DH-7	TG	-837	n.a.	9.6	-373	7.2	6.9	5.6	n.m.	-309[6]
DH-7	TG	-883	n.a.	9.4	-355	7.5	8.8	5.4	n.m.	
DH-8	TG	-645	n.a.	9.0	-353	0.03	0.03	n.m.	n.m.	
DH-8	TG	-697	n.a.	8.5	-274	0.19	0.17	4.2	n.m.	-90[6]
DH-8	TG	-749	n.a.	8.4	-298	0.18	0.21	3.7	n.m.	
DH-8	TG	-872	n.a.	8.8	-305	0.07	0.08	3.1	n.m.	
DH-8	TG	-978	n.a.	8.8	-364	0.19	0.2	1.7	n.m.	
DH-9[4]	TG	-235	n.a.	8.4	-277	0.12	<0.05	1.8	n.m.	
DH-9[4]	TG	-316	n.a.	8.5	-319	0.46	<0.05	1.8	n.m.	
DH-9[4]	TG	-961	n.a.	8.3	-250	0.53	<0.05	3.1	n.m.	
DH-10[4]	TG	-338	n.a.	8.5	-254	0.06	<0.05	15.6	n.m.	
DH-12	TG	-226	-57	9.3	-28	<0.05	<0.05	<0.04	n.m.	
DH-12	TG	-452	-283	9.2	-33	<0.05	<0.05	<0.04	n.m.	
DH-12	TG	-409	-240	8.9	-36	<0.05	<0.05	<0.04	n.m.	
DH-12	TG	-367	-198	8.9	-90	<0.05	<0.05	<0.04	n.m.	
DH-12	TG	-312	-143	9.2	-34	<0.05	<0.05	<0.04	n.m.	
DH-13	TG	-67	-26	8.1	57	<0.05	<0.05	6.9	n.m.	
DH-13	TG	-425	-384	8.4	-7	<0.05	<0.05	5.5	n.m.	
MIU-4	TG	-99	-26	9.2	-304	0.07	<0.05	3.1	n.m.	
MIU-4	TG	-273	-227	9.4	75	0.06	<0.05	<0.3	n.m.	
MIU-4	TG	-533	-527	9.2	17	<0.05	<0.05	<0.3	n.m.	

* Bhl refers to borehole (all of which lie within a 10 km x 10 km area roughly centered on the Tono mine); Frm denotes formation (see Fig. 1); depth refers to sampling depth (meters below ground level, mbgl), which is taken to be the midpoint between packers; uncnf stands for vertical distance from the sampling depth to the TG-TL unconformity; Eh_c refers to calculated Eh assuming equilibrium for the indicated redox couple; n.a denotes not applicable (*i.e.*, because the TG-TL unconformity was not encountered in the borehole); n.m indicates not measured. [1] minimum depth; [2] maximum elevation; [3] approximate vertical distance from the unconformity; [4] sample may be contaminated with drilling fluid; [5] calculated assuming equilibrium for the reaction $SO_4^{2-} + 9H^+ + 8e^- = HS^- + 4H_2O$ (log K = 33.7, at 25°C); [6] calculated assuming equilibrium for the reaction $Fe^{3+} + e^- = Fe^{2+}$(log K = 13.01, at 25°C).

Figure 1. Geological cross section through the Tono mine area. The Neogene Mizunami Group includes the Lower and Upper Toki Lignite-bearing Formations (TL and TU, respectively), Akeyo Formation (A) and Oidawara Formation (O), and consists of lacustrine/marine sequences of conglomerates and tuffaceous sandstones, siltstones and mudstones. The Pliocene Seto Group includes the Tokiguchi Porcelain Clay, which is overlain by gravels composed of chert, rhyolite and granite. Groundwater is locally recharged in the vicinity of the fault indicated in the figure by the solid and broken line, and flows from NW to SE along the unconformity between the Cretaceous Toki granite (TG) and the Lower Toki Lignite-bearing Formation.

REDOX FRONTS AND REDOX-CONTROLLING REACTIONS

Redox environment near the TG-TL unconformity

The TG-TL unconformity represents the approximate location of a redox front separating relatively oxidizing groundwaters in the Toki granite from strongly reducing pore fluids in sedimentary rocks of the Mizunami Group (Fig. 2). Reducing groundwaters are present in the Toki granite (Table I), but the relation between sampling depth and distance from the unconformity is unknown for these solutions. The oxidizing groundwaters thus appear to occupy a region several hundred meters thick wedged between two reducing systems: one located just above, and the other well below, the unconformity. Different sampling techniques have been used to measure Eh. Surface flow-through cell measurements (DH-12, DH-13 and MIU-4 samples, Table I) may be less reliable than down-hole techniques used to measure Eh *in-situ*. Thus the relatively oxidizing solutions (Eh > 0) measured in fluids slightly above the unconformity (DH-12/ -161 mbgl and MIU-4/ -74 mbgl, Table I) and reducing groundwaters (Eh < 0) below the unconformity (MIU-4/ -99 mbgl, Table I) may be measurement artifacts.

Eh-pH relations

Insights into potential redox-controlling reactions are inferred from the equilibrium stability relations shown in Fig. 3. Reducing groundwaters plot near the pyrite/solution and SO_4^{2-}/HS^- equilibrium boundaries. Pyrite is present in trace amounts in the TL and TU, and also occurs as fresh, unweathered crystals in relatively deep, intact zones of the Toki granite. The intact zones have experienced less rapid groundwater flow than the more intensely fractured zones in the upper TG. Calculated Eh values assuming equilibrium for the SO_4^{2-}/HS^- redox couple are

Figure 2. Distribution of measured redox potentials in relation to the TG-TL unconformity.

roughly consistent with the limited available Eh measurements in groundwaters from the Lower Toki Lignite-bearing Formation (Fig. 2).

The relatively oxidizing groundwaters plot well above the pyrite/solution and SO_4^{2-}/HS^- equilibrium boundaries (Fig. 3). This is consistent with the observation that pyrite crystals in moderately and intensely fractured zones of the TG commonly exhibit dissolution textures at

Figure 3. Eh-pH diagrams for the $Fe\text{-}O_2\text{-}S\text{-}CO_2\text{-}H_2O$ system at 25°C and 1 bar. Activity of Fe species = 10^{-6} (Fig. 3a) and 10^{-5} (Fig. 3b). Fugacity of $CO_2(g) = 10^{-5}$ (Fig. 3a) and 10^{-3} (Fig. 3b). Activity of S species = 10^{-5}. The ranges in Fe activities and $CO_2(g)$ fugacities considered in these figures bound the ranges observed in most Tono groundwaters. Dashed lines in Fig. 3b are as labeled in Fig. 3.a.

depths to about 800 mbgl, suggesting that this mineral may have reacted with groundwaters that are relatively oxidizing [2], and also consistent with SEM-EDS analyses indicating the presence of Fe(III)-oxyhydroxides in microfractures in the Toki granite at depths to at least 132 mbgl [2].

Redox controlling reactions

The presence of Fe(III)-oxyhydroxides at considerable depths in the Toki granite is important because reactions among these minerals may be sufficiently fast (*e.g.*, [7]) to control redox potentials in accordance with heterogeneous reactions that can be generally written:

$$Fe(OH)_3(s) + 3H^+ + e^- = Fe^{2+} + xH_2O, \tag{1}$$

where $Fe(OH)_3$ (s) refers to an Fe(III)-oxyhydroxide and the value of x depends on the oxyhydroxide s stoichiometry [*e.g.*, $x = 3$ for $Fe(OH)_3(am)$, $x = 2$ for goethite (α-FeOOH)]. To evaluate this possibility, the Eh corresponding to reaction (1) is calculated using [*e.g.*, 5]:

$$Eh = E^{0*} - 2.303\frac{RT}{F}\left(3\mathrm{pH} + \log\{Fe^{2+}\}\right) \tag{2}$$

where,

$$E^{0*} = E^0 + 2.303\frac{RT}{F}\log K^*, \tag{3}$$

and R refers to the gas constant, T denotes temperature, F stands for the Faraday constant, E^0 represents the standard half-cell potential for the reaction $Fe^{2+} = Fe^{3+} + e^-$ (0.771 V) and K^* refers to an equilibrium constant for the reaction:

$$Fe(OH)_3(s) + 3H^+ = Fe^{3+} + xH_2O \tag{4}$$

The concentration of Fe^{2+} (*i.e.*, $\{Fe^{2+}\}$), in Eqn. (2) must be evaluated for conditions at Tono using the following equation, which accounts for speciation of ferrous iron among $FeOH^+$, $FeHCO_3^+$ and $FeCO_3(aq)$,:

$$\{Fe^{2+}\} = \frac{Fe(II)_{tot}}{1 + \frac{\beta_1}{\{H^+\}} + \beta_2\{HCO_3^-\} + \frac{\beta_3\{HCO_3^-\}}{\{H^+\}}}, \tag{5}$$

where $Fe(II)_{tot}$ refers to total analytical concentration, and β_1, β_2 and β_3 denote association constants for $FeOH^+$, $FeHCO_3^+$ and $FeCO_3(aq)$, respectively. The values adopted in the present study at $T = 25°C$, are $\log \beta_1 = -9.3$, $\log \beta_2 = 2.7$ and $\log \beta_3 = -5.6$ [6]. The Fe(III) oxyhydroxides considered include freshly precipitated, amorphous $Fe(OH)_3(am)$ ($\log K^* = 4.3$ [6]), a solid of intermediate crystallinity representing aged $Fe(OH)_3$ (am) ($\log K^* = 3.0$ [7]), fine-grained goethite ($\log K^* = 1.1$ [8]) and coarse-grained goethite ($\log K^* = -2.2$ [8]). Particle-size effects on the solubilities of these minerals are accounted for using the approach described in reference [7].

Results are summarized in Fig. 4, where Eh values calculated using Eqn. (2) are plotted as a function of the quantity (3pH + log $\{Fe^{2+}\}$), and compared to Eh measurements (Table I) for groundwaters in which $Fe(II)_{tot}$ exceeds the detection limit (≈ 0.05 ppm). As can be seen, there is reasonably good agreement between calculated and measured Eh values among all the groundwater samples if it is assumed that the crystallinity of the oxyhydroxide can vary from freshly precipitated amorphous $Fe(OH)_3(am)$ to fine-grained goethite. Precipitation of $Fe(OH)_3(am)$ is instantaneous, and the growth rate of an X-ray or SEM identifiable phase from this solid precursor may take hours to years depending on temperature and aqueous concentrations of Fe(II) and Fe(III) [7]. Although the results in Fig. 4 suggest redox control by the Fe(III)-oxyhydroxides, it is not possible to conclude generally that these solids also control the Eh of samples in which Fe(II) concentrations are below the detection limit. This limit [*i.e.*, 0.05 ppm Fe(II)] may also represent the minimum concentration of Fe(II) needed to obtain stable and reproducible Eh measurements in systems containing Fe(III) solids and dissolved Fe(II) [5].

REDOX-FRONT MIGRATION

The propagation velocity of an oxidizing front across the unconformity from the upper, fractured and relatively oxidizing groundwater zone of the Toki granite into the reducing Lower Toki Lignite-bearing Formation is estimated using the following equation derived from the stationary-state approximation to coupled fluid flow and water-rock interaction, (*e.g.*, [9][10]):

$$v_f = \frac{v\{\psi_j\}}{\sum_{r=1}^{M} \left(\frac{\upsilon_{j,r}}{\overline{V}_r}\right)\{\phi_r\}}. \qquad (6)$$

In this equation v_f refers to the velocity of the redox front, v stands for the Darcy velocity of the fluid, $\upsilon_{j,r}$ represents the stoichiometric coefficient for the j-th aqueous reactant in a balanced dissolution reaction (which may include oxidation/reduction) involving the r-th mineral, $\overline{V}_r$ denotes molar volume, and $\{\psi_j\}$ and $\{\phi_r\}$ refer to differences in the generalized concentration of the j-th reactant and volume fraction of the r-th mineral measured between upstream and downstream points on either side of the front.

We assume that dissolved oxygen (DO) is the only oxidant present in solutions migrating into the TL from the TG, and j therefore refers only to the aqueous species $O_2(aq)$. Although other potential oxidants, including Fe^{3+} and SO_4^{2-}, could be considered in the model, we neglect them at this preliminary level of analysis pending further characterization of reactions associated with the redox front. Three constraints on DO concentrations are assumed: 1) the measured Eh and pH of relatively oxidizing TG groundwaters sampled in the KNA-6 borehole (Table I) and equilibrium for the half-cell reaction $O_2(aq) + 4H^+ + 4e^- = 2H_2O(l)$ (DO ≈ 10^{-52} ppm), 2) the analytical detection limit (DO = 2 ppm) , and 3) equilibrium with atmospheric $O_2(g)$ ($P_{O2(g)}$ = 0.21 bar) at 25°C (DO = 8.5 ppm). Dissolved oxygen in the TL is assumed to be fixed by the Eh and pH measured in the KNA-6 borehole (Table I), and equilibrium for the $O_2(aq)$ half-cell reaction noted above (DO ≈ 10^{-72} ppm). Groundwater flow models and relative ^{14}C groundwater ages [2] suggest that the horizontal Darcy flux along the unconformity is about 0.08 m yr^{-1}. Here we assume that groundwater flows into the TL from the TG at this rate, and ignore additional inflow from the surface through sediments of the Mizunami Group. It is assumed that $O_2(aq)$

Figure 4. Comparison of redox potentials calculated assuming dissolution/precipitation reactions involving an Fe(III)-oxyhydroxide are redox controlling versus measured Eh values in groundwater samples from the TG and TL. Error bars correspond to the precision of the Eh measurements (± 10 mV). Sample labels refer to borehole/sampling depth (see Table I).

migrating into the TL reacts with pyrite according to the reaction $FeS_2 + 15/4O_2(aq) + 1/2H_2O(l) = Fe^{3+} + H^+ + 2SO_4^{2-}$, for which $\upsilon_{j,r} = 3.75$. The volume fraction of pyrite in the TL is assumed to be 0.004 [11], and the molar volume of this mineral is 23.94 $cm^3\ mol^{-1}$[6].

Results using Eqn. (6) and the above assumptions and constraints indicate that $v_f = 7 \times 10^{-57}$ m yr^{-1} if DO in the infiltrating TG groundwaters = 10^{-52} ppm, 7.9×10^{-6} m yr^{-1} if DO = 2 ppm, and 3.4×10^{-5} m yr^{-1} if DO = 8.5 ppm. Thus, during the 10 million years that U is thought to have been immobilized in the Tono ore body, a redox front would not have migrated a detectable distance into the TL if DO in the infiltrating TG groundwaters = 10^{-52} ppm. The front would have migrated about 80 m if DO = 2 ppm and 340 m if DO = 8.5 ppm. In the latter two cases, the front would have passed completely through the TL, contrary to observations.

CONCLUSIONS

The unconformity underlying the Tono uranium deposit coincides with the location of a redox front separating relatively oxidizing groundwaters in the Toki granite from strongly reducing pore fluids in the Lower Toki Lignite-bearing Formation. Stable and reversible redox potentials measured *in-situ* and in surface flow-through cells appear to be controlled by the Fe(III)-oxyhydroxide — Fe^{2+} redox couple, but it is unclear whether this is also the case for groundwaters in which total dissolved Fe(II) is below the detection limit. The propagation of the redox front

from the TG into the TL is predicted to be essentially immeasurable over 10 million years if the concentration of $O_2(aq)$ in TG groundwaters is consistent with present-day measurements of Eh and pH, and equilibrium for the half-cell reaction $O_2(aq) + 4H^+ + 4e^- = 2H_2O(l)$. Front velocities calculated by conservatively assuming that $O_2(aq)$ concentrations are near the analytical detection limit for this species are sufficiently fast that the front would have migrated through the TL within 10 million years. The immobilization of uranium within the Tono deposit for this period of time thus appears attributable to oxidation-reduction reactions that minimize $O_2(aq)$ concentrations primarily in the TG, and secondarily in the TL.

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