

JNC TJ7400 2005-049

鉍物を用いた長期的地球科学環境の解析調査

(核燃料サイクル開発機構 契約業務報告書)

2004年3月

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要旨

本業務では花崗岩中の割れ目に産する方解石中の微量元素に基づき、方岩石沈殿時の酸化還元環境を推察する手法を開発した。

本手法では、方解石と共存した地下水中の幾つかの陽イオンの濃度の範囲を実験により求められた方解石中に共沈する陽イオンの分配係数より求め、それら陽イオンの酸化還元平衡式を仮定し、推察した方解石沈殿時の地下水中の陽イオンの濃度にもとづいて酸化還元平衡式を計算することで酸化還元電位を求めた。陽イオンが複数の価数を取り得る場合には、それぞれの価数の陽イオンの活動度を推察し、それぞれの価数の酸化還元電位を推察するための **Nernstian** 曲線を求めた。

予察的な結果では、土岐花崗岩中の地下水の **U**、**Fe**、**Mn** 濃度は、多くの場合、割れ目に産する方解石中の **U**、**Fe**、**Mn** 濃度から推察した値とほぼ一致している。このことは、方解石が沈殿した時点の地下水中のこれらの元素の濃度が、現在の地下水中の **U**、**Fe**、**Mn** の濃度とほぼ一致することを示している。

UO₂ (am) と細粒針鉄鉍を仮定した酸化還元平衡式から推察できる **Eh** および **pH** の値が重複している範囲は、それぞれの鉍物が共存し、土岐花崗岩中の方解石およびその方解石が沈殿した時の地下水と平衡であるための条件を示している。つまり、この領域は方解石形成時の地下水における **Eh-pH** 条件を示している。この領域は白金電極を用いて計測した現在の土岐花崗岩中の深部の地下水から得られる値とよく一致しており、現在の地下水の酸化還元状態が方解石沈殿時の酸化還元状態から変化していないことを示している。ただし、本手法における各元素の分配係数や酸化還元平衡条件については、更に検討を進める必要がある。

本報告書は三菱商事株式会社が、核燃料サイクル開発機構との契約により実施した業務の結果である。

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Interpretation of paleoredox environments based on the trace-element content of authigenic calcites

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March 2004

Summary

This study develops an approach that can be used to interpret redox conditions in paleo-groundwaters based on the trace-element content of late-stage fracture calcites. Ranges in total concentrations of selected cations in groundwaters coexisting with calcite are first calculated using analytical data on mineral chemistry and experimentally determined partition coefficients for co-precipitation of the cations in calcite. In cases where the cations can exist in two or more oxidation states, activities of the free divalent cations are also calculated and these activities are then used to calculate the Eh of half-cell reactions having different Nernstian slopes on an Eh-pH diagram. Domains defined by the intersection of the resultant curves are used to interpret paleo-redox environments that are consistent with an assumption of equilibrium for the respective half-cell reactions.

Preliminary results indicate that U, Fe and Mn concentrations in granite groundwaters of the Tono region are in most cases bounded by calculated values based on the U, Fe and Mn contents of late-stage calcites. This suggests that the concentrations of these elements in present-day groundwaters are comparable to those in groundwaters that were present at the time of calcite precipitation.

Overlapping ranges in calculated Eh-pH values for heterogeneous reactions involving $\text{UO}_2(am)$ and fine-grained goethite define specific redox environments that are necessary for both these minerals to coexist at equilibrium with an aqueous phase and with calcites having Fe and U contents comparable to those observed in calcites of the Toki granite. This region thus defines credible bounds on Eh-pH conditions in groundwaters that were present when these calcites formed. These bounds are closely consistent with *in-situ* Eh measurements obtained using Pt electrodes and groundwater samples from deep boreholes in the Toki granite, suggesting that the redox environment of contemporary groundwaters is comparable to that of groundwaters that were present at the time of calcite precipitation. It should be emphasized that there are significant uncertainties in the experimental partition coefficients used in this approach, and that the key assumption of redox equilibrium, which underpins the approach, may not be valid in all cases.

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1 Background

The Japan Nuclear Cycle Development Institute (JNC) is investigating the hydrogeology and hydrochemistry of the deep groundwater system in the Tono area of Gifu-ken, central Japan. Calcite mineralization associated with the fracture flow system in the basement Toki granite is being studied as part of these investigations. The morphology, isotopic composition and trace-element content of calcite crystals lining fracture surfaces will be used as indicators of paleohydrochemical and paleohydrogeological conditions.

The British Geological Survey (BGS) is assisting JNC in this effort through the provision of analyses and interpretations of the microchemical and petrographic characteristics of at least 20 samples of fracture calcites. The BGS will analyze the trace element compositions of the samples using Laser Ablation Microprobe – Inductively Coupled Plasma-Mass Spectrometry (LAMP). Concentrations of the following elements will be determined in each analysis: Ca, Mg, Fe, Cu, Mn, Sr, Ba, Pb, U, Th, La, Ce, Pr, Nd, Sm, Eu and Y. At least 6 such analyses will be obtained for each sample. Optical petrographical images and high-quality optical cold-cathodoluminescence (CL) images will be obtained to help target areas of specific interest for the LAMP analyses. The BGS will also evaluate and interpret the mineral chemical data in relation to calcite petrography.

2 Objectives

The objective of the present study is to assist JNC in carrying out thermodynamic interpretations of the LAMP analytical data and other characterization data obtained by JNC and the BGS. A comprehensive work program, summarized below, will be needed to accomplish this objective. It is important to emphasize, however, that studies carried out during FY03 address only Tasks 2 and 3.

1. *Literature review.* A literature review is needed to evaluate studies in other fields that have used a similar approach to that described in Section 3. Such studies have focused mainly on paleo-redox conditions inferred from the trace-element contents of carbonate cements in shallow fresh-water aquifers. An unpublished study for Nagra that purportedly describes a similar approach, and which details the strengths and limitations of the approach, should also be reviewed.
2. *Evaluation/selection of trace-element partition coefficients.* Recent critical evaluations of partition coefficients for cations co-precipitated in carbonate minerals should be reviewed. In FY03, values will be selected for the elements considered in the models described in Section 3. Total reported ranges in these values will also be compiled. These ranges are important because they may reflect differences in calcite precipitation kinetics and (or) the effects of coupled substitutions among different trace elements.
3. *Development of thermodynamic models.* Thermodynamic models will be developed for selected pairs of redox-sensitive trace elements to be determined in the LAMP analyses (*e.g.*, Fe, Mn, Cu, Pb and/or U). Models for U and Fe that were developed in the previous study for JNC, noted above, will be reviewed and revised if necessary. An exploratory effort will also be undertaken in FY03 to develop a model for Mn. Models for Fe and Mn may be particularly relevant to the present study because the CL properties of calcite depend on the relative concentrations of co-precipitated Fe(II) and Mn(II), which suggests that these CL properties could be correlated in principle with the redox environment at the time of precipitation. Development of a suitable model for Mn(II) may be difficult, however, because aqueous Mn concentrations are likely to be controlled by the solubility of complex, non-stoichiometric oxyhydroxides incorporating mixed valence states of Mn, and because the composition and crystallinity of these oxyhydroxides may vary with the environment in which they formed.

4. *Model application.* The LAMP analyses to be obtained by the BGS in FY 03, plus earlier BGS LAMP analyses of fracture calcites in drillcore from MIU-3, will be interpreted using the thermodynamic models developed in this project. The models will be used for two purposes:
- to estimate total concentrations of Ca and trace elements in groundwaters present at the time these elements were co-precipitated in calcite, and
 - to infer upper and lower bounds on the range of Eh-pH conditions in these groundwaters.
5. *Synthesis/integration.* Interpretations of paleohydrochemical conditions using the thermodynamic models developed in this project will be integrated with the results of other studies carried out by JNC and the BGS characterizing the isotopic and petrographic properties of fracture calcites. Results will be examined primarily for evidence of similarities and differences in the chemistry of present-day and paleogroundwaters of the Tono region.

3 Description of thermodynamic models

The general modeling approach used in the present study was developed in an earlier study for JNC by Monitor Scientific, LLC. In this approach, ranges in total concentrations of selected cations in groundwaters coexisting with the surface of a calcite crystal at the time of its precipitation are first calculated using the LAMP analytical data and experimentally determined partition coefficients for co-precipitation of the cations in calcite. In cases where the cations can exist in two or more oxidation states, activities of the free divalent cations are also calculated and these activities are used to calculate the Eh of half-cell reactions having different Nernstian slopes on an Eh-pH diagram. Domains defined by the intersection of these slopes can be interpreted to indicate paleo-redox conditions if the underlying assumption of equilibrium is valid for the half-cell reactions considered. Caution is needed in such interpretations, however, because there are significant uncertainties in the experimental partition coefficients, and in other aspects of the thermodynamic calculations, and because redox disequilibrium among certain redox couples is a common characteristic of groundwater systems.

Thermodynamic models that were developed in this study for interpretation of paleo-redox conditions in groundwaters of the Toki granite are summarized in Table 3_1. The model for U is based on the observation that groundwaters in the Tono region often appear to be at equilibrium with respect to an amorphous UO_2 solid (Fig. 3_1). The model for Fe is based on the observation that the redox potentials of groundwaters in the Toki granite, measured *in-situ* using a Pt electrode installed in downhole chemical probes, appear to be closely approximated by potentials corresponding to half-cell reactions involving amorphous Fe(III) oxyhydroxide or fine-grained goethite (Fig. 3_2). The model for Mn is based on the assumption that a “fictive” MnO_2 solid that is considerably more stable than pyrolusite effectively represents the complex Mn oxides and oxyhydroxides that are likely to be present in the Toki granite (Barnaby and Rimstidt, 1989).

Data supporting these models are given in Table 3_2. Most of the equilibrium constants are taken from Arthur *et al.* (2003). Standard Gibbs energies of formation (from the elements) at 25°C and 1 bar for MnHCO_3^+ and $\text{MnCO}_3(aq)$ from Nordstrom *et al.* (1990) were used to calculate values of K_{11} and K_{12} . The approach used to evaluate particle-size effects on the stability of goethite is

Table 3_1. Thermodynamic models of redox conditions interpreted from the U, Fe and Mn contents of calcite.

1. Assumptions

- $T = 25^\circ\text{C}$,
- $P = 1 \text{ bar}$
- ionic concentrations = activities
- equilibrium for all homogeneous and heterogeneous reactions.

2. Calculate total dissolved Ca concentrations in groundwaters equilibrated with calcite as a function of pH and $P_{\text{CO}_2(\text{g})}$:

$$[\text{Ca}] = K_{cc} \left(\frac{[\text{H}^+]^2}{K_3 P_{\text{CO}_2(\text{g})}} + \frac{1}{K_1} + \frac{[\text{H}^+]}{K_2} \right),$$

where,

$[\text{Ca}]$ – total dissolved concentration of Ca (mol kg⁻¹),

$P_{\text{CO}_2(\text{g})}$ – partial pressure of CO₂(g) (bar)

K_{cc} – equilibrium constant for the reaction $\text{CaCO}_3(c) + \text{H}^+ = \text{Ca}^{2+} + \text{HCO}_3^-$,

K_1 – equilibrium constant for the reaction $\text{CaCO}_3(aq) + \text{H}^+ = \text{Ca}^{2+} + \text{HCO}_3^-$,

K_2 – equilibrium constant for the reaction $\text{CaHCO}_3^+ = \text{Ca}^{2+} + \text{HCO}_3^-$, and

K_3 – equilibrium constant for the reaction $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(l) = \text{H}_+ + \text{HCO}_3^-$

3. Calculate corresponding total dissolved concentrations of all divalent U, Fe and Mn species using experimental partition coefficients for the co-precipitation of these species in calcite:

$$[\text{Me(II)}] = \frac{X_{Me}^{cc} [\text{Ca}]}{X_{Ca}^{cc} \lambda_{Me}^{cc}},$$

where,

$[\text{Me(II)}]$ – total dissolved concentration of divalent species of the metal Me (*i.e.*, U, Fe, Mn)

X_{Me}^{cc} – mol fraction of the divalent cation in calcite,

X_{Ca}^{cc} – mol fraction of Ca in calcite (≈ 1), and

λ_{Me}^{cc} – partition coefficient for coprecipitation of Me in calcite.

4. U model

For the half-cell reaction $\text{UO}_2^{2+} + 2e^- = \text{UO}_2(am)$

$$Eh = 0.193 + 0.03 \log[\text{UO}_2^{2+}]$$

where,

$$[UO_2^{2+}] = \frac{[U(II)]}{\left(1 + \frac{1}{K_4[H^+]^3} + \frac{K_3^2 P_{CO_2(g)}^2}{K_5[H^+]^4} + \frac{K_3^3 P_{CO_2(g)}^3}{K_6[H^+]^6}\right)},$$

and,

$[UO_2^{2+}]$ – concentration of the free aqueous species UO_2^{2+} (mol kg⁻¹),
 K_4 – equilibrium constant for the reaction $UO_2(OH)_3^- + 3H^+ = UO_2^{2+} + 3H_2O(l)$,
 K_5 – equilibrium constant for the reaction $UO_2(CO_3)_2^{2-} + 2H^+ = UO_2^{2+} + 2HCO_3^-$, and
 K_6 – equilibrium constant for the reaction $UO_2(CO_3)_3^{4-} + 3H^+ = UO_2^{2+} + 3HCO_3^-$

5. Fe Model

For the half-cell reaction “ $Fe(OH)_3(s)$ ” + $3H^+ = Fe^{2+} + xH_2O(l)$, 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 $Fe(OH)_3(am)$ and $x = 2$ for goethite (α - $FeOOH$)],

$$Eh = E^{0*} - 0.059(3pH + \log[Fe^{2+}]),$$

where,

$$E^{0*} = E^0 + \frac{2.303RT}{F} \log K^*,$$

$$[Fe^{2+}] = \frac{[Fe(II)]}{\left(1 + \frac{K_7}{[H^+]} + \frac{K_8 K_3 P_{CO_2(g)}}{[H^+]} + \frac{K_9 K_3 P_{CO_2(g)}}{[H^+]^2}\right)},$$

and,

$[Fe^{2+}]$ – concentration of the free aqueous species Fe^{2+} (mol kg⁻¹),
 E^0 – standard potential for the reaction $Fe^{2+} + e^- = Fe^{3+}$ (0.771 V)
 R – gas constant (0.001987 kcal °K⁻¹ mol⁻¹),
 F – Faraday constant (23.061 kcal V⁻¹ eq⁻¹),
 K^* – equilibrium constant for the reaction “ $Fe(OH)_3(s)$ ” + $3H^+ = Fe^{3+} + xH_2O(l)$ [$\log K^* = 4.3$ ($Fe(OH)_3(am)$), = 1.1 (fine-grained goethite), and = -2.2 (coarse-grained goethite),
 K_7 – equilibrium constant for the reaction: $Fe^{2+} + H_2O(l) = FeOH^+ + H^+$,
 K_8 – equilibrium constant for the reaction: $Fe^{2+} + HCO_3^- = FeHCO_3^+$,
 K_9 – equilibrium constant for the reaction: $Fe^{2+} + HCO_3^- = FeCO_3(aq) + H^+$.

6. Mn model

For the half-cell reaction “ MnO_2^* ” + $4H^+ + 2e^- = Mn^{2+} + 2H_2O(l)$, where “ MnO_2^* ” represents a fictive Mn(IV) oxide that is assumed to be more stable than pyrolusite (*i.e.*, ΔG_f^0 for “ MnO_2^* ” = -131.3 kcal mol⁻¹, see Barnaby and Rimstidt, 1989):

$$Eh = 0.806 - 0.03(4pH + \log[Mn^{2+}]),$$

where,

$$[Mn^{2+}] = \frac{[Mn(II)]}{\left(1 + \frac{K_{10}}{[H^+]} + \frac{K_{11}K_3P_{CO_2(g)}}{[H^+]} + \frac{K_{12}K_3P_{CO_2(g)}}{[H^+]^2}\right)}$$

and,

$[Mn^{2+}]$ – concentration of the free aqueous species Mn^{2+} (mol kg⁻¹),
 K_{10} – equilibrium constant for the reaction $Mn^{2+} + H_2O(l) = MnOH^+ + H^+$,
 K_{11} – equilibrium constant for the reaction $Mn^{2+} + HCO_3^- = MnHCO_3^+$,
 K_{12} – equilibrium constant for the reaction $Mn^{2+} + HCO_3^- = MnCO_3(aq) + H^+$.

Table 3_2. Data supporting thermodynamic models of paleo-redox conditions.

Parameter	Value	Range
K_{cc}	$10^{1.85}$	
K_1	$10^{7.0}$	
K_2	$10^{-1.05}$	
K_3	$10^{-7.81}$	
K_4	$10^{19.25}$	
K_5	$10^{3.75}$	
K_6	$10^{9.43}$	
K_7	$10^{-9.32}$	
K_8	$10^{2.72}$	
K_9	$10^{-5.6}$	
K_{10}	$10^{-10.62}$	
K_{11}	$10^{1.51}$	
K_{12}	$10^{-5.87}$	
λ_{U}^{cc}	0.04	0.01 – 0.26
λ_{Fe}^{cc}	2.7	1.5 – 7.7
λ_{Mn}^{cc}	15.0	3.1 - 51
U^{cc} (ppb)		0.1 – 10.0
Fe^{cc} (ppm)		1,000 – 10,000
Mn^{cc} (ppm)		1,000 – 10,000
$\log P_{CO2(g)}$	$= -5.5303 + 1.1712pH - 0.17628pH^2$	

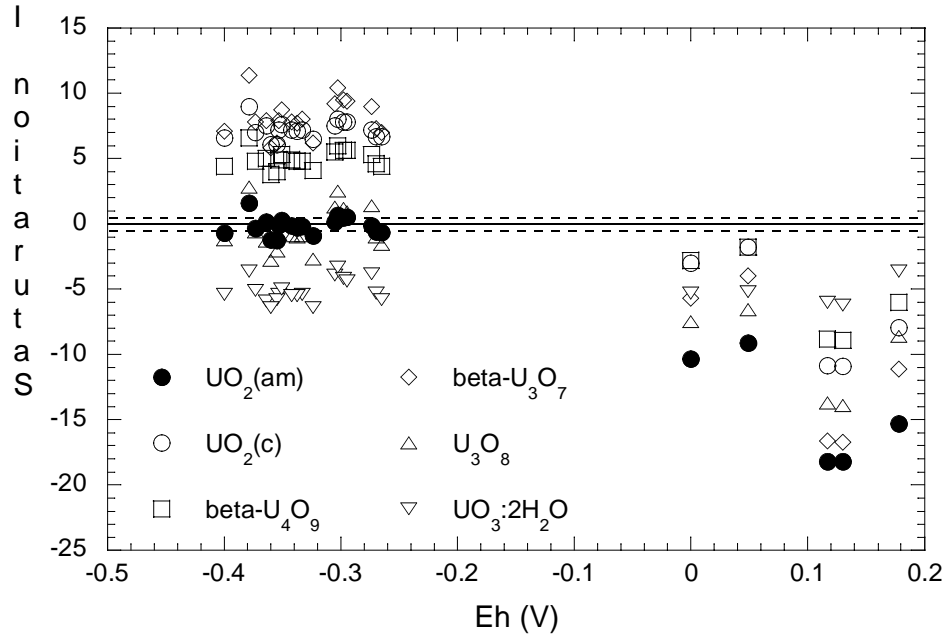


Figure 3_1. Calculated saturation indexes (SI) for various U(IV) and U(VI) oxides in contact with groundwaters of the Tono region (Arthur et al., 2003). SI values near 0 for $UO_2(am)$ suggest that reducing groundwaters are equilibrated with this solid.

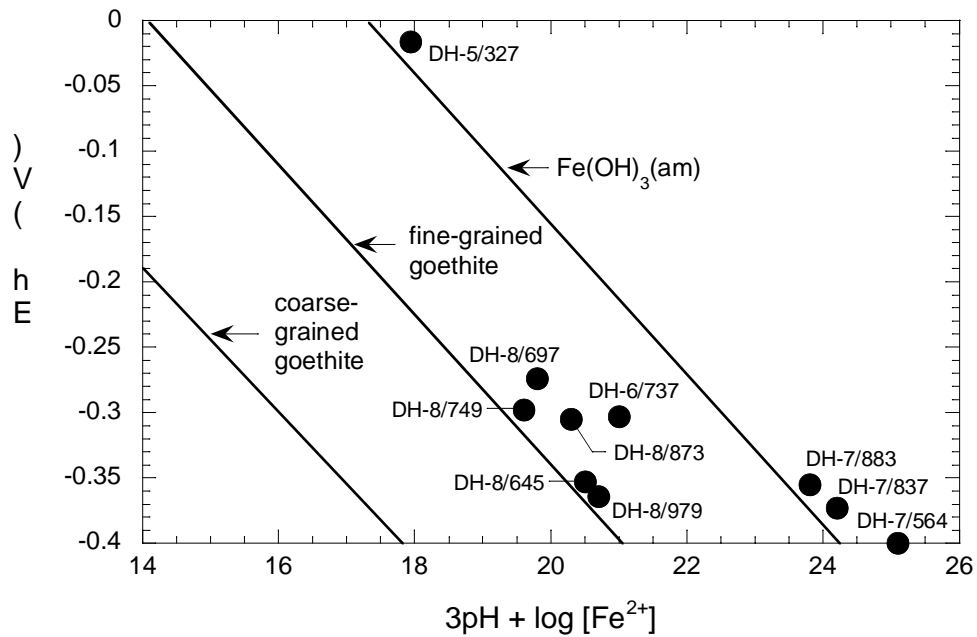


Figure 3_2. Comparison of redox potentials calculated assuming heterogeneous reactions involving an Fe(III)-oxyhydroxide are redox controlling versus in-situ Eh values measured using a Pt electrode in downhole chemical probes. Sample labels refer to boreholes drilled into the Toki granite and sampling depth (mbgl).

described by Langmuir (1997). The partition coefficients for U, Fe and Mn in Table 3_2 are from Curti (1999) and Rimstidt *et al.* (1998). Bounding ranges in the concentrations of these elements in late-stage, fracture-lining calcites in the Toki granite (*i.e.*, the parameters U^{cc} , Fe^{cc} and Mn^{cc} in Table 3_2) are based on LAMP analyses reported by Milodowski *et al.* (2001). The polynomial expression relating $P_{CO_2(g)}$ to pH is based on an empirical correlation between these parameters groundwaters of the Toki granite (Fig 3_3).

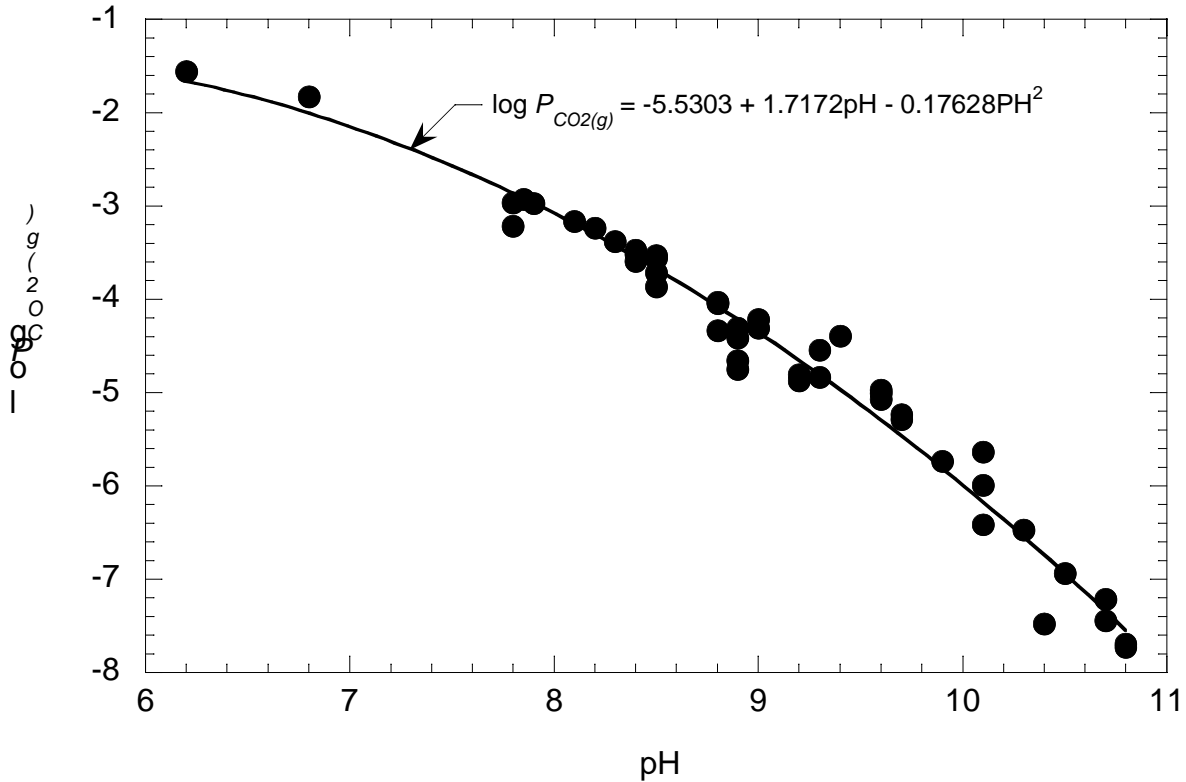


Figure 3_3. Empirical correlation between pH and $P_{CO_2(g)}$ in groundwaters of the Toki granite.

4 Discussion of results

Calculated aqueous concentrations of U(II; *i.e.*, as total UO_2^{2+}), Fe(II) and Mn(II) using the models described in Section 3 are compared in Figs. 4_1, 4_2 and 4_3, respectively, with concentrations of the respective elements observed in present-day groundwaters of the Toki granite. As can be seen in Fig. 4_1, total U concentrations in the contemporary groundwaters are bounded by calculated values based on the U contents of late-stage calcites. This suggests that U concentrations in the present-day groundwaters are comparable to those in groundwaters that were present at the time of calcite precipitation.

Figs. 4_2 and 4_3 indicate similar agreement for Fe and Mn, respectively, with a few notable exceptions. The Fe and Mn concentrations of deep groundwaters from borehole DH-7 are much higher than values predicted using the respective models and measured Fe and Mn contents of fracture calcites (Fig 4_2). The concentration of Mn in groundwater from borehole DH-5 is also

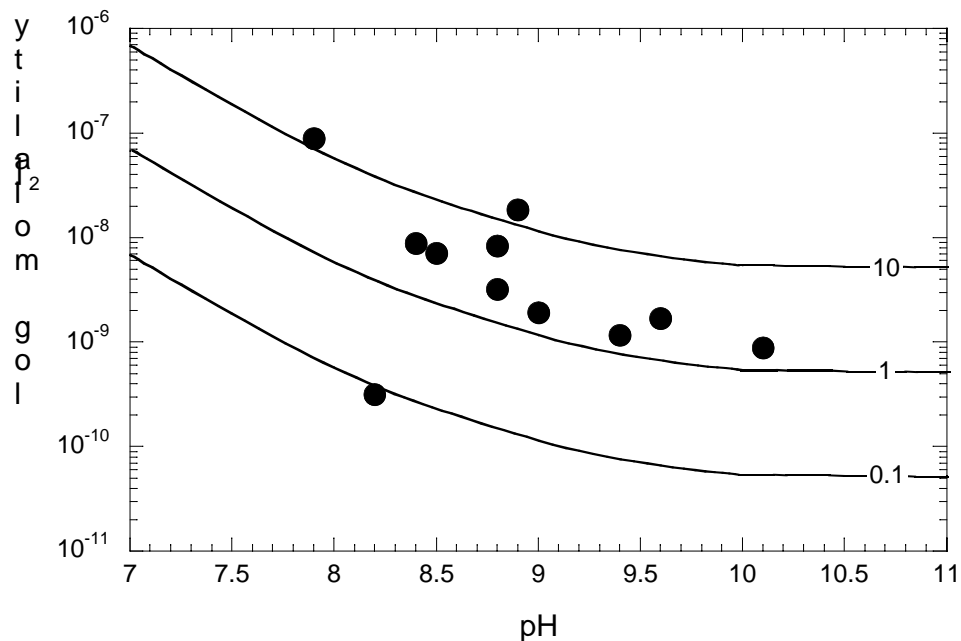


Figure 4_1. Comparison of aqueous U concentrations in contemporary groundwaters of the Toki granite (symbols) with their calculated counterparts using the models in Table 3_1 and measured U contents of authigenic calcites (lines). The labels on the calculated curves represent U concentrations in calcite (ppb).

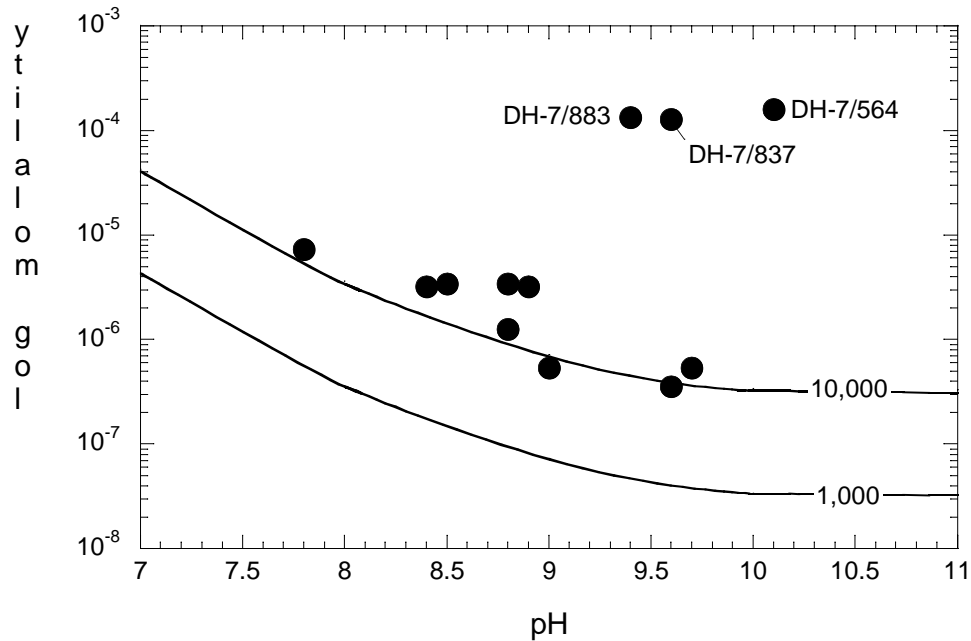


Figure 4_2. Comparison of aqueous Fe concentrations in contemporary groundwaters of the Toki granite (symbols) with their calculated counterparts using the models in Table 3_1 and measured Fe contents of authigenic calcites (lines). The labels on the calculated curves represent Fe concentrations in calcite (ppm).

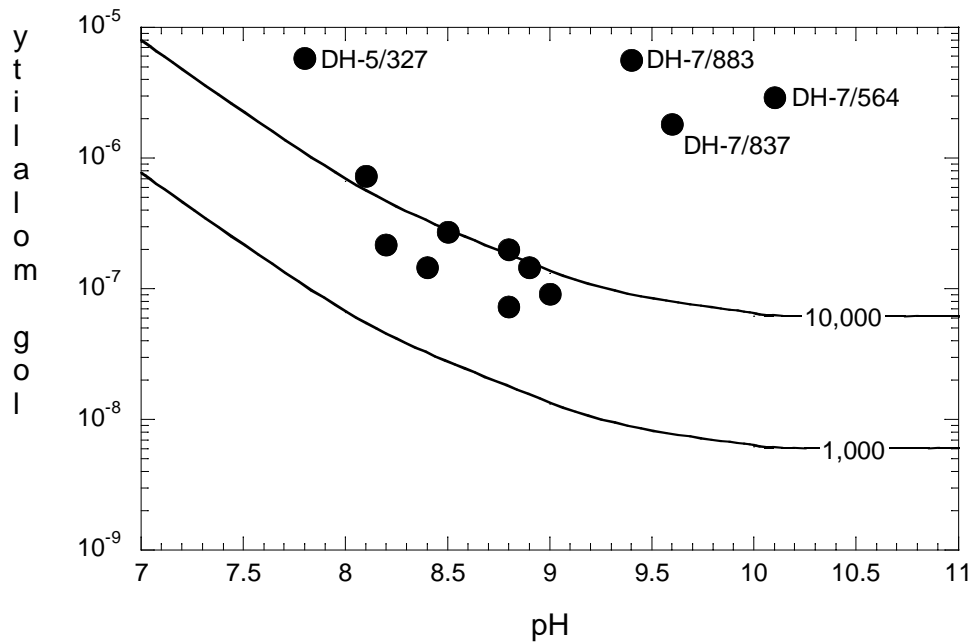


Figure 4_3. Comparison of aqueous Fe concentrations in contemporary groundwaters of the Toki granite (symbols) with their calculated counterparts using the models in Table 3_1 and measured Fe contents of authigenic calcites (lines). The labels on the calculated curves represent Fe concentrations in calcite (ppm).

distinctly higher than the calculated range (Fig. 4_3). These results suggest that while the Fe and Mn concentrations of most contemporary groundwaters are comparable to those in groundwaters that were present at the time of calcite precipitation, other present-day waters have considerably higher concentrations. Referring to Fig. 3_2, it is interesting to note that the *in-situ* redox potentials of these high-Fe, high-Mn waters appear to be controlled by heterogeneous equilibrium involving $\text{Fe}(\text{OH})_3(am)$.

Redox potentials calculated using the models described in Section 3 are plotted versus pH in Fig. 4_4. The solid lines in the figure bound potentials calculated using the U model and the observed U contents of late-stage calcites. The short-dashed lines demarcate three bands corresponding to the Fe contents of these calcites and the Fe model for $\text{Fe}(\text{OH})_3(am)$ [upper band], fine-grained goethite (middle band) and coarse-grained goethite (lower band). The dot-dash-dot lines bound potentials calculated using the Mn model and measured Mn contents in the fracture calcites. It is important to emphasize that the curvature among the calculated Eh boundaries in Fig. 4_4 results from changes in the aqueous speciation of the respective elements due to changes in carbonate content and pH.

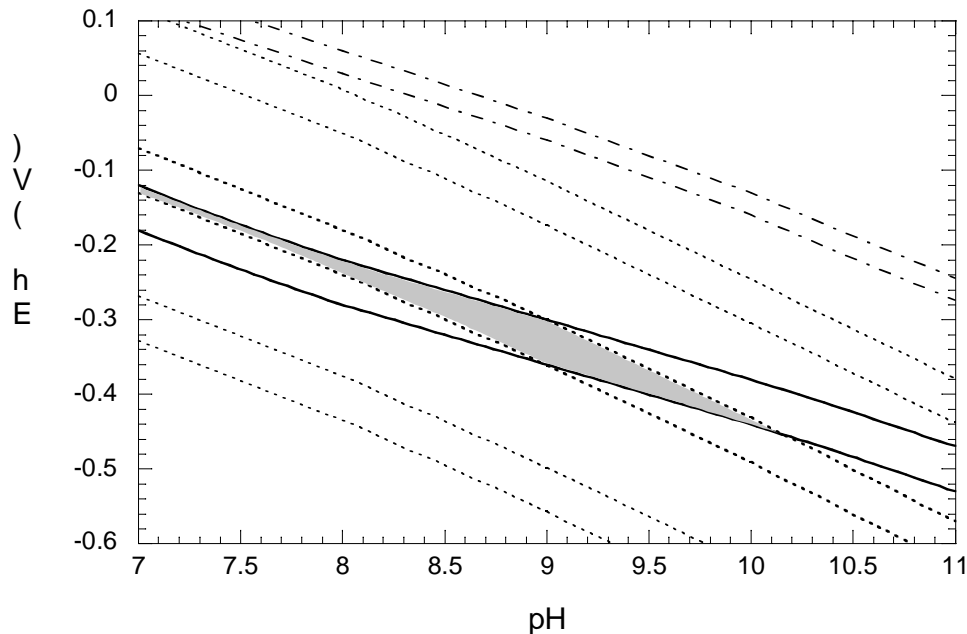


Figure 4_4. Calculated ranges in Eh-pH conditions for redox couples involving U, Fe and Mn based on the concentrations of these elements in fracture-lining calcites from the Toki granite.

As can be seen in Fig. 4_4, none of the calculated bands overlap except those for $\text{UO}_2(am)$ and fine-grained goethite. The overlapped region, indicated in the figure by the cross-hatched pattern,

defines specific Eh-pH conditions that are necessary for both $\text{UO}_2(am)$ and fine-grained goethite to coexist at equilibrium with an aqueous phase and with calcites having Fe and U contents comparable to those observed in calcites of the Toki granite. This region thus provides credible bounds on Eh-pH conditions in groundwaters that were present when these calcites formed. Mn(IV) oxides were apparently unstable under these conditions, as evidenced by the relatively low Mn contents of calcites in the Toki granite.

Figure 4_5 provides a comparison of the compatible $\text{UO}_2(am)$ -goethite-calcite Eh-pH conditions noted above with *in-situ* Eh measurements obtained using Pt electrodes and groundwater samples from deep boreholes in the Toki granite. As can be seen, there is good agreement between the calculated and measured potentials in deep groundwaters that are relatively reducing. This suggests that the Eh of the contemporary groundwaters is comparable to the Eh of groundwaters that were present at the time of calcite precipitation. Two groundwaters that are relatively oxidizing have measured Eh values that are compatible with equilibrium constraints imposed by

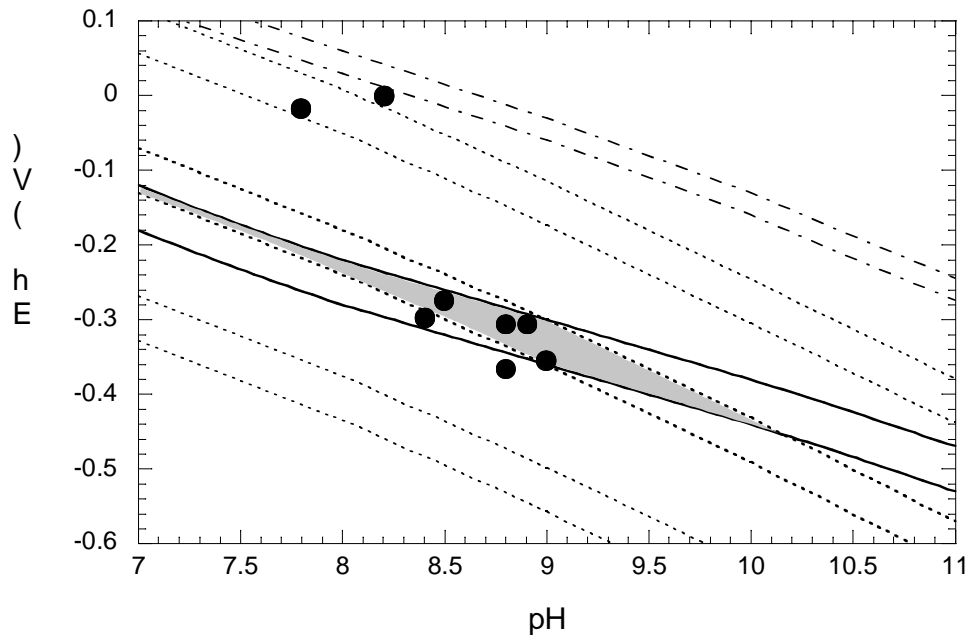


Figure 4_5. Comparison of calculated and measured redox potentials as a function of pH. heterogenous equilibrium with $\text{Fe}(\text{OH})_3(am)$ and with the Fe contents of fracture calcites, but which are incompatible with $\text{UO}_2(am)$ equilibrium and the U contents of these calcites.

5 Conclusions and recommendations

An approach to evaluate redox conditions in paleo-groundwaters of the Tono region was developed and tested in the present study. Ranges in total concentrations of selected cations in groundwaters coexisting with the surfaces of late-stage, fracture calcites are first calculated in this approach using LAMP analytical data on mineral chemistry and experimentally determined partition coefficients for co-precipitation of the cations in calcite. In cases where the cations can exist in two or more oxidation states, activities of the free divalent cations are also calculated and these activities are then used to calculate the Eh of half-cell reactions having different Nernstian slopes on an Eh-pH diagram. Domains defined by the intersection of the resultant curves are used to interpret paleo-redox conditions assuming that equilibrium is valid for the half-cell reactions considered.

Results indicate that U, Fe and Mn concentrations in contemporary groundwaters of the Toki granite are in most cases bounded by calculated values based on the U, Fe and Mn contents of late-stage calcites. This suggests that the concentrations of these elements in present-day groundwaters are comparable to those in groundwaters that were present at the time of calcite precipitation. Iron concentrations in deep groundwaters from borehole DH-7, and Mn concentrations in one sample from borehole DH-5, are, however, significantly greater than those interpreted from the Fe and Mn contents of calcite.

An overlap in calculated ranges in Eh-pH values for heterogeneous reactions involving $\text{UO}_2(am)$ and fine-grained goethite defines specific redox conditions that are necessary for both these minerals to coexist at equilibrium with an aqueous phase and with calcites having Fe and U contents comparable to those observed in calcites of the Toki granite. This region thus provides credible bounds on Eh-pH conditions in groundwaters that were present when these calcites formed. These bounds are closely consistent with *in-situ* Eh measurements obtained using Pt electrodes and groundwater samples from deep boreholes in the Toki granite, suggesting that the redox environment of contemporary groundwaters is comparable to that of groundwaters that were present at the time of calcite precipitation. It is important to emphasize that caution is needed in these interpretations, however, because there are significant uncertainties in the

experimental partition coefficients, and in other aspects of the thermodynamic calculations, and because redox disequilibrium among certain redox couples is a common characteristic of groundwater systems.

It is recommended that the models developed thus far should be further refined, tested and extended using the new LAMP analyses to be obtained by the BGS in FY03. The models should be used for two purposes:

- to estimate total concentrations of Ca and trace elements in groundwaters present at the time these elements were co-precipitated in calcite, and
- to infer upper and lower bounds on the range of Eh-pH conditions in these groundwaters.

Interpretations using the models should be integrated with the results of other studies characterizing the isotopic and petrographic properties of fracture calcites. Results should be examined primarily for evidence of similarities and differences in the chemistry of present-day groundwaters and paleogroundwaters of the Tono region.

6 References

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