PNC TN8410 91-253

NATURAL ANALOGUE STUDY ON THE LONG-TERM DURABILITY OF BENTONITE

-Time-temperature condition and water chemistry on illitization at the Murakami deposit,Japan-

Jan.,1992

POWER REACTOR AND NUCLEAT FUEL DEVELOPMEMT CORPORATION

TOKAI WORKS

動力炉・核燃料開発事業団（Power Reactor and Nuclear Fuel Development Corporation)1992

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１９９２年１月

NATURAL ANALOGUE STUDY ON THE LONG-TERM DURABILITY OF BENTONITE

－Time-temperature condition and water chemistry on illitization at the Murakami deposit, Japan－

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要　　旨

高レベル廃棄物の処分システムに用いる緩衝材の候補材であるベントナイトの長期耐久性を、天然の変質事例を調査することによって評価した。

新潟県の村上鉱床におけるベントナイトのイライト化変質を対象に、ＸＲＤ分析、全岩化学分析、放射年代測定、鉱床地域の温度分布履歴計算、水／岩石反応試験などをおこない、イライト化変質のための①温度－時間条件と、②化学的環境条件（水質）の推定を試みた。その結果、温度が340 ℃から100 ℃まで低下するのに350 万年要し、イライト化率は80％であることがわかった。同様に240 ℃から100 ℃まで低下するのに300 万年要し、イライト化率は40％、160 ℃から100 ℃まで低下するのに200 万年要し、イライト化率は０％であった。水質は、海水に類似しているものと推定された。

なお、本資料は1991年フランス、ストラスブールで開催されたＥＭＲＳ，Fall Meetingの論文集に投稿したものである。

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NATURAL ANALOGUE STUDY ON THE LONG-TERM DURABILITY OF BENTONITE
- Time-temperature condition and water chemistry on illitization at the Murakami deposit, Japan. -

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ABSTRACT

Time-temperature conditions and water chemistry on illitization at the Murakami deposit in central Japan were determined. The extent of the illitization and time-temperature condition estimated were as follows: the duration for conversion from 0 to 80% illite (volumetric ratio) was approximately 3.5Ma in the temperature range from 340 to 100℃. Conversion from 0 to 40% requires approximately 3.0Ma in the temperature range from 240 to 100℃. During 2.0Ma in the temperature range from 160 to 100℃, however, illite was scarcely observed. Water chemistry is estimated from two approaches, namely laboratory experiment and numerical analysis. The former is an interactive experiment between seawater and the tuff of the deposit. The latter is a calculation based on the difference of bulk composition between illitized and non-illitized tuff. The extent of each ionic concentration is inferred to be as follows: K^+ ; 560 to 6400, Mg^{2+} ; 800 to 1700, Ca^{2+} ; 360 to 2900, Na^+ ; 9400 to 15000 (mg/l).

INTRODUCTION

Smectite-rich clays alter to illite at high temperature or in the presence of a sufficient supply of potassium. In the repository environment, illitization is considered to require extremely long times which cannot be covered by laboratory experiment. A natural analogue is the only means by which very slow mechanisms can be identified and by which long-term predictions of models can be tested for pertinence. The selection of appropriate natural analogue is the key issue in determining whether the natural analogue study will be successful. The authors regard the illitization of the Murakami bentonite-illite deposit in central Japan as a "natural experiment". This deposit originated from the thermal effect of an igneous extrusive rock. Environmental conditions of the "experiment" are mainly time-temperature, water chemistry, and the water/rock volumetric ratio. Geologic characteristics of the deposit were favorable to determine the environmental conditions quantitatively because:
(1) As the igneous activity is simple, the illitization period and the thermal conditions can be explicitly determined.
(2) The original host rock, which contains the bentonite, is fairly homogeneous.
(3) The mineral assemblage and the bulk composition of the host rock are similar to those of compacted bentonite.

The preliminary study by Kamei et al. [1] of the Murakami deposit generated a concept for determining the time-temperature conditions for illitization associated with igneous extrusion. In this paper, we estimate the time-temperature conditions and the ionic concentration of the pore fluid related to the illitization of the deposit.

Illitizations with igneous activity have been previously reported by Nadeau et al.[2], and Brusewitz[3]; however, there are few detailed studies in which environmental conditions have been reported.

GEOLOGIC SETTING

Figure 1 shows a geologic map and a cross-section of this deposit area. The original host rock of the illite deposit is a homogeneous rhyolitic tuff, approximately 80 meters thick. The extrusive rock is biotite rhyolite in the form

of a funnel, and is exposed at the surface 500m wide and 1000m long. We identified thirteen kinds of marine diatom fossils from the tuff. These diatoms were classified into NPD7B zone after Akiba[4]. Fission track ages were determined for zircons extracted from fourteen samples of the tuff. These values range from 7.3 ± 0.4 to 5.6±0.3Ma. These facts indicate that: (1) the tuff is marine-based, and (2) the deposition age of the tuff range from 7 to 6Ma approximately. On the other side, a Rb-Sr mineral isochron age and K-Ar ages for the intrusive rock range from 6.2± 0.8 to 4.7± 1.7Ma. Therefore, the extrusion occurred immediately after the tuff deposition under marine conditions.

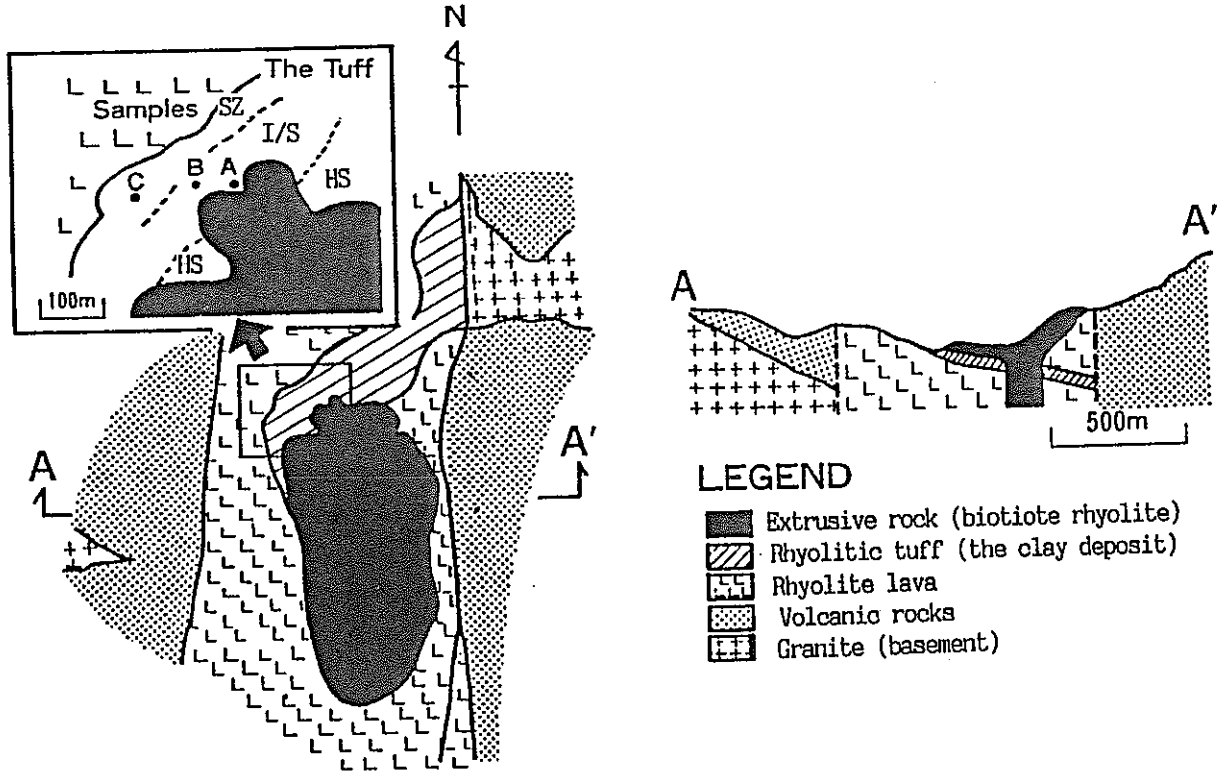

Figure 1. A geologic map and a cross-section of the Murakami deposit.

ALTERATION OF THE DEPOSIT

X-ray diffraction analyses and microscopic observation revealed the distribution of alteration minerals and the extent of illitization. The tuff, as the host rock, was divided into the following five zones defined by the lateral variation in alteration mineral assemblages: pyrophyllite(P), illite(I), High-crystallinity smectite(HS), illite/smectite mixed layers (I/S), and smectite-zeolite(SZ). These five zones are arranged in this order from the contact to the outer part (Figure 2). The main volume of each sample from the P, I, and HS zones consist of alteration phases. These rocks are so-called "mono-mineral". It can be recognized under a microscope that original textures do not remain. Accordingly, the tuff of P, I, and HS zones are considered to have been altered under high water-rock ratio. In contrast, in the tuff from I/S and SZ zones, the original textures are still recognized (Figure 3). Furthermore, these samples contain various alteration minerals in minor amounts. So, the tuff from I/S and SZ zones are considered to have resulted from of reaction under low water-rock ratio conditions. The I/S and SZ zones are significant to the natural analogue study because the decrease of illite ratio in I/S mixed layered clays may be traced from the I/S to SZ zone.

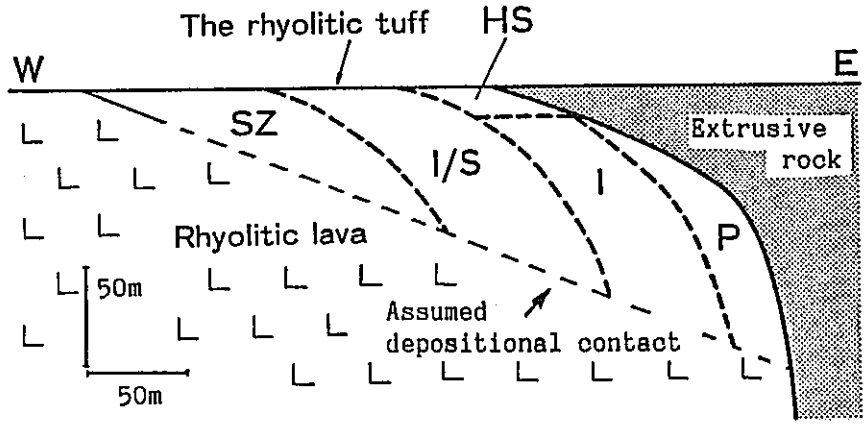

Figure 2 . A schematic cross section indicating distribution of alteration minerals. P,pyrophyllite; I,illite; HS,high-crystallinity smectite; I/S,illite-smectite mixed layers; SZ,smectite-zeolite.

Samples and Extent of the Illitization

Three clay samples were obtained on the surface. Samples A, B, and C were named in this order from near the contact to the outside as shown in Figure 1. Table 1 shows mineral assemblages of these samples. We determined illite ratio in I/S mixed layers for each sample using method after Watanabe[5]. The illite ratios for samples A, B, and C were approximately 80, 40, and 0 vol.% respectively.

Table 1 . The mineral assemblages of the samples A, B, and C.

Sample A (I/S zone)	qt≫I/S ≒ py ≒ Kf ≒ pl > ill
B (I/S zone)	qt≒ α-crist≫mor ≒pl> I/S≒ill ≒py ≒ilm
C (SZ zone)	α-crist> smec ≒ qt ≒mor ≒fer ≒Kf ≒pl> cal≒py

qt,quartz; I/S,illite/smectite mixed layers; py,pyrite; Kf,K-feldspar; pl,plagioclase; ill,illite; α-crist, α-cristobalite; mor,mordenite; ilm,ilmenite; smec,smectite; fer,ferrierite; cal,calcite.

ENVIRONMENTAL CONDITIONS

Time-Temperature Condition

A Rb-Sr age and K-Ar ages were determined for biotite and plagioclase of the

Figure 3. Textures of the tuff from SZ(1), I/S(2), and I(3)zones. Bar =0.3mm.

extrusive rock. "Closure temperatures" have been reported to these minerals on Rb-Sr and K-Ar systems (Wagner et al.[6], Harrison et al.[7]). Fission-track ages were determined for zircons extracted from the igneous rock. "Annealing temperature" has been proposed for zircon on fission track age determination (Hurford [8]). Combining the determined radiometric ages with the value for each assumed closure temperature (or annealing temperature) provides the cooling history of the intrusive rock as the heat source. Figure 4 shows this cooling history. The cooling rate is approximately -70℃/Ma. (The value reported by Kamei et al.[1], -45℃/Ma, has been revised.)

Using the value, -70℃/Ma, we calculated the thermal history of the deposit area in two dimensions with the aid of the "FINAS" (Finite element nonlinear structural analysis system) computer software (Iwata [9]). TableⅡ shows input data for thermal conductivity, specific heat, and density for rocks, in this deposit. Initial temperature of the heat source was assumed 350℃ (at the time of 6.2 Ma before the present) based on the geologic setting.

TableⅡ. Input data for thermal conductivity, specific heat, and density of the rocks, in this deposit.

	Thermal Conductivity [kcal/m h ℃]	Specific Heat [kcal/kg℃]	Density [kg/m³]
Rhyolitic Tuff	0.57	0.36	1900
Rhyolite	1.15	0.15	2600
Andesite	1.27	0.20	2700
Granite	2.69	0.15	2600

The shape of the igneous rock body at depth is, however, not known in detail, because the upper portion has been eroded. Accordingly, ten cases with varying shape were calculated. Figure 5 shows the bounds of the calculation in the case of a domed shape. In this figure, the "eroded stratum" was assumed to have same physical properties as the rhyolite. From these results, we concluded that the thermal condition in the tuff was not significantly affected by the assumed shape of the extrusive rock. The cooling history at the collection points of samples A, B, and C can be estimated by these calculations. TableⅢ shows the time-temperature conditions for each sample. The time scales are based on the assumption that most of the illitization occurred above 100 ℃.(Aoyagi et al.[10] estimated approximately 100 ℃ for the appearance of I/S mixed layers in a Japanese oil field area. The Murakami deposit is part of this area.)

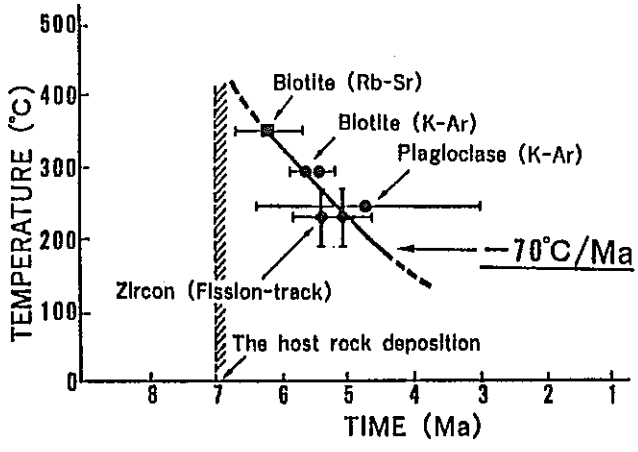

Figure 4. The cooling history of the igneous extrusive rock.

TableⅢ. The time-temperature conditions.

Samples	ill. % *	Time-temperature conditions
A	80	340→100 ℃, 3.5 Ma
B	40	240→100 ℃, 3.0 Ma
C	0	160→100 ℃, 2.0 Ma

*; illite ratio in I/S mixed layers.

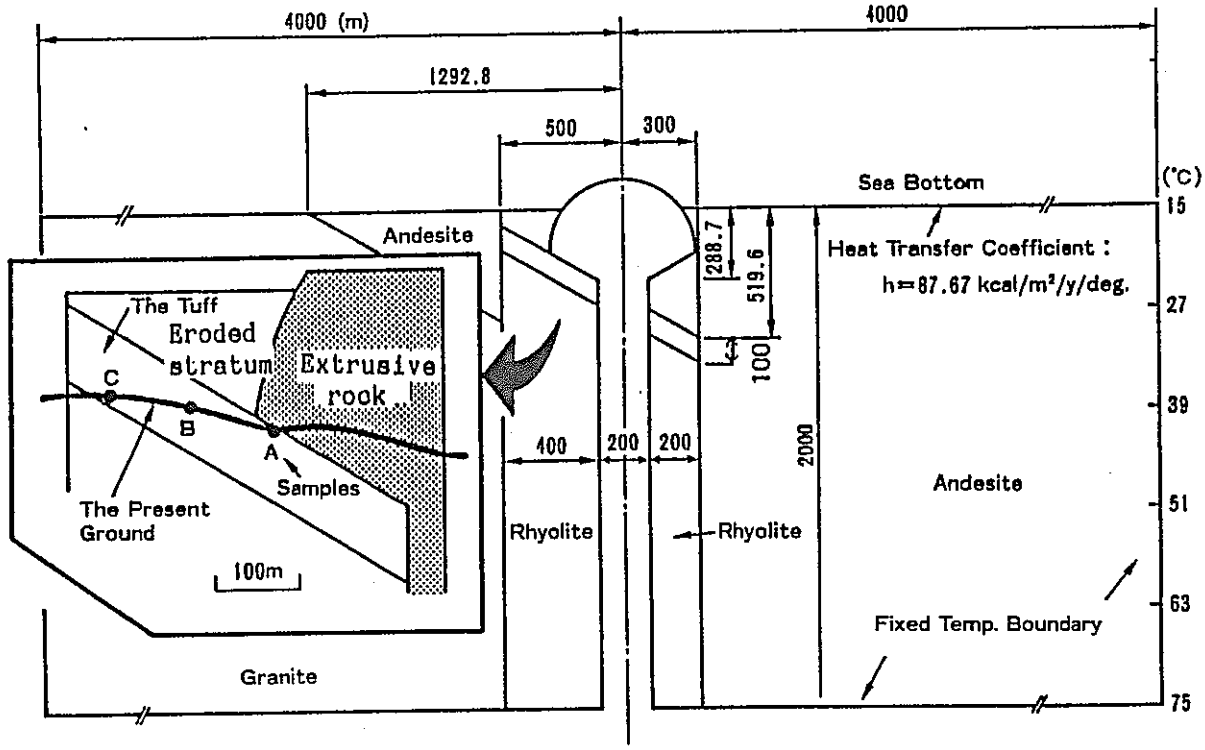

Figure 5. The bounds of the calculation in the case for which the igneous extrusive rock was domed-shaped.

Water chemistry

In order to estimate water chemistry (ionic concentration) during illitization, we performed an experiment and a calculation under the following assumptions; (i) That the pore fluid in the tuff prior to the reaction is seawater, because of the geologic setting, and (ii) the chemical composition of the tuff is uniform before the reaction in all parts and corresponds to that of sample C, which was obtained from a non-illitized section of the tuff (see Figure 1).

(1)Experiment

Sample C was subjected to an interaction test in seawater in a teflon vessel. The temperature was 150℃ for 30 days. The seawater/rock sample (powder) volumetric ratios were set at 2, 5, and 20. (In the "natural experiment", the water/rock ratio cannot be determined accurately. The original texture has, however, remained even in the tuff containing mixed layered clays of 80 % illite. In addition, samples from the I/S zone contain alteration minerals in minor amounts. Accordingly, the water/rock ratio could be quite small.) The ionic concentrations of K^+, Mg^{2+}, Ca^{2+}, and Na^+ were measured in the leachate. These ions are considered to exert an influence on illitization (e.g. Roberson et al.[11], Howard et al.[12]). The ionic concentrations are given in Table V. They do not appear to depend significantly on the water/rock volumetric ratios.

(2)Calculation

Variation in chemical composition during the water/rock interaction is shown schematically in Figure 6. The bulk compositions and dry densities of sample A, as a rock after the reaction, and sample C, as a rock before the reaction, were determined (Table Ⅳ).

Table Ⅳ. Dry-densities and chemical compositions of samples A and C.

	Sample A	Sample C
Dry-density (g/cm^3)	1.324	1.451
Chemical composition (wt%)		
SiO_2	72.3	71.4
TiO_2	0.11	0.11
Al_2O_3	14.1	13.2
Fe_2O_3	2.13	1.11
FeO	0.24	0.14
MnO	0.02	0.02
MgO	1.00	0.80
CaO	0.17	0.62
Na_2O	0.65	1.35
K_2O	3.65	4.28
P_2O_5	0.04	0.03
H_2O^+	4.52	5.67
TOTAL	98.85	98.77

In the model shown in Figure 6, equation (1) was considered to be applicable:

$$W i_2 = W i_1 + R/W (S i_1 - S i_2) \quad (1),$$

Where, $W i_1$; Concentration of the component "i" in the solution before the reaction.
$W i_2$; Concentration of "i" in the solution after the reaction,
$S i_1$; Concentration of "i" in the rock per unit volume before the reaction,
$S i_2$; Concentration of "i" in the rock after the reaction,
R ; Volume of the rock,
W ; Volume of the solution.

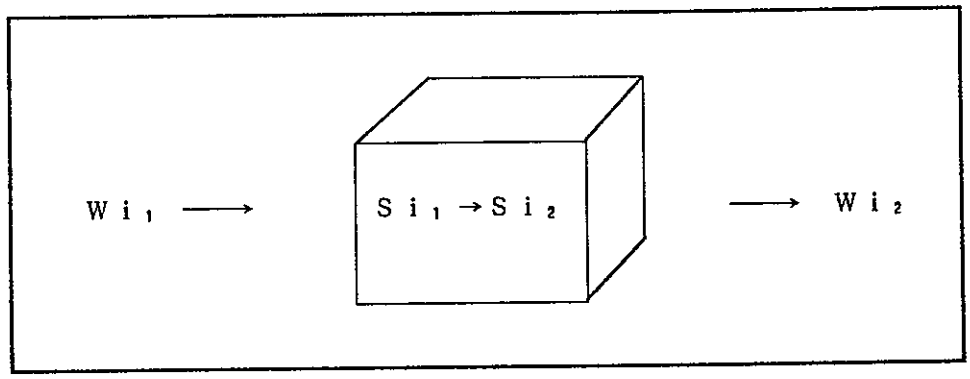

Figure 6. A model of variation of chemical composition during a water/rock interaction.

The ionic concentrations of the solution before the reaction were assumed to be the same as those of seawater: $K^+ = 400$, $Mg^{2+} = 1300$, $Ca^{2+} = 400$, $Na^+ = 11000$ (mg/l). Water/rock volumetric ratios were set at 2, 5, and 20, the same as in the the experiment described above. The results were also shown in TableV. The values calculated are consistent with the values obtained in the experiments, especially in the case where the water/rock ratio is 20. However, we have obtained little information concerning the water/rock ratio during illitization of the deposit.

This ratio has yet to be determined. ,Figure 7 is an integrated diagram showing range of each ionic concentration determined by the experiments and by the calculations.

Table V . Ionic concentrations based on experiments and calculations.

Water/rock *	Experiment 2	Experiment 5	Experiment 20	Calculation 2	Calculation 5	Calculation 20	
K^+	610	560	620	6400	2800	1000	(mg/l)
Mg^{2+}	1700	1400	1500	800	1100	1250	
Ca^{2+}	1100	360	750	2900	1400	650	
Na^+	9400	11000	10000	15000	13000	11400	

*: Volumetric ratio.

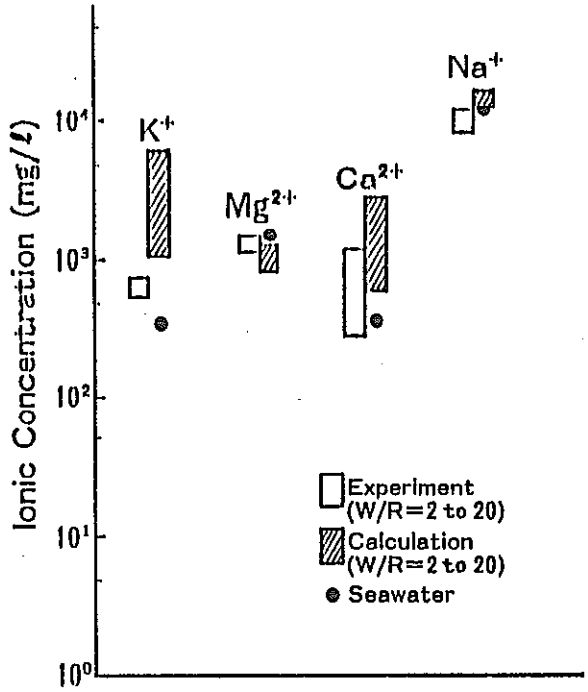

Figure 7. Ranges of each ionic concentration determined by the experiments and by the calculations.

CONCLUSIONS

Illitization at the Murakami deposit can be regarded as an experiment in nature. The extent of illitization as deduced from the "natural experiment" and the environmental conditions as determined by experiment were estimated quantitatively. The time-temperature conditions for each extent of illitization are as follows: 80 vol.% illitization ; 3.5 Ma, 340 to 100 ℃. 40 % ; 3.0 Ma, 240 to 100 ℃. 0% ; 2. 0 Ma, 160 to 100 ℃.

Water chemistry of pore fluid on the illitization was estimated by experiments and by calculations: K^+ , 560 to 6400; Mg^{2+} , 800 to 1700; Ca^{2+}, 360 to 2900; and Na^+, 9400 to 15000 (mg/l). These values do not differ significantly from those of seawater.

ACKNOWLEDGEMENTS

The authors are sincerely grateful to Messrs. Sakuramoto Y., Futakuchi K., and Takano H. (Dia consultants Co.) for their useful suggestions, field survey and XRD analyses, to Mr.Sato M.(Sato Mining Co.) for obtaining samples, to Mr.Aoyama Y.(Computer Software Development Co.) for computer simulation, to Sumitomo Metal Mining Co. for chemical analyses, to Kyoto Fission Track Co. and Teledyne Isotopes Co. for radiometric age determinations, to Mr. Kawasaki M.(Inspection Development Co.) for the leaching test, and to Prof.Watanabe T.(Joetsu Univ. of Education), Dr. Shikazono N.(Keio Univ.) for valuable discussions.

REFERENCES

[1] Kamei G., Arai T., Yusa Y., Sasaki N., Sakuramoto Y., Mat. Res. Soc. Symp. Proc., 176, 657-663 (1990).
[2] Nadeau P.H., Reynolds R.C.Jr., Clays and Clay Minerals, 29, 4, 249-259 (1981).
[3] Brusewitz A.M., Clays and Clay Minerals, 34, 4, 442-454 (1986).
[4] Akiba F., Init. Rep. DSDP, U.S. Govt. Printing Office, Washington, 87, 393-481 (1985).
[5] Watanabe T., Clay Science, 7, 97-114 (1988).
[6] Wagner G.A., Reimer G.M., Jager E., Mem. 1st Geol. Mineral. Univ. Padova, 30 (1977).
[7] Harrison T.M., Armstrong R.L., Naeser C.W., Harakal J.E., Jour. Earth. Sci., 16, 400 (1979).
[8] Hurford A.J., Contrib. Mineral. Petrol., 92, 413 (1986).
[9] Iwata K., PNC N9520 89-019 FINAS:RM002, VERSION 11.0 (1989),(in Japanese).
[10] Aoyagi K., Kazama T., Sedimentology 27, 179-188 (1980).
[11] Roberson H.E., Lahann R.W., Clays and Clay Minerals 29, 2, 129-135 (1981).
[12] Howard J.J., Roy D.M., Clays and Clay Minerals 33, 2, 81-88 (1985).