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THE THERMAL HISTORY OF MURAKAMI DEPOSIT, JAPAN.

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ESTIMATION OF ILLITIZATION RATE OF SMECTITE FROM
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要 旨

緩衝材の候補材料であるベントナイトは、スメクタイトを主成分とする。本研究の目的は天然環境下でのスメクタイトのイライト化変質を調査し、スメクタイトの長期安定性を評価することである。調査対象として、ベントナイト層とこれを貫く火成岩体が分布している地域を選定し、火成岩体の熱に伴うスメクタイトのイライト化を調査した。火成岩体中のいく種類かの鉱物について放射年代を測定し、これらの値とそれぞれの閉止温度を組み合わせて熱源（火成岩体）の冷却速度を見積った。この値をもとに、イライト化反応時間を計算等で求めたところ、340万年以上となった。X線回折分析により、この間、スメクタイトは40%のイライトを含む、イライト/スメクタイト混合層鉱物に変化したことがわかった。

イライト化変質に関与した水の組成を推定するため、イライトの構造水の水素同位体比(D/H)を測定した。その結果、この反応に関与した水のD/Hは、海水のそれに近い値をもっていることがわかった。

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ABSTRACT

The research on illitization of smectite in the natural environment affords information on the long-term durability of bentonite which is the candidate for buffer material.

Murakami bentonite deposit in central Japan, where the bentonite and rhyolitic intrusive rock were distributed, was surveyed and the lateral variation of smectite to illite in the aureole of the rhyolite was studied.

The radiometric ages of some minerals from the intrusive rock and the clay deposit were determined. Comparison of the mineral ages (obtained by K-Ar, Rb-Sr and fission-track methods) with closure temperature estimated for the various isotopic systems allowed the thermal history of the area. The age of the intrusion was 7.1 ± 0.5 Ma(; Mega d'annees), and the cooling rate of the intrusive rock was estimated to be approximately 45 °C/Ma.

Sedimentation ages of the clay bed were mostly within the range from 18 to 14 Ma. However, the fission-track age of zircon in the clay containing illite/smectite mixed layers was 6.4 ± 0.4 Ma, which was close to that of the intrusion. The latter value could be explained as the result of annealing of fission-tracks in zircon. The presence of annealing phenomena and the estimated cooling rate concluded that illitization had occurred in the period of 3.4 Ma at least under the temperature range from above 240 ± 50 to 105 °C. Illite-smectite mixed layers occurred from smectite in the process. The proportion of illite was about 40 %. Approximately, 29 kcal/mol as a value of activation energy was calculated to the illitization.

The hydrogen isotopic ratio (D/H) of constitution water of the illite was determined. The values that were calculated for the water, which were related to the illitization, fell within the range of hydrogen isotopic ratios of seawater.

INTRODUCTION

Bentonite clay consists principally of smectite. Smectite converts to illite if it is subjected to elevated temperatures or if sufficient cation exchange can take place with potassium in porewater.

Smectite-illite conversion occurring in natural environment can be classified into four processes :

- (1)Diagenesis
- (2)Regional metamorphism
- (3>Contact metamorphism
- (4)Hydrothermal alteration

Illitization that is related to contact metamorphism, is the most suitable as a subject for natural analogue study on bentonite. The reaction term and thermal condition should be revealed on the natural analogue study. Studying a contact metamorphism is possible to yield the data of the reaction term and the thermal condition.

Murakami bentonite-illite deposit in central Japan was investigated, because the bentonite bed is rather homogeneous, its mineral assemblage is similar to that of compacted bentonite. The thermal history is possible to be comprehended because of its simple igneous activity.

In this study, the mode of occurrence on illite was revealed by a geological survey. The thermal history was presumed by comparison of the ages with each closure temperature.

To reveal the water chemistry of solution relative to the illitization is also important, but it is difficult to reveal directly the chemical composition. However, hydrogen isotope composition of constitution water of illite affords informations to assume the origin of the solution.

GEOLOGY

The geological map of Murakami deposit area is shown in Figure 1. Lava and tuff, both of rhyolitic, distributed in a graben with a width of about one kilometer. The reported values of the deposition are over the range of 18 to 14 Ma (Muramatsu [2]). The fossils of foraminifera or mollusca indicate that the tuff is originally marine-based (Metal Mining Agency of Japan [3]). The tuff is also altered into a so-called bentonite bed. As alteration minerals in the tuff, smectite, mordenite, and laumontite are identified by X-ray diffraction analysis. An igneous rock (biotite rhyolite) intrude into the tuff and lava. The intrusive rock is exposed in an area about 500 meters wide and 1000 meters long. The contact surface between the intrusive rock and the tuff dips about 30° near the ground surface. This intrusive rock body was assumed to form a funnel. Idealized geological section is shown in Figure 2. The diameter of the intrusive rock body is unknown at a horizon of deeper than 50 meters below the ground surface. On the assumption that, the shape of the intrusive rock body is symmetrical(as shown in Figure 2), the diameter may be shorter than 200 meters.

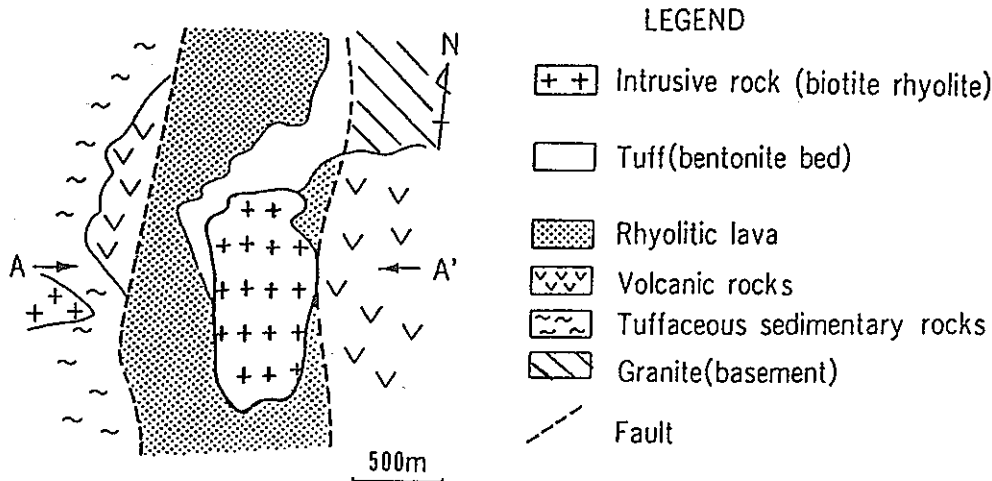


Fig.1 A geological map of the Murakami deposit area.

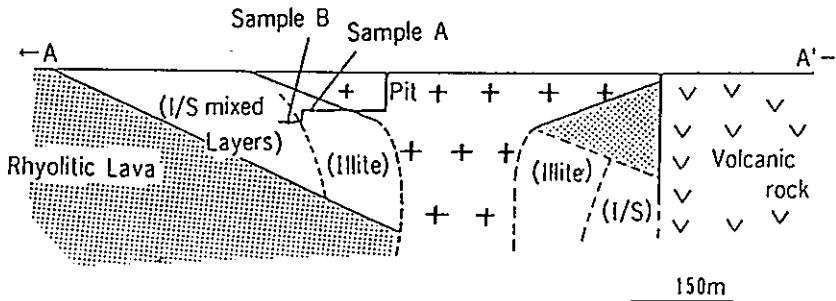


Fig.2 An idealized geological section of the Murakami deposit area.

SAMPLES

A sample of the intrusive rock was taken from the freshest-looking ground surface, and two clay samples were obtained from the Murakami mine gallery area. At this mine, illitized tuff is quarried for use as the raw material in pottery.

Collecting points of the clay samples were 15 (sample A) and 30 meters (sample B) apart from the boundary between the igneous intrusive body and the clay bed. X-ray diffraction analysis showed that the sample A contained only illite as a clay mineral, but the sample B contained illite-smectite mixed layers with a very small amount of kaolinite. The illite ratio of the mixed layers was determined to be about 40% by using the method of Weir et al.[4](Fig.3).

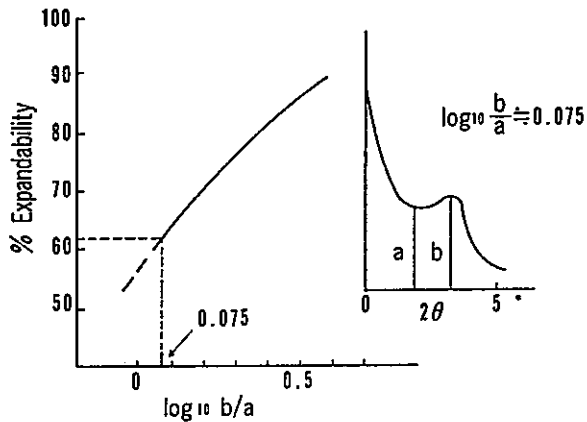


Fig.3 The proportion of expandable layers of sample B ; about 60 %. The right side graph is a XRD chart for sample B, which has been treated with ethylene glycol. The left side graph is a plot of $\log_{10} b/a$ against % expandability ; after Weir et al.[4].

THERMAL HISTORY

Rb-Sr mineral isochron age and K-Ar ages were determined in the intrusive rock and the clay samples. Fission-track ages were also determined in zircons extracted from the intrusive rock and the clay samples (Table I , II).

"Closure temperatures" were known to each mineral on Rb-Sr and K-Ar systems respectively (e.g. Jager et al.[5], Dodson[6], Wagner et al.[7], Harrison & McDougall[8], Hurford[1]) (Table III). By plotting on a graph the mineral ages compared against the presumed closure temperatures the cooling rate for the intrusive rock was able to be established (Fig.4). The rate was estimated to be approximately 45 °C/Ma .

Table I K-Ar and Fission-track ages of the samples from Murakami deposit.

	K-Ar (Ma)	F.T. (zircon) (Ma)
Intrusive rock	5.6±0.3(biotite) 4.7±1.7(plagioclase)	5.4±0.4[—] *
Sample A (illite)	6.5±0.6	7.2±0.4[5.3]
Sample B (ill./smec.)	4.9±0.7	6.4±0.4[6.1]

*[] ; Calculated except shortened fission-tracks.

Table II Rb-Sr mineral isochron age of the intrusive rock.

Rb-Sr mineral isochron (Ma)		
Intrusive rock	7.1±0.5	⁸⁷ Sr/ ⁸⁶ Sr I.R. * 0.70365 ± 0.0020
	⁸⁷ Rb/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr
whole rock	1.106	0.70402±0.00008
biotite	49.7	0.70864±0.00033
plagioclase	0.039	0.70343±0.00015

* I.R. ; Initial Ratio.

Table III Reported values of closure temperature.

Minerals	Temperature (°C)			References
	K-Ar	Rb-Sr	F.T.	
biotite	300	350	—	Wagner et al., [7]
plagioclase	250	—	—	Harrison et al., [10]
zircon	—	—	240 ± 50	Hurford [1]

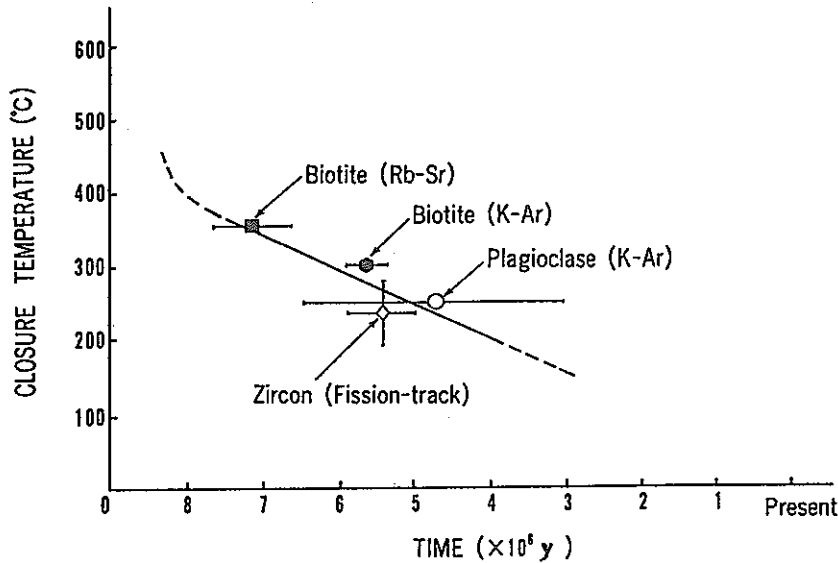


Fig.4 The cooling curve for the intrusive rock body.

Annealing of Zircon

Fission-track ages of zircons from the intrusive rock and clay samples were shown in Table I. The fission-track was known to shorten or to disappear with elevated temperature (e.g. Hurford[1], Naezer et al.[9], Harrison et al.[10], Nishimura & Mogi[11]). Some shortened tracks survived in zircons from the sample A and B. The ages in brackets in Table I were calculated with the exception of the shortened tracks. The ages were obviously younger than those of the clay bed deposition, and were close to that of the intrusion. It was concluded that the zircons were annealed by the heat from intrusive rock, and the fission-track ages were reset. Hurford[1] estimated that a mean closure temperature was 240±50°C for the retention of fission-tracks in zircon. Therefore, the sample B was subjected to more than 240 ± 50°C at the time of approximate 6 Ma.

Preliminary Study of Simulated Thermal History of the Bentonite Deposit

The thermal history of the area surrounding the intrusive rock body was simulated by the thermal analysis code "TRUMP"(Fig.4). The thermal history was simulated axisymmetrically a distance of 2 kilometers around the vertical centre line of the intrusive rock body. The intrusive rock body was assumed to be in the form of a cylinder, which had a diameter of 200 meters. As an initial condition, the temperature at the contact surface at the time of 7.1 Ma was established to be 350 °C on the basis of the Rb-Sr mineral isochron age and its closure temperature. The present temperature was established to 25 °C temperature in the gallery. The cooling rate of the intrusive rock body was regarded as constant ; 45 °C/Ma. The input data concerned with the bentonite were as follows:

density $\rho = 2.2 \text{ g/cm}^3$
 specific heat $C = 0.36 \text{ cal} \cdot \text{deg}^{-1} \cdot \text{g}^{-1}$
 thermal conductivity $K = 1.31 \times 10^{-3} \text{ cal} \cdot \text{m}^{-1} \cdot \text{h}^{-1} \cdot \text{deg}^{-1}$

Sample B locality was an area of about 30 meters from the contact surface. The fission-track age of zircon from sample B was $6.4 \pm 0.4 \text{ Ma}$. Fig.4 showed that the temperature at the sample B locality was about $280 \text{ }^\circ\text{C}$ at the age. This value was concordant with the closure temperature of zircon; $240 \pm 50^\circ\text{C}$. The cooling rate of approximate $40 \text{ }^\circ\text{C/Ma}$ could be also estimated at the locality.

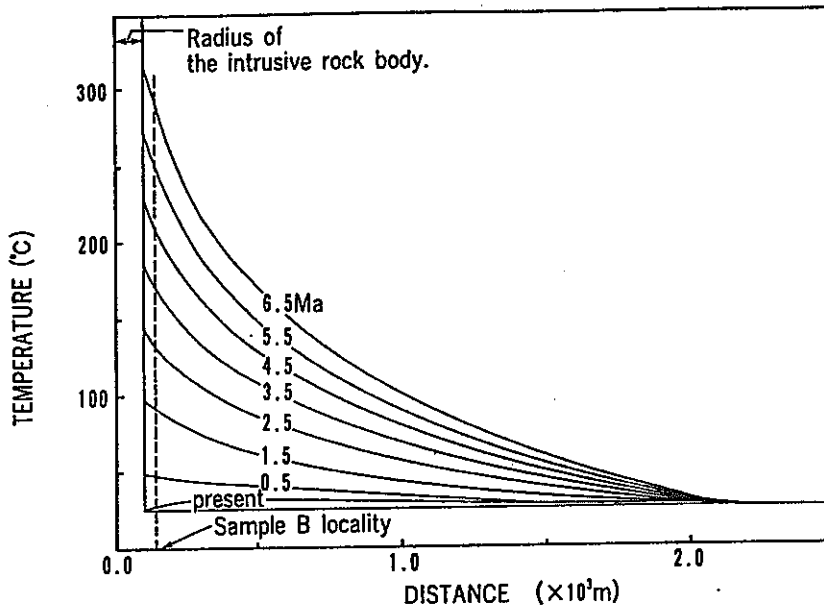


Fig.5 A Simulated thermal history of the area surrounding the intrusive rock body.

The Illitization Period

Aoyagi[12] and Kazama[13] showed that the illite-smectite mixed layers started to generate at 104°C . Oda et al.,[14] also estimated temperature for appearance of mixed layers was 105°C at Japanese oil fields : Murakami deposit belonged to the area. In the above instances, $105 \text{ }^\circ\text{C}$ was assumed as a minimum temperature of illitization in the Murakami deposit area. At the sample B locality, the temperature at the time of 6.4 Ma was presumed to be $240 \pm 50^\circ\text{C}$. If the cooling rate at the locality was constant and was $40 \text{ }^\circ\text{C/Ma}$ (see Fig.5), the period from 240 to $105 \text{ }^\circ\text{C}$ was about 3.4 Ma .

In the period of more than 3.4 Ma , we found that smectite converted to illite-smectite mixed layers ; the illite ratio is approximate 40% .

WATER CHEMISTRY

Hydrogen isotopic compositions (D/H) of water in the form of hydroxyl groups in the illite and the smectite-illite mixed layers mineral, were measured in order to estimate solution chemistry related to the illitization. The extraction of constitutional water from the clay minerals was performed using the methods of Friedman & Smith[15], Godfrey[16], and Epstein & Taylor[17].

The D/H ratio was shown as follows :

$$\delta D(\%) = \{ (D/H)_{\text{sample}} / (D/H)_{\text{SMOW}} - 1 \} \times 1000 \quad (1).$$

where, SMOW refers to Standard Mean Ocean Water.

The values of δD were -57.1 and -50.2 ‰ for the illite (sample A) and the mixed layers mineral (sample B) respectively.

At 200 °C, the equilibrium values of Δ ($\Delta = 10^3 \ln \alpha$) was -39.8 for illite (O'neil & Karaka[18]), where, α was fractionation factor between clay and water:

$$\alpha_{\text{clay-water}} = (D/H)_{\text{clay}} / (D/H)_{\text{water}} \quad (2).$$

The values of δD for the water related with the illitization at the Murakami deposit were calculated using the fractionation factor ; -18.8 ‰ for the illite and -11.7 ‰ for the mixed layers mineral. On the other hand, the δD value of present groundwater at Murakami mine is -41.4 ‰. Besides, δD values of present Japanese meteoric water fall within the range from -40 to -100 ‰ (matsubaya[19]). The water for the illitization is obviously rich in deuterium than the present groundwater or the meteoric water, and the calculated δD values for the water are close to those of seawater ; nearly equal to 0 ‰.

DISCUSSION

The activation energy for the illitization at Murakami deposit is calculated on the basis of the estimated thermal history. The illitization rate is expressed by the following equation (Eberl & Hower[20] and Sudo[21]):

$$\ln X = A \cdot \int_T^{T_0} dt/dT \cdot \exp(-E/RT)dT \quad (3).$$

Where, X : % expandability ; the proportion of smectite layers in mixed layer phases,

A : Arrhenius constant,
t : Reaction time (days),
To: Initial temperature,
T : Temperature after t days,
E : activation energy,
R : gas constant.

The proportion of smectite layers in mixed layers of sample B is measured to be about 60 %. The sample is estimated to be $240 \pm 50^\circ\text{C}$ at least on the basis of the annealing condition of fission tracks observed in the zircons. The temperature at the end of the illitization is supposed to be 105°C . Therefore, the illitization period is estimated to be more than 3.4 Ma under the cooling rate of $40^\circ\text{C}/\text{Ma}$.

If the illitization period is 3.4 Ma, the values of activation energy is calculated approximately 29 kcal/mol by means of Eq.3. The value of activation energy is close to that calculated by Roberson & Lahann[22] : which is about 30 kcal/mol. The reaction experiments after Roberson & Lahann[22] were conducted in closed vessels containing 400 ppm K^+ and 9400 ppm Na^+ at 270 and 350°C . The ionic concentration illustrated that of seawater. Water chemistry of the solution might be similar to that of seawater because of the geological setting in the Murakami deposit area and the hydrogen isotopic properties of the illite.

CONCLUSION

Some of the principal conclusions are as follows:

- (1) The cooling rate of the intrusive rock, which is a heat source of the illitization is estimated to be about $45^\circ\text{C}/\text{Ma}$.
- (2) The fission-track age of zircon in the clay sample is reset by the heat from the intrusive rock body. By applying the closure temperature for fission-tracks in zircon, the clay sample is subjected to more than $240 \pm 50^\circ\text{C}$.
- (3) The illitization period is presumed to be above 3.4 Ma by comparison the annealing condition for fission-tracks with the calculated cooling rate for the clay bed (about $40^\circ\text{C}/\text{Ma}$).
- (4) Smectite converts to illite-smectite mixed layers in the period. The

proportion of illite is approximately 40 %.

(5) The hydrogen isotopic compositions of the water relative to the illitization and the geological setting assume that the water chemistry of solution for the reaction may be similar to that of seawater.

(6) In the test calculation, the activation energy is approximately 29 kcal/mol for the illitization.

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