K-Ar dating by smectite extracted from bentonite formations

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Abstract: We attempt to apply K-Ar dating to extracted smectite from bentonite formations collected by different age formations from Japan, China, and America. The results show that the K-Ar ages of smectite are younger than the expected geological age estimated from the stratigraphic data or other research data. The time differences increase with increased age, and K-Ar ages in this study also increase with increased age. For example, smectite in the old strata of bentonite has an older age than smectite in the young strata. K-Ar dating by smectite has the greatest potential for indicating the crystallized age of smectite.

1 Introduction

Smectite is crystallized by diagenesis and hydrothermal alteration in nature and is produced in fault gouges. The dating of smectite has significance for mining and evaluating fault activity. However, the K-Ar dating of smectite is difficult to analyze because smectite does not include potassium. Also, illite layers crystallized from smectite layers progress with the potassium fixation process in the interlayer increases with formation temperature. The potassium fixation at early alteration mainly occurs by the solid–solid exchange, and the reaction progresses the dissolution-precipitation reaction and increases the illite layers [1]. The mixed layer clay that consists of 80% smectite and 20% illite layers ($g = 0$) (I/S) is generally identified as pure smectite, and it is rare for smectite to not have potassium.

K-Ar dating of smectite has been performed by several researchers [2, 3]. The K-Ar dating results by Clauer et al. [2] agree with the values obtained by both Rb-Sr and K-Ar data by smectite from the D.S.D.P. samples. Also, Elliott [3] has reported that the smectite K-Ar ages agree with the K/T boundary from the over and under layers. Thus, smectite may have formed a volcanic glass deposit on the K/T boundary based on REE and K-Ar data.

2 Samples

Dating samples were collected from bentonite with five different ages (table 1). The oldest

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sample was collected from the late Jurassic in China, while the youngest sample was collected from the late Miocene in Japan. Samples for dating were original rocks that were directly collected fresh rocks from the wall of a mining tunnel. The bentonite of Kunimine is alternated with shale. The bentonite excavated from the mining tunnel comprised a total of 31 layers that varied in thickness from several centimeters to 2 m. Also, #1 bentonite lies on the lowest layer while #29 lies on the upper layer of the Kunimine mine in Yamagata, Japan. All samples of bentonite mainly consist of Al octahedral type smectite and quartz, and the whole smectite almost consists of S100%, $g = 0$ (Table 1). Lastly, plagioclase, alkali feldspar, mica, and zeolite were rarely detected by XRD.

Table 1. Samples and expected strata age.

				Other dating age	$\Delta 2\theta_1$	$\Delta 2\theta_2$
	country	time	Formation	Ma $\pm$ 1 σ	degrees	degrees
Kunimine #29	Japan	Late Miocene	upper formation of the Mizusawa F.	13.9 $\pm$ 0.9 (FT) ^[4]	5.22	5.28
Kunimine #1	Japan	Late Miocene	lower formation of the Mizusawa F.	9.6 $\pm$ 0.3 (FT) ^[4]	5.14	5.32
Kushiro	Japan	Eocene	the Harutori F.	39.54 $\pm$ 0.56 (SHRIMP) ^[5]	5.17	5.28
Wyoming TY	America	Late Cretaceous	Clay Spur bentonite	95 (40Ar/39Ar) ^[6]	5.22	5.27
Jilin Liufangzi	China	Late Jurassic	Liufangzi bentonite	150	5.20	5.27

$\Delta 2\theta_{1,2}$ use Reichweite (g) calculation

3 Sample preparation and analysis method

Smectite was extracted by elutriation from original rock. The collection level was 10 cm (200 mL) from the top of the suspended water after 8 h of precipitation. Three cylinders with a height of 50 cm and a volume of 1 L were used for samples. The supernatant of the first suspension solution was transferred to the second cylinder, and then the second suspension solution was transferred to the third cylinder. Clays for analysis were collected between a depth of 10 cm and a top of the third cylinder water after 8 h standing. The enrichment of samples was used by high-speed centrifugation for the third supernatant, and the water level of the first cylinder after sampling was recovered to 200 mL for the solution level decreased. The dilution volume of the first cylinder (1 L) amounted to about 30 L. The extracted clay seemed clear like gel. The diameters of the samples ranged between 0.3 to 10 $\cdot$ m and 0.2 to 1.0 $\cdot$ m. Also, the samples from Kunimine bentonite showed rougher 1 to 10 $\cdot$ m particles.

To evaluate the contaminations, K-Ar dating was performed on the deposition particles of the first cylinder. Extracted clay samples have pure smectite, and this result was confirmed by XRD. The contamination samples mainly consisted of quartz and feldspar. Then, 0.5 g of Smectite was extracted by elutriation from an original rock of 500 g. The time of enrichment was 2 to 6 months. The permeability of the bentonite formation is rather small, and smectite contacts the heterogeneous pH 7 distilled water for a long period in the cylinder. Furthermore, potassium is trapped in bentonite due to the formation of smectite.

Ar analysis performed ³⁸Ar spike methods [7] by HIRU [8], and the sample pre-heating temperature was between 180 and 200 $^{\circ}$ C under vacuum conditions (10⁻⁷ Torr) in the glass

tree folder for 3 days [7]. The melting temperature of the samples for Ar degassing was about 1500 °C, and Ar gas was infused into MS finished purification to use the Ti–Zr getter pump. Weakly adsorbed ^{40}Ar originated atmosphere and potassium detached from the smectite was used for elutriation and pre-heating, and potassium analysis was normally performed by AAS. In contrast, ICP was used for samples with less potassium [9], and potassium contents were calculated by averaging three ICP measurement values.

4 Results

Fig. 1 shows an FE-SEM image of smectite. Every smectite forms a cornflake texture consisting of flared flakes [10]. The small lath [11] particles pile up along the edge of flakes (Fig. 1a, b). The small lath particles cannot be observed in suspended smectite after rubbing powder (Kunimine #29r) onto glass plates (Fig. 1c, d).

Fig. 1. FE-SEM image in original rocks. (a) Kunimine #1 Bentonite (b) Wyoming Spur Bentonite, cornflake texture developed, and small lath particles (arrows) adsorbed on the edge of blade by overgrowth (c) Kunimine #29r, precipitated on SEM holder after rubbed smectite (d) High magnification of #29r, small lath particles cannot be seen on the edge.

Fig. 2 shows the dating data. The horizontal axis is the K–Ar data from this study, and the perpendicular axis is the expected age based on the geological data. The samples with an air contamination ratio over 96% were omitted from Fig. 2.

K–Ar ages indicated the same ages for different particle sizes. However, the contamination rate of the atmosphere increased with decreased particle size. Also, smectite ages show the same ages of around 40 Ma as other dating methods and stratigraphical times. The gaps between the stratigraphical time and K–Ar ages of smectite increase with increasing ages.

Fig. 2. K-Ar ages. Smectite shows younger age increases with increasing age. Contaminations coincide with the expected stratigraphic age.

Fig. 3. The smectite-contamination curve of Wyoming and Kunimine #29. Smectite ratio = smectite / (smectite + contamination).

Ages from contamination are older than smectite ages, and the contamination ages agree well with stratigraphical ages. These ages are inferred from the eruption ages by volcanism.

5 Discussion

5.1 Textures of authigenic smectite

To estimate the formation age of smectite by the K-Ar dating, it is important that smectite contains authigenic clay mineral. Smectite formed cornflake shape within the bentonite also adsorbed small lath particles on the edge of the flared flakes. However, the lath particles cannot be confirmed with the rubbed smectite.

The cornflake texture and adsorption of small lath particles indicate the process of precipitation and crystal growth from pore water. Fibrous laths were observed on the edge of flared flakes and crystallized in the a-b plane of the smectite-illite mixed layer [10]. Laths appear to have formed as an overgrowth texture on the wall surface of ordered I/S and illite [11].

To estimate the formation ages of smectite by K-Ar dating, it is important that lath particles be normally observed on the edge of the smectite flake.

5.2 Influence of contamination

Other minerals cannot be identified from the extracted smectite by XRD profiles. However, if potassium contents of smectite are 0 wt%, K-Ar values indicate very small contamination ages. The contamination and extracted smectite mixing curves are shown in Fig. 3. Smectite ages are different from contamination ages for smectite contents of 90 wt%. In the case of contamination contents lower than 10 wt%, samples with fewer wt% contamination contents have ages that correspond with extracted smectite at 100 wt% ages.

The strongest XRD peak of 5 wt% biotite or K-feldspar, and 95 wt% smectite mixed samples reached 500 to 1000 cts under the same XRD conditions. Also, contents of contamination in extracted clay samples had already reached a level lower than a few wt%.

Consequently, extracted clay ages show that smectite formation ages even if very few other minerals were contaminated into smectite extracted sample.

5.3 Degases of Ar

Smectite ages indicated younger ages than stratigraphical ages of the formation, and this gap increased with increased age. Potassium is dissolved into solution under high temperatures. Also, I/S is formed due to potassium fixation into the interlayer of smectite. Metastable smectite was detected in bentonite despite the bentonite being crystallized several million years ago, showing that potassium is not supplied from pore water to the interlayer for a long period. ^{40}Ar is formed by radioactive decay from ^{40}K without changing a positron. Radiogenic ^{40}Ar atomic is fixed in the ^{40}K atomic-occupied site on the spot, and K-Ar ages tend to be young with the formation of I/S [12].

Illite layers are recrystallized by the dissolution and precipitation of illite layers if smectite layers fall below 50% [1]. I/S, which consists of large concentrations of expansive layers, grows large crystals with the dissolution and precipitation of small particles, and the degassing of Ar from smectite with ages less than 40 Ma occurs at very small concentrations. In contrast, Ar degassing ratios increase as time increases. Then, K-Ar ages of smectite indicate younger ages than the stratigraphic ages detected.

6 Summary

Smectite ages by K-Ar dating indicated younger ages than stratigraphical ages of the formation. This gap increases with increased age. However, smectite ages coincide with bentonite formation ages <40 Ma. The mixing curve made by purification smectite and contamination enables the dating of smectite.

Smectite formation ages can be analyzed by the K-Ar method by the confirmation of small lath particles.

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