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FURTHER INVESTIGATIONS OF A CONVERSION SERIES OF DIOCTAHEDRAL MICA/SMECTITES IN THE SHINZAN HYDROTHERMAL ALTERATION AREA, NORTHEAST JAPAN

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Abstract—A complete conversion series for mica/smectites was found in a hydrothermal alteration envelope around Kuroko-type ore deposits at the Shinzan area, Akita Prefecture, Northeast Japan. The minerals are an alteration product of volcanic glass of Miocene age and are commonly associated with zeolites and silica minerals. Degrees of ordering of interstratification of the minerals change discontinuously from Reichweite $g = 0$ (100–55% expandable layers) to $g = 1$ (45–20% expandable layers), and from $g = 1$ to $g = 2$ (<20% expandable layers). This pattern of conversion differs from the behavior of mica/smectites during burial diagenesis which undergo a continuous change in ordering type, and from the behavior of rectorite which displays a constant expandability and ordering (45–55%) over a wide range of conditions. Differences between these minerals were also found in the relationships between expandability and total layer charge, and between expandability and number of non-exchangeable interlayer cations. In mica/smectites from the Shinzan area, chemical changes in the interlayers and tetrahedral and octahedral sites are consistent with a reaction in which K-enrichment and K-fixation in the interlayers are controlled by an increase in negative layer charge. This conversion occurred in response to a steep geothermal gradient and migrating hydrothermal solutions.

Key Words—Burial diagenesis, Interstratification, K-fixation, Mica, Rectorite, Smectite.

INTRODUCTION

Interstratified dioctahedral mica/smectites can be generated by various processes, e.g., during the diagenetic conversion of montmorillonite to illite. This reaction has been studied by many workers (Burst, 1969; Perry and Hower, 1970; Weaver and Beck, 1971; Foscolos and Kodama, 1974; Hower *et al.*, 1976; Środoń, 1979). The structural and chemical changes of the minerals involved in the reaction are sensitive indicators of the degree of diagenesis.

Mica/smectites are also abundant in hydrothermal alteration areas. In Japan, occurrences have been reported mainly from the hydrothermal alteration envelopes surrounding pyrophyllite-sericite ore deposits and Kuroko-type ore deposits. The pyrophyllite-sericite ores (Roseki) commonly contain rectorite-like minerals (Shimoda and Sudo, 1960; Sudo *et al.*, 1962; Brindley and Sandalaki, 1963; Kodama *et al.*, 1969; Matsuda *et al.*, 1981a, 1981b), whereas the Kuroko-type deposits, composed of various sulfides and sulfates are surrounded by hydrothermal alteration aureoles with mica/smectites (Shimoda, 1970, 1972; Shirozu and Higashi, 1972; Higashi, 1974, 1980: Inoue *et al.*, 1978). In 1978, Inoue *et al.* reported a complete conversion series of mica/smectites from this type of deposit from the Shinzan area, northeast Japan, where the minerals occur as alteration products of felsic volcanic glass.

In the present study, the conversion series of mica/smectites of hydrothermal origin is characterized and compared with a series of mica/smectites of diagenetic origin and with a rectorite series from Roseki-type ore deposits.

OCCURRENCE OF MICA/SMECTITES IN THE SHINZAN AREA

Samples were obtained from eight drillholes in the Shinzan area, Akita Prefecture, as shown in Figure 1. Although a large part of the area is covered by Quaternary sediments, two Miocene formations, which are largely pyroclastic, were drilled in the area. These formations have been subjected to hydrothermal alteration and can be grouped into six zones based on the assemblages of authigenic minerals as listed in Table 1. A zonal arrangement from a sericite-chlorite zone nearest the center of hydrothermal activity, which is assumed by the exposure of Cu-Pb-Zn impregnation, to a montmorillonite zone or zeolite zones in the margin is depicted in Figure 2. Interstratified mica/smectites occur extensively between the sericite-chlorite zone and montmorillonite or zeolite zones. Although the percentage of expandable layers in mica/smectites in-

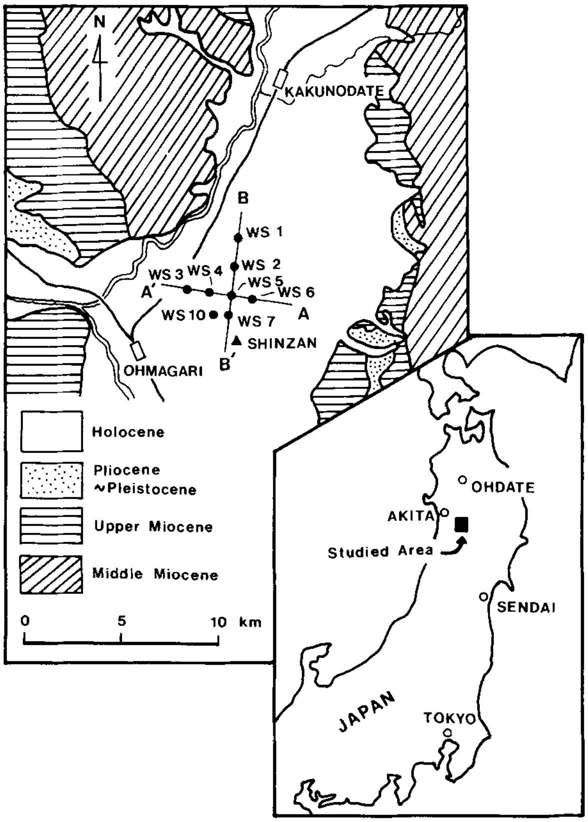

Figure 1. Locality of drillholes and general geology of the Shinzan area, Japan.

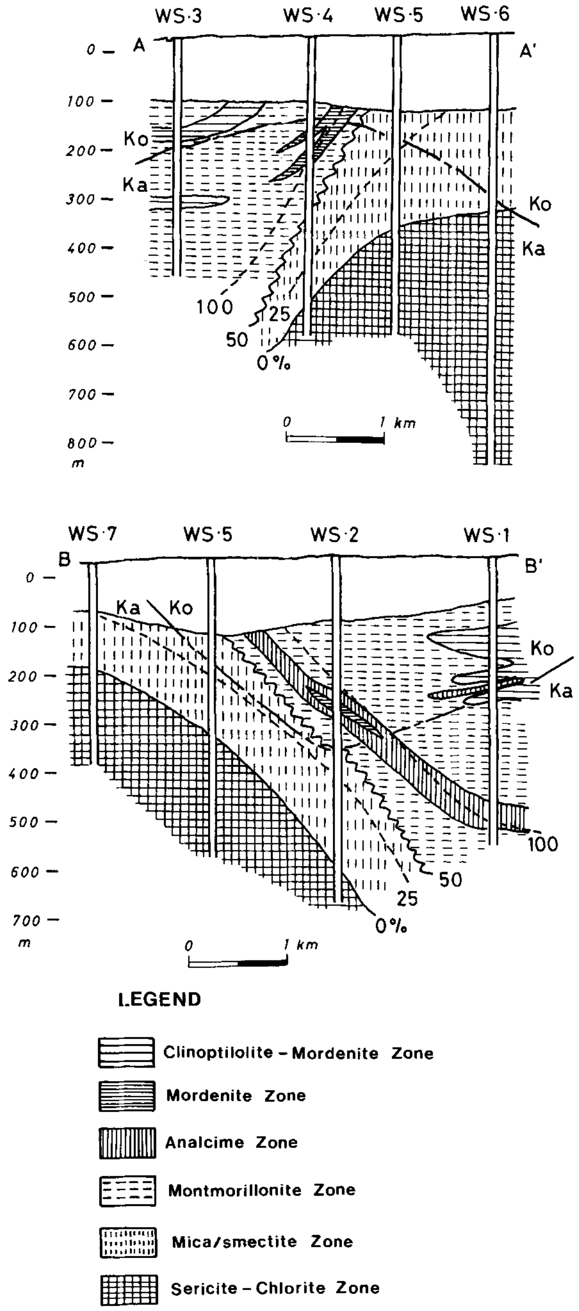

Figure 2. Vertical sections showing the zonal distribution of authigenic minerals in the Shinzan area. Long-dashes show the stratigraphic boundary between the Kawajiri (Ka) and the Kotsunagizawa (Ko) Formations (Miocene). Short-dashes show the contours of percentage of expandable layer in mica/smectites.

creases gradually from the sericite-chlorite zone to the montmorillonite or zeolite zones, the mica/smectite zone described here is characterized by mica/smectites that contain less than about 50% expandable layers. The vitric materials have been largely replaced by clay minerals, zeolites, and silica minerals, but original vitric textures are commonly detectable in the altered sediments.

EXPERIMENTAL METHODS

X-ray powder diffraction (XRD) analysis

XRD analysis was performed on oriented specimens held at 55 ± 5% R.H. and on specimens kept in ethylene glycol (EG) vapor heated at 60°–65°C for more than 20 hr. K- and Mg-saturated specimens were run in order to determine the percentage of expandable layers in mica/smectites after EG treatment, according to the method of M. Sato (1973) based on the Kakinoki and Komura (1952) equation.

Chemical analysis

Following storage of the mica/smectite in a 0.1 N $SrCl_2$ solution, the Ca, Mg, Na, and K contents of the supernatant solution were determined by atomic absorption and flame emission spectroscopy. The remaining clay was washed in distilled water and decomposed by HF and H_2SO_4. Adsorbed Sr was determined by atomic absorption spectroscopy. The bulk chemical composition was determined for untreated specimens.

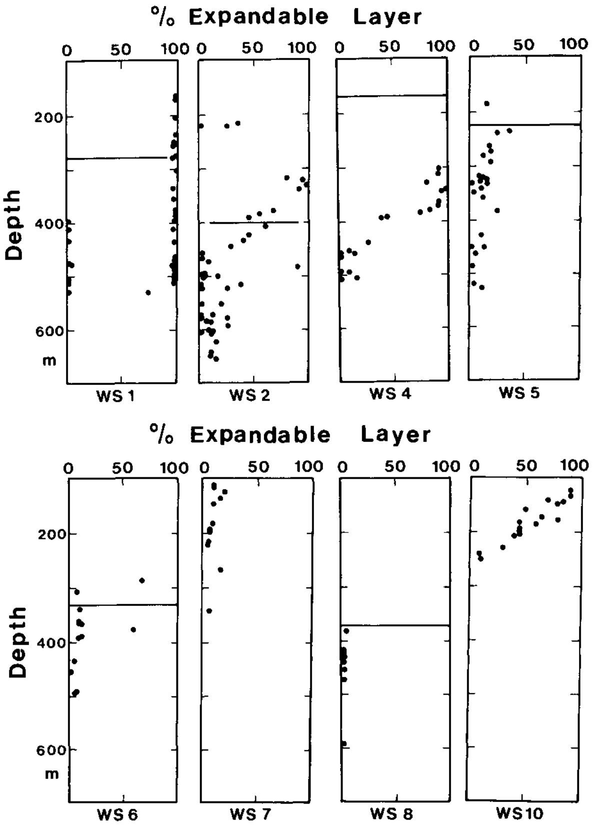

Figure 3. Variation in percentage of expandable layer of mica/smectites with increasing depth of eight drillholes at the Shinzan area (after Inoue *et al.*, 1978).

A more detailed description of the analytical techniques used can be found in Inoue *et al.* (1978) and Inoue (1983); complete data are reported in Inoue *et al.* (1978) and Inoue (1980).

Cation-exchange reaction

Ca-K and Na-K ration-exchange reactions were carried out using montmorillonite from Aterazawa in Yamagata Prefecture (Inoue and Minato, 1979). Exchange

Table 1. Authigenic mineral assemblages of alteration zones.

Zone	Mineral assemblage
Sericite-chlorite zone	Sericite, chlorite, quartz
Mica/smectite zone	Mica/smectites, quartz, (chlorite, sericite, montmorillonite)
Montmorillonite zone	Montmorillonite, quartz, opal
Analcime zone	Analcime, mica/smectites, montmorillonite, chlorite, quartz
Mordenite zone	Mordenite, montmorillonite, mica/smectites, quartz
Clinoptilolite-mordenite zone	Clinoptilolite, (mordenite), montmorillonite, opal

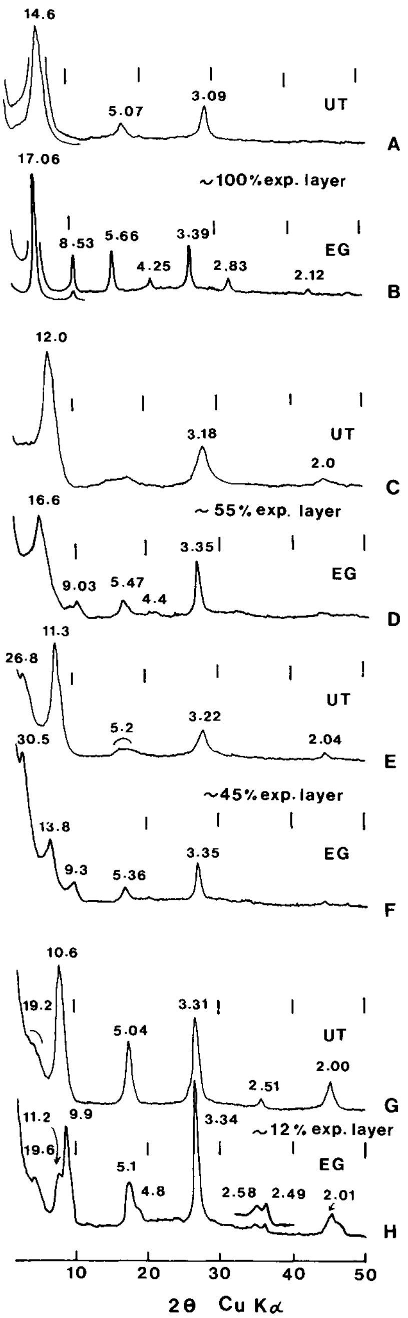

Figure 4. Representative X-ray powder diffraction patterns of mica/smectites with various expandabilities from the Shinzan area.

(A), (B): drillhole WS-2, 183.50 m, ~100% exp. layers
(C), (D): drillhole WS-2, 383.80 m, ~55% exp. layers
(E), (F): drillhole WS-4, 392.80 m, ~45% exp. layers
(G), (H): drillhole WS-5, 281.45 m, ~12% exp. layers
(A), (C), (E), (G): untreated specimens
(B), (D), (F), (H): ethylene-glycol treated specimens

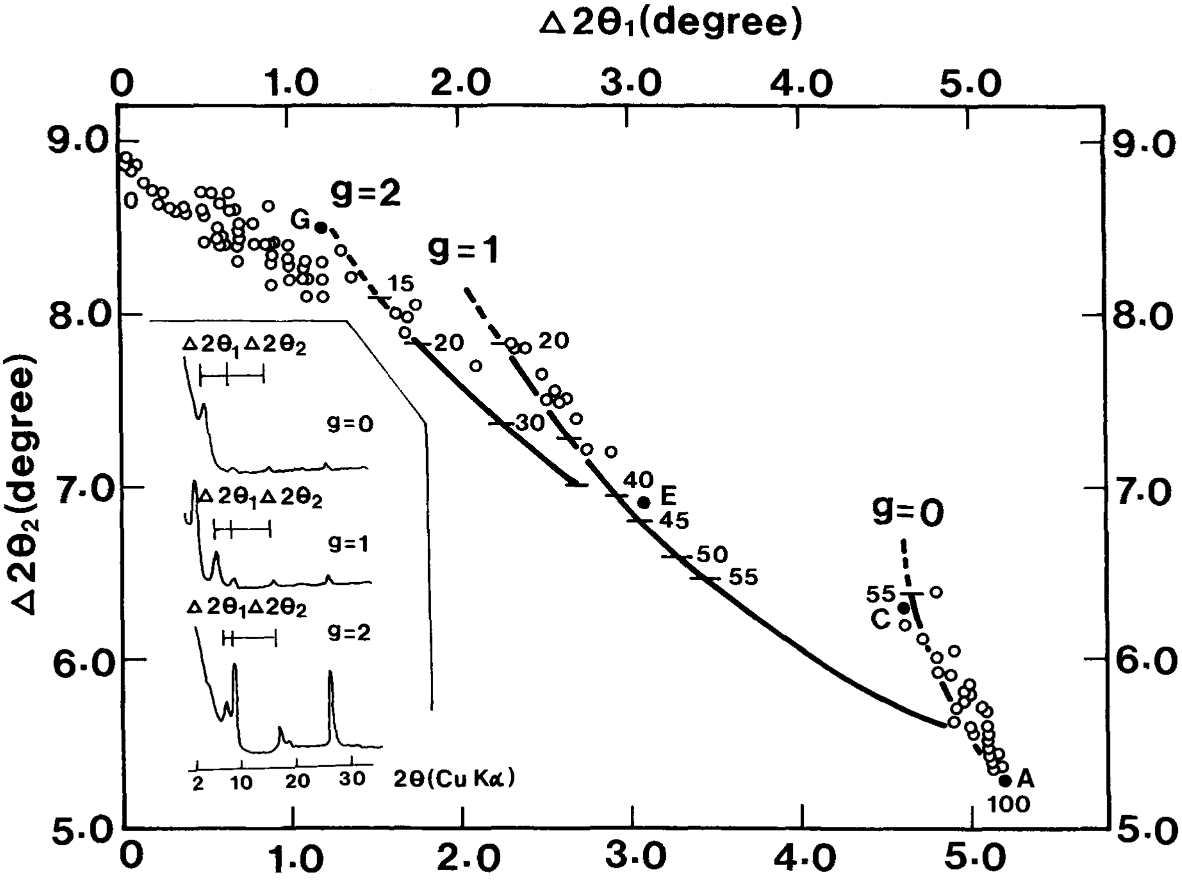

Figure 5. Diagram showing $\Delta 2\theta_1$ vs. $\Delta 2\theta_2$ relation for mica/smectites from the Shinzan area. The solid circles B, D, F, and H correspond to samples shown in Figure 4. See text for definition of $\Delta 2\theta_1$ and $\Delta 2\theta_2$.

isotherms were determined at a fixed total normality (0.1 N) and at various temperatures.

CONVERSION SERIES OF MICA/SMECTITES IN THE SHINZAN AREA

Reaction trend in interstratification

The expandability of mica/smectites decreases continuously with increasing depth in each drillhole. The feature is especially conspicuous in drillholes WS-2, WS-4, and WS-10 (Fig. 3). Figure 2 shows that expandability increases laterally from the center of the hydrothermal alteration aureole to the margin.

Comparing the typical XRD patterns of mica/smectites with various expandabilities (Figure 4) with calculated patterns (Reynolds and Hower, 1970; M. Sato, 1973; Watanabe, 1980), it is clear that the degree of ordering of interstratification in the mica/smectites increases systematically with decreasing expandability of the minerals (Inoue *et al.*, 1978).

Recently, Watanabe (1981) devised a diagram for the identification of the degree of ordering of interstratified mica/smectites; he used spacing of 10.1 Å and 16.9 Å for the mica and smectite components, respectively. The technique uses three basal XRD reflections which are sensitive to the variation of the degree of ordering: a peak (l_1) at 5.1–7.6°2θ, a peak (l_2) at 8.9°–10.2°2θ, and a peak (l_3) at 16.1°–17.2°2θ (CuKα radiation) after EG treatment (see the lower left part of Figure 5). If the angular differences are represented as $\Delta 2\theta_1 = l_2 - l_1$ and $\Delta 2\theta_2 = l_2 - l_2$, there is a distinct relationship between $\Delta 2\theta_1$ and $\Delta 2\theta_2$ that shows systematic changes with expandability at constant Reichweite values. When the data for mica/smectites in the present study are plotted on the Watanabe's diagram ($\Delta 2\theta_1$ vs. $\Delta 2\theta_2$ diagram, Figure 5), the relationship between expandability and interstratification of mica/smectites becomes clearer: mica/smectites containing more than about 55% expandable layers correspond to a random interstratification of Reichweite g = 0 (e.g., XRD patterns of Figure 4c and 4d), and those containing about 45–20% and less than about 20% expandable layers have an ordered interstratification of g = 1 (e.g., Figure

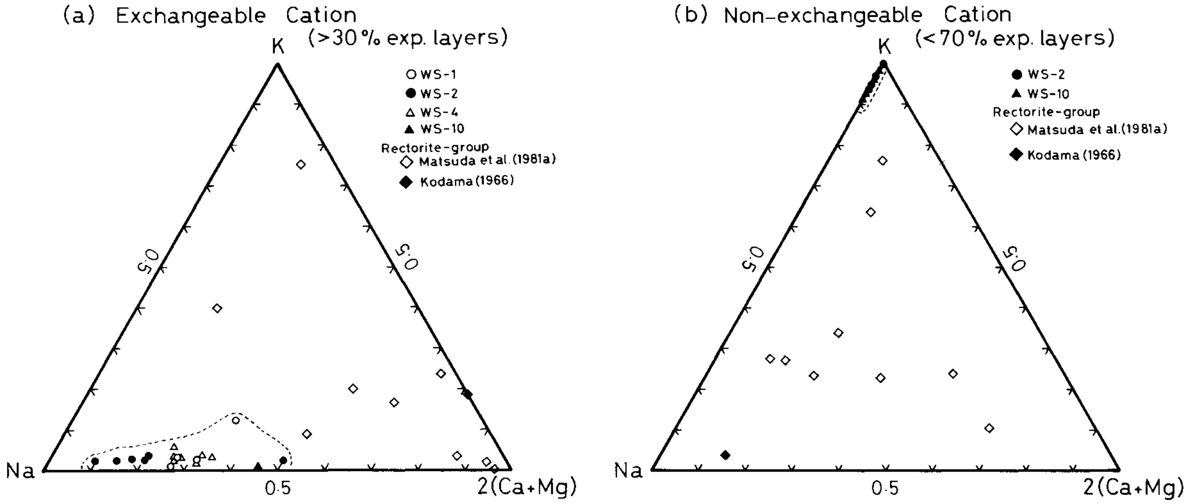

Figure 6. Composition of interlayer cations of mica/smectites from the Shinzan area and of rectorite-like minerals from Roseki deposits. (a) exchangeable cations of mica/smectites with more than 30% expandable layers; (b) non-exhcangeable cations of mica/smectites with less than 70% expandable layers.

4e and 4f) and $g = 2$[1] (e.g., Figure 4g and 4h), respectively. Most of the plots for mica/smectites with less than about 10% expandable layers tend to be biased toward lower $\Delta 2\theta_1$ values from the extrapolated curve of $g = 2$. If these specimens contain discrete sericite, the value of $\Delta 2\theta_1$ should become smaller. This deviation from the $g = 2$ curve suggests that these mica/smectites may have another type of interstratification with a longer-range ordering than $g = 2$. As shown in Figure 5, occurrences of perfectly ordered mica/smectites with 55–45% expandable layers are rare, and plots are scarce in fields between the $g = 0$ and $g = 1$ curves, and between the $g = 1$ and $g = 2$ curves.

Reaction trend in chemical composition

Bulk chemical composition of mica/smectites from the Shinzan area changes continuously with decreasing expandability (Inoue *et al.*, 1978). The composition of interlayer cations of mica/smectites from the Shinzan area is given in Figure 6. The exchangeable interlayer cations of mica/smectites with more than 30% expandable layers are mainly Na and Ca; exchangeable K and Mg contents are very small (Figure 6a). Interlayer Ca is more common in drillholes from the marginal zones (WS-1 and WS-4) and in the upper part of drillhole WS-2. Sodium is a predominant exchangeable interlayer cation in mica/smectites coexisting with analcime. Potassium is a predominant non-exchangeable interlayer cation in mica/smectites with less than 70% expandable layers; the non-exchangeable Na and Ca contents are negligible (Figure 6b).

The chemical variation in the 2:1 silicate layer of mica/smectites is shown in Figure 7 in terms of the pyrophyllite ($Al_2Si_4O_{10}(OH)_2$), muscovite ($KAl_2Si_3AlO_{10}(OH)_2$), and leucophyllite ($KAlMgSi_4O_{10}(OH)_2$)

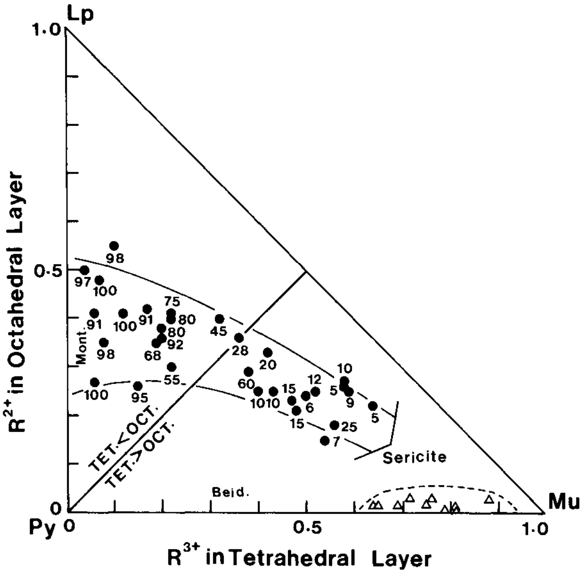

Figure 7. Chemical compositions in the 2:1 silicate layer of mica/smectites from the Shinzan area (●) and of rectorite-like minerals from Roseki deposits (△) (after Matsuda *et al.*, 1981a). The figures indicate the percentage of expandable layer of mica/smectites. Lp: leucophyllite, Mu: muscovite, Py: pyrophyllite, Mont.: montmorillonite, Beid.: beidellite.

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[1] Watanabe (1980) calculated the same XRD patterns of mica/smectites with $g = 2$ as IMII-ordering ($g = 3$) by Reynolds and Hower (1970), based on the X-ray diffraction theory for one-dimensionally disordered crystal by Kakinoki and Komura (1952).

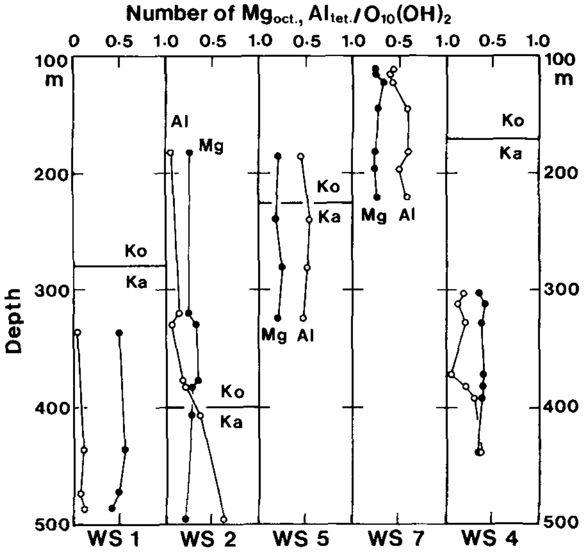

Figure 8. Change of the numbers of the octahedral Mg and tetrahedral Al per $O_{10}(OH)_2$ in mica/smectites increasing the depth in boreholes of the Shinzan area. The solid and open circles indicate octahedral Mg and tetrahedral Al, respectively. Lateral lines indicate the stratigraphic boundary between the Kawajiri (Ka) and the Kotsunagizawa (Ko) Formations.

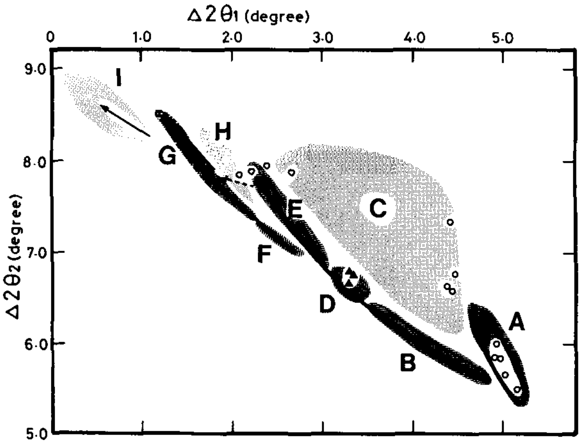

Figure 9. Schematic diagram of structural conversion trend of mica/smectites of different origins. ○ = Gulf Coast (Perry and Hower, 1970); ▲ = rectorite-like minerals from Roseki deposits; ← = conversion trend in the Shinzan area.

contents. Ferric and ferrous iron were regarded as substituting for Al and Mg, respectively. As shown in Figure 7, the mica/smectites with nearly 100% expandable layers have a typical montmorillonitic composition. With decreasing expandability, the tetrahedral Al content increases from 0 to 0.65, and the octahedral Mg content decreases from 0.5 to 0.2; consequently, the smectite is gradually converted to a mica with sericitic composition. The dominant source of negative layer charge changes from the octahedral to the tetrahedral site at about 30% expandable layers. Figure 8 shows the vertical changes in the numbers of octahedral Mg and tetrahedral Al cations per $O_{10}(OH)_2$ in mica/smectites from the drillholes.

COMPARISON WITH MICA/SMECTITES FORMED IN DIFFERENT ENVIRONMENTS

Structural conversion

In the $\Delta 2\theta_1$ vs. $\Delta 2\theta_2$ diagram (Figure 9), nine fields can be distinguished, each of which represents a particular feature of interstratification in mica/smectites on the basis of probability theory. The interstratification of mica/smectites of field A is in a structure of $g = 0$, $P_M = P_{MM} = P_{IM}$ and $P_I = P_{II} = P_{MI}$, where P_I and P_M indicate the probabilities of occurrence of mica and expandable layers within a stacking arrangement, and P_{II} and P_{MM} are the transition probabilities from mica to mica and from expandable layer to expandable layer, respectively. Field B is represented by the interstratification: in $g = 1$, $0.5 < P_M < 1.0$, $P_{II} = 0$ and $P_{MM} \neq 0$; field C: in $g = 1$, if $P_I > P_M$, $P_{MM} \neq 0$, or if $P_I < P_M$, $P_{II} \neq 0$; field D: in $g = 1$, $P_I = P_M \simeq 0.5$, $P_{II} = P_{MM} \simeq 0$ and $P_{IM} = P_{MI} \simeq 1$; field E: in $g = 1$, $0 < P_M < 0.5$, $P_{MM} = 0$ and $P_{II} \neq 0$; field F: in $g = 2$, $0.33 \leq P_M$ and dominant occurrence of IMI-domain within a stacking arrangement; field G: in $g = 2$, $0.33 > P_M$, $P_{MM} = 0$, $P_{MIM} = 0$, $P_{MIIM} \neq 0$, and dominant occurrence of IMII-domain; field H: in $g = 2$, $P_{MM} = 0$ and $P_{MIM} \neq 0$, and field I is represented by another type of interstratification with a long-range ordering greater than $g = 2$. The interstratification in mica/smectite with a given expandability can have various degrees of ordering from $g = 0$ to $g = 1$ and from $g = 1$ to $g = 2$.

The conversion trend in the Shinzan area is represented in Figure 9 by A → E → (H→) G → I. For comparison, some of the diagenetic mica/smectites from the Gulf Coast of the United States (Perry and Hower, 1970) are plotted in the figure and are scattered in fields C and H. The dispersion of the points may be partly due to contamination by detrital mica and smectite. The conversion trend of the diagenetic mica/smectites is represented by A → C → E → H (→ G → I). A similar trend for diagenetic mica/smectites was found from the Kamisunagawa area in Hokkaido and the Ohashizawa area in Yamagata by Shimoda *et al.* (1983). Thus, the conversion trend of hydrothermal mica/smectites in the Shinzan area is roughly similar to those of diagenetic origin, but, it is distinct in that the former does not pass into field C and probably not into field H. As mentioned above, fields C and H may be regarded as transitional zones from a random structure of $g = 0$ to an ordered structure of $g = 1$ and from $g = 1$ to another ordered structure of $g = 2$, respectively. In terms of a structural conversion from smectite to mica, the degree of ordering of interstratification of hydrothermal mica/smectites changes discontinuously from $g = 0$ to $g = 1$

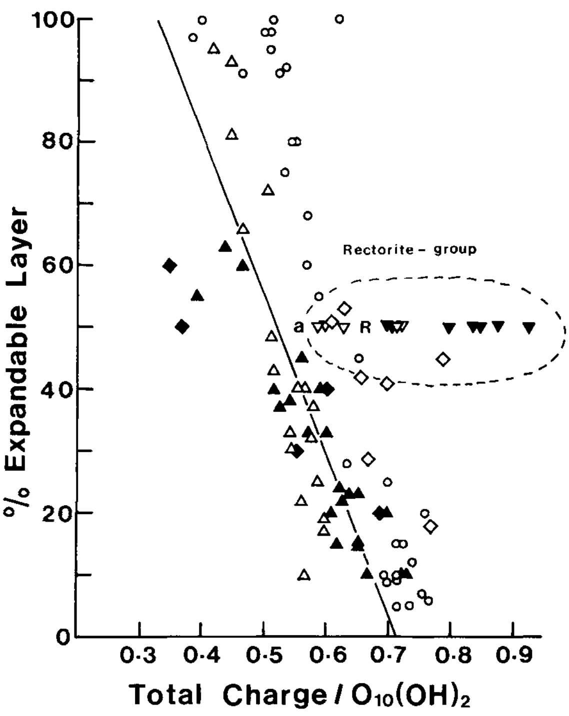

Figure 10. Relationship between the percentage of expandable layer and total layer charge per $O_{10}(OH)_2$ in mica/smectites of different origins; hydrothermal mica/smectites (○ = this study), diagenetic mica/smectites (▲ = Hower and Mowatt, 1966; △ = Eslinger *et al.*, 1979; ◇ = Foscolos and Kodama, 1974; ◆ = Weaver and Pollard, 1973) and rectorite-like minerals (▼ = Matsuda *et al.*, 1981a, 1981b; ▽ = Weaver and Pollard, 1973; a: Brindley, 1956; R; Kodama, 1966). The line is the average one of total layer charges in montmorillonite and illite drawn between 0.33 and 0.72.

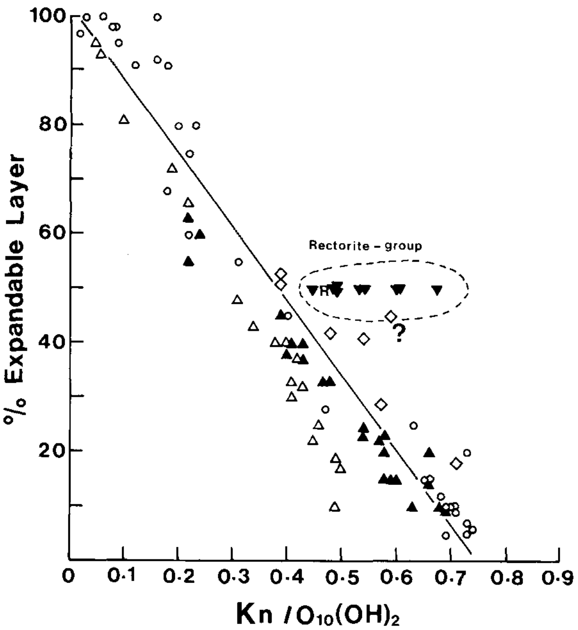

Figure 11. Relationship between the percentage of expandable layer and number of non-exchangeable interlayer cations (K_n) per $O_{10}(OH)_2$ in mica/smectites of different origins; hydrothermal mica/smectites (○ = this study), diagenetic mica/smectites (▲ = Hower and Mowatt, 1966; △ = Eslinger *et al.*, 1979; ◇ = Foscolos and Kodama, 1974) and rectorite-like minerals (▼ = Matsuda *et al.*, 1981a, 1981b; R: Kodama, 1966). The curve indicates a regression one for mica/smectites which have predominantly non-exchangeable K^+ in the interlayer.

and from g = 1 to g = 2, whereas the conversion is continuous in diagenetic clays.

In the hydrothermal alteration and diagenetic environments, the interstratification represented by fields B, D, and F seems to be difficult to realize in the course of structural conversion (Figures 5 and 9). In particular, mica/smectites with a perfectly ordered interstratification in field D are very rare. On the other hand, rectorite-like minerals in field D are common in Roseki deposits. This difference is probably attributable to difference in crystallo-chemical properties of component layers in each mica/smectite, as described below.

Chemical properties

The relationships between the percentage of expandable layer and the total layer charge, and between the percentage of expandable layer and the number of non-exchangeable interlayer cations are shown in Figures 10 and 11, respectively. The relationships are useful in the characterization of mica/smectites of different origins. In Figure 10, a line has been between the average total layer charges of montmorillonite ($0.33/O_{10}(OH)_2$) and illite ($0.72/O_{10}(OH)_2$) after Weaver and Pollard (1973). The points for diagenetic mica/smectites tend to swarm near the line, whereas points for those in the present study tend to be biased toward the right side from the line; that is, toward the greater total layer charge. Smectites in the alteration zones around Kuroko deposits usually have greater total layer charge than the above average value of montmorillonite (Shirozu and Iwasaki, 1980). Sericites of hydrothermal origin generally have greater total layer charge than diagenetic illites (Weaver and Pollard, 1973). Therefore, the deviation from the average line in hydrothermal mica/smectites may be due to greater layer charges of both component layers.

The points for rectorite-like minerals are distinctively biased toward greater layer charge (Figure 10). As shown in Figure 6b, rectorite-like minerals commonly contain considerable amounts of Na and Ca as non-exchangeable interlayer cations. The hydration energy of Na and Ca is greater than that of K. Na and Ca with greater hydration energy will hold water molecules more tightly in the interlayer. It is likely that development of greater negative layer charge in the 2:1 silicate layer is responsible for dehydration of the

Table 2. Temperature, pH, and major cations[1] in Kuroko ore-forming solution.

T (°C)	250° ± 50°C
pH (25°C)	4.5 ± 0.5
Cl	33,000 ppm
Na	18,500 ppm
K	4000 ppm
Ca	500 ppm
Mg	1–10 ppm
SO_4	10^{-4} ppm
Equivalent fraction	K/(Na + K) = 0.113 K/(2Ca + K) = 0.803

[1] Data partly revised from Shikazono (1976).

interlayer Na and Ca, and for collapse of the basal spacing (Eberl, 1980; Inoue, 1983).

Figure 11 shows the relationship between the percentage of expandable layer and number of non-exchangeable cations (K_n) per $O_{10}(OH)$ unit in mica/smectites of different origins. In the mica/smectites which contain dominantly K as non-exchangeable interlayer cations (Figure 6b), the correlation for the above relationship is excellent. The relation is expressed approximately by a linear regression equation: % expandable layers = $-137\ K_n + 103$. On the other hand, the plots for rectorite-like minerals with non-exchangeable Na and Ca are biased from the regression curve toward larger amounts of non-exchangeable interlayer cations. This bias is also attributable to the greater layer charge of the rectorite-like minerals as shown in Figure 10.

Thus, the mica/smectites having dominantly non-exchangeable interlayer K from the present study and those of diagenetic origin (Hower and Mowatt, 1966; Foscolos and Kodama, 1974; Eslinger *et al.*, 1979) are chemically different from rectorite-like minerals. These differences influence the degree of ordering of interstratification of mica/smectites even if the minerals have the same expandability, as pointed out by Eberl and Hower (1977).

GENESIS OF MICA/SMECTITES IN THE SHINZAN AREA

Physico-chemical environments forming mica/smectites

The physico-chemical characteristics of Kuroko ore-forming solutions have been described by many geochemists (Kajiwara, 1973; T. Sato, 1973; Ichikuni, 1975; Shikazono, 1976). A representative example is given in Table 2. Oxygen- and sulfur-isotope and fluid-inclusion studies show that the temperatures of precipitation of metal sulfides were about 250° ± 50°C. It may be assumed that the temperature of hydrothermal solution at the conduit of the Kuroko mineralization at the Shinzan area was around 250°C. The oxygen-isotope temperatures in a Kuroko-type deposit (Hattori and Muehlenbachs, 1980) indicate that the maximum temperature at the boundary between the sericite-chlorite zone and the mica/smectite zone was about 200°C. Analcime may be stable to about 190°C at 2 kb in the reaction analcime + quartz = albite + H_2O (Campbell and Fyfe, 1965). According to Utada (1968) and Iijima and Utada (1971), analcime decomposes at about 100° ± 20°C in burial diagenetic environments, where the geothermal gradient approximates 2°C/100 m. Although the stability of analcime is still controversial, the analcime zone (Figure 2) was probably formed at about 100° ± 20°C. The upper stability temperature of clinoptilolite-mordenite zones is about 60°–90°C (Utada, 1968). Based on the above temperature estimates, it is likely that the mica/smectites in the Shinzan area formed between 80° and 200°C.

Burial diagenetic mica/smectites formed in a relatively wide range of depth, 3000 m to 4000 m according to Perry and Hower (1970) and Hower *et al.* (1976). On the contrary, the mica/smectite zone in the Shinzan area developed over a considerably narrower range (Figure 2) mainly because of the steep thermal gradient in this area during the hydrothermal alteration. The estimated geothermal gradient, based upon the above-mentioned temperatures, is about 10°C/100 m.

Migration of chemical components during conversion reaction of mica/smectites

Table 3 shows the chemical composition of estimated original volcanic glass (3a) and typical mica/smectites (3b–3g) at various degrees of interstratification from the Shinzan area. Assuming that the original chemical composition was uniform throughout the sediments of the Shinzan area, the variation of chemical composition in Table 3 can be explained as follows. In the center of hydrothermal activity, sericite (Table 3b) and chlorite were formed by reaction of the hydrothermal solution with the volcanic glass at high temperatures. Away from the center of hydrothermal activity, the hydrothermal solutions gradually penetrated tuffs and were diluted with interstitial pore solutions. The reaction of the felsic glass with the solution at lower temperatures probably produced smectite, similar to that in the specimen (Table 3g) which has a typical montmorillonitic composition and which contains small amounts of exchangeable Ca^{2+}. Then, the early-formed smectite came into contact with percolating hydrothermal solutions. At higher temperatures, Na^+, Ca^{2+}, and Si^{4+} were leached from the early-formed smectite, and K^+ in the solution was gradually fixed to form mica/smectites with lower expandabilities (Table 3c–3f). The leached Ca^{2+} migrated to the margin and was fixed as carbonates or mordenite, while Na^+ was fixed as analcime in the marginal zones. The Na-concentration of hydrothermal solution responsible for the formation of analcime was considerably high (Utada

Table 3. Chemical compositions of fresh glass as a precursor and mica/smectites with various expandabilities as products in the Shinzan area.

	a[1] fresh glass	b WS-2 495.6 m	c WS-4 440.6 m	d WS-2 383.8 m (wt %)	e WS-2 377.8 m	f WS-2 320.4 m	g WS-2 183.5 m
SiO_2	71.3	50.42	50.97	52.65	52.62	54.43	55.41
TiO_2	0.25	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Al_2O_3	12.1	29.42	22.27	20.83	19.80	21.13	19.28
Fe_2O_3	1.9	3.41	2.90	2.51	2.61	1.76	2.77
MnO	0.08	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MgO	0.2	2.21	3.46	2.98	3.39	2.58	2.91
CaO	1.37	0.05	0.18	0.11	0.22	0.14	0.82
Na_2O	3.60	0.31	1.08	1.75	2.11	2.77	1.41
K_2O	2.56	7.97	4.79	3.31	2.09	0.76	0.13
H_2O	6.64	5.77	13.55	15.61	16.47	15.41	16.90
Total	100	99.56	99.20	99.75	99.31	98.98	99.63
% exp. layer		5%	28%	55%	68%	95%	100%

[1] By electron microprobe, after Iijima (1974).

and Ishikawa, 1973), a speculation that is supported by the observation that the exchangeable interlayer cations of mica/smectites coexisting with analcime are dominantly Na (Table 3e).

According to the above-estimated formation temperature of the analcime zone, the expandability of mica/smectites in the analcime zone of the Shinzan area should have decreased to near 50%, compared with those of common burial diagenetic mica/smectites (Perry and Hower, 1970). In fact, however, the expandability of mica/smectites coexisting with analcime is at least 70–80% (Figure 2). Na-saturated smectite is stable to higher temperatures in the solution with high Na-activity (i.e., ~400°C; Eberl and Hower, 1977). These facts suggest that the development of the mica/smectite zone and the progress of the conversion reaction were controlled by the cation composition of hydrothermal solution as well as by temperature.

Process for the enrichment and fixation of K in the interlayer

During the course of the conversion of smectite to mica through intermediate mica/smectites, Na^+ and Ca^{2+} in the interlayers of smectite were exchanged for K^+ in the hydrothermal solution, and the K ion was fixed in the interlayers.

Several factors might have contributed to K-enrichment in the interlayer during the hydrothermal alteration. Potassium smectite may have formed by the following exchange reaction:

$$M^z\text{-smectite} + zK^+ = zK\text{-smectite} + M^z$$

where M is Na^+ or Ca^{2+}, and z is the valence of M ion. The smoothed isotherms for the above reaction are shown in Figure 12. Assuming that the solution has the cation composition listed in Table 2 and that the amounts of the other cations in the solution are neglected for simplicity, equivalent fractions of K^+ in Na-K- and Ca-K-smectites can be calculated to be at least 0.25 and 0.4 at 50°C from the isotherms in Figure 12. In fact, the hydrothermal solution responsible for the formation of mica/smectites at the marginal zones probably contained more Na^+ than the hypothetical solution shown in Table 2. Assuming the composition of the solution to be constant, the equivalent fraction of K^+ in smectite will become smaller with increasing temperature. Thus, the enrichment of K^+ in the interlayers of smectite cannot be explained by increasing temperature alone.

Considering only an exchange reaction between Na^+ and K^+, which is reasonable in the solution with small amounts of Ca^{2+} as shown in Table 2, the K-selectivity of smectite increases with increasing negative layer charge (Inoue, unpublished data). Even at a constant temperature, K^+ will concentrate in the interlayers of smectite as negative layer charge increases by the substitution of tetrahedral Si by Al, as described above. On the other hand, the more the negative layer charge

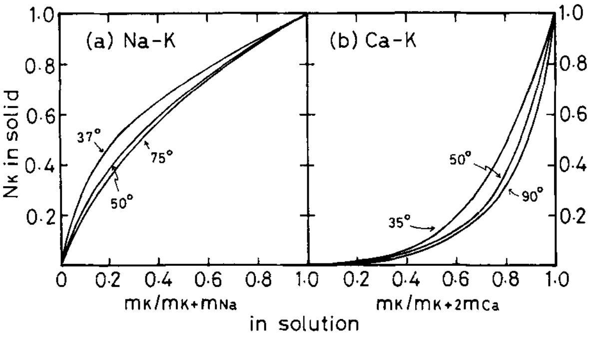

Figure 12. Smoothed isotherms for Na-K (a) and Ca-K (b) exchange reactions in montmorillonite at a total normality of 0.1.

of smectite increases, the greater is the exothermicity of the Na-K exchange reaction for smectite (Inoue, unpublished data). This greater exothermicity inhibits K-enrichment in the interlayer. But, taking into consideration the fact that Na-K exchange reactions of vermiculite are endothermic (Inoue, unpublished data), it may be inferred that smectite with a negative layer charge greater than a certain threshold prefers K^+ with increasing temperature. Eventually, some of smectite layers may break down with increasing temperature, and, as a consequence, dissolved Al may substitute for tetrahedral Si in the remaining smectite. The smectite with greater negative layer charge has a greater selectivity for K^+ even in solutions of low K-concentration (e.g., Inoue *et al.*, 1981).

To convert smectite layers to mica, it is necessary that K^+ is fixed in the interlayers. Smectites can fix a specific amount of interlayer K^+, the amount of K-fixation increasing with increasing negative layer charge (Inoue, 1983). Hence, increasing negative layer charge can be responsible for the K-enrichment and K-fixation in the interlayers of smectite, and as a result smectite converts to mica through intermediate mica/smectites. Furthermore, most of the K^+ in mica/smectites with less than 70% expandable layers is non-exchangeable (Figure 6), and the percentage of non-exchangeable K^+ to the total amount of interlayer cations is larger than that of mica component layer (Inoue, 1983). This fact suggests that the rate of K-fixation reaction in the interlayer occurs faster than the subsequent structural modification that leads to the conversion of smectite to mica through intermediate mica/smectites.

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Резюме—Полные серии видоизменения для слюд/смектитов были найдены в кармане гидротермического изменения вокруг Куроко-типа залежей руды в Шинзан области, Акита префектура, Северно-восточная Япония. Минералы являются продуктом видоизменения вулканического стекла миоценовой эпохи и обычно связываются с цеолитами и кремнеземными минералами. Степени упорядочения переслаивания минералов изменяются прерывисто от числа Рейхвейта g = 0 (100–55% расширяющихся слоев) до g = 1 (45–20% расширяющихся слоев) и от g = 1 до g = 2 (<20% расширяющихся слоев). Этот образец превращения отличается от поведения слюды/смектитов в течение периода диагенеза погребений, которые претерпевают непрерывное изменение типа упорядочения, и от поведения ректорита, который проявлет постоянную способность к расширению и упорядочению (45–55%) в широким диапазоне условий. Различия межлу этими минералами были также найдены и в области соотношений между расширяемостью и полным зарядом слоя, и между расширяемостью и числом необмениваемых межслойных катиогов. Химические изменения в прослойке и в четырехгранных и восьмигранных местах в слюдах/смектитах из Шинзан области согласуются с реакцией, в которой обогащение прослойки калием и фиксация калия в прослойке контролируется увеличением отрицательного заряда слоя. Это превращение происхоит как реакция на большой геотермальный градиент и миграцию гидротермальных растворов. [E.G.]

Resümee—Eine vollständige Umwandlungsserie von Glimmer/Smektite wurde in einer hydrothermalen Umwandlungszone um Erzlagerstätten vom Kuroko-Typ im Shinzangebiet, Akita Prefecture, NO Japan, gefunden. Die Minerale sind Umwandlungsprodukte von vulkanischem Glas aus dem Miozän und treten im allgemeinen zusammen mit Zeolithen und SiO_2-Mineralen auf. Der Ordungsgrad der Wechsellagerung in den Mineralen ändert sich diskontinuierlich von der Reichweite g = 0 (100–55% expandierbare Lagen) bis g = 1 (45–20% expandierbare Lagen), und von g = 1 bis g = 2 (<20% expandierbare Lagen). Dieses Umwandlungsschema unterscheidet sich vom Verhalten Glimmer/Smektite, das durch Versenkungsdiagenese hervorgerufen wird, in dem eine kontinuierliche Veränderung im Ordnungszustand stattfindet. Es unterscheidet sich auch vom Verhalten von Rektorit, der über einen großen Bedingungsbereich eine konstante Expandierbarkeit und Ordnung (45–55%) zeigt. Unterschiede zwischen diesen Mineralen wurden auch in der Beziehung zwischen Expandierbarkeit und Gesamtladung der Schichten und zwischen Expandierbarkeit und Anzahl der nichtaustauschbaren Zwischenschichtkationen gefunden. In den Glimmer/Smektit-Wechsellagerungen aus dem Shinzangebiet hängen chemische Veränderungen in den Zwischenschichten sowie auf den tetraedrischen und oktaedrischen Plätzen mit einer Reaktion zusammen, bei der die K-Anreicherung und K-Fixierung in den Zwischenschichten durch eine Zunahme der negativen Schichtladung kontrolliert wird. Diese Umwandlung ist die Folge eines steilen geothermischen Gradienten und wandernder hydrothermaler Lösungen. [U.W.]

Résumé—Une série de conversion complète pour des mica/smectites a été trouvée dans une enveloppe d'altération hydrothermique autour de dépôts de minéraux du type Kuroko dans la région Shinzan, Préfecture d'Akita, Japon du Nord-Est. Les minéraux sont un produit de l'altération de verre volcanique d'age Miocène, et sont souvent associés avec des zéolites et des minéraux silices. Les degrés d'ordonnement d'interstratification des minéraux changent de manière discontinue de Reichweite g = 0 (100–55% de couches expansibles) à g = 1 (45–20% de couches expansibles) et de g = 1 à g = 2 (<20% de couches expansibles). Ce procédé de conversion diffère du comportement de mica/smectites pendant la diagénèse d'ensevelissement; celles-ci subissent alors un changement de type d'ordonnement continuel; et aussi du comportement de la rectorite qui montre un potentiel d'expansion et un ordonnement (45–55%) constants sur une large gamme de conditions. Des différences entre les relations de potentiel d'expansion et la charge totale de couche, et du potentiel d'expansion et du nombre de cations intercouche non-échangeables de ces minéraux ont aussi été trouvées. Dans les micas/smectites de la région Shinzan, des changements chimiques dans les intercouches et dans les sites tétraèdraux et octaèdraux sont compatibles avec une réaction dans laquelle l'enrichissement de K et la fixation de K dans les intercouches sont contrôlés par une augmentation de la charge négative de couche. Cette conversion s'est produite en réaction à un raide gradient géothermique et à des solutions hydrothermiques émigrantes. [D.J.]