

CHANGE IN LAYER CHARGE OF SMECTITES AND SMECTITE LAYERS IN ILLITE/SMECTITE DURING DIAGENETIC ALTERATION

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Abstract—The changes in amount and location of layer charge during diagenetic alteration have been investigated for smectites and smectite layers of illite/smectite interstratified minerals (I/S) by X-ray powder diffraction analysis with various expansion behavior tests: 1) ethylene glycol (EG) solvation (XRD); 2) K-saturation and EG solvation; 3) Li-saturation, heating at 250 °C and glycerol or EG solvation (Greene-Kelly test); and 4) alkylammonium saturation. In the course of low-temperature diagenesis but before the onset of illitization, mean layer charge of smectites continuously increases from approximately 0.56 to 0.73 per $O_{20}(OH)_4$ with increasing depth, and tetrahedral charge also increases continuously from approximately 0.21 to 0.38 per $O_{20}(OH)_4$ (beidellitization). The continuous increase in tetrahedral charge without change in peak intensity and shape suggests that the solid-state Al for Si substitution mechanism appears to predominate within beidellitization. After illitization, the content of the beidellitic layers continuously decreases, while the mean layer charge of expandable layers and the content of illite layers in I/S increase. This suggests that the conversion of a beidellitic layer to an illitic layer preferably occurs during early illitization. Thus, before illitization, beidellite-like layers are formed from precursor smectite, and during the early stage of illitization, the high charged beidellitic layers are probably consumed to form illite layers.

Key Words—Beidellitization, Charge Location, Diagenesis, Greene-Kelly Test, Illite/Smectite, Layer Charge, Smectite.

INTRODUCTION

The smectite to illite conversion through interstratified illite/smectite (I/S) minerals has been described for various environments: sedimentary (Perry and Hower 1970; Boles and Franks 1979), hydrothermal (Steiner 1968; McDowell and Elders 1980; Inoue and Utada 1983), contact metamorphic (Nadeau and Reynolds 1981) and metasomatic ones (Velde and Brusewitz 1982). The proportion of illite to smectite layers within I/S and the layer ordering progressively increased during the conversion, herein termed illitization. Illitization may be related to water that contributes to petroleum migration (Burst 1969) and to silica that is consumed for sandstone cementation (Boles and Franks 1979). The mechanism and kinetics of illitization have an influence upon the migration and redistribution of various materials within low temperature geological environments and the performance of backfill barriers of radioactive waste repositories. Furthermore, the conversion is thermally driven and is potentially useful as a paleotemperature indicator (Nadeau and Reynolds 1981). Thus, it is important to un-

derstand how illitization proceeds not only for clay mineralogists but also for geochemists, petroleum geologists and geotechnical engineers involved with geological disposal.

Many studies have proposed two end-member hypotheses of illitization mechanism that can be described as either solid-state transformation (Hower et al. 1976) or dissolution-precipitation (Boles and Franks 1979; Nadeau et al. 1985a). However, recent morphological data of particle diameters and thickness distribution measured by transmission electron microscopy, mostly indicate that smectite dissolves (Whitney and Velde 1993) and illite crystallizes by Ostwald ripening (Eberl and Srodon 1988; Inoue et al. 1988; Eberl et al. 1990; Lanson and Champion 1991, Eberl 1993). Most of these morphological studies, except for that by Whitney and Velde (1993), have emphasized the mechanism of the late illitization. Moreover, little is shown about the change of smectite itself before illitization, while it has been suggested that the chemistries of smectite layers in I/S must change before illite is formed (Perry and Hower 1970). According to Whitney and Northrop (1988), Inoue et al. (1988) and Whitney (1992), the illitization is not a single reaction, but consists of two or more stages with different mechanisms. Thus, there is no reason to as-

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sume that a single reaction mechanism occurs during early and late illitization. The reaction mechanism applied to late illitization should not be directly applied to the early illitization. A great deal of research focuses on the mechanisms before and during early illitization for understanding the illitization mechanisms from the beginning to the end.

Although smectite and illite are structurally and chemically similar, there is a marked difference in expandability of their interlayers. Because the expandable interlayers within smectite provide geochemically active sites for reactions such as ion exchange, the important change during illitization is a loss of the expandability. It is known that the expandability of smectite is considerably affected by the amount and location of layer charge (Glaeser and Mering 1968; Kodama and Ross 1974; Suquet et al. 1975; Suquet et al. 1977; Sato et al. 1992). Once the net layer charge of smectite layers is sufficiently large, it is followed by K fixation and interlayer collapse (Howard 1981; Howard and Roy 1985). The collapsing process from wetting and drying cycles is related to the layer charge of the original smectite (Eberl et al. 1986). To understand the mechanism of illitization, the following points must be made clear: 1) how the layer charge is developed, that is whether illite with high charge forms directly from solution or does illite form solid-state from low charged smectite via high charged smectite; and 2) what types of expandable layers exist in I/S, that is, whether the expandable layers are montmorillonite with octahedral charge or beidellite with tetrahedral charge.

From earlier studies, the layer charge of smectite layers in I/S has been calculated from an overall chemical composition of the I/S on the assumption that each illite layer in I/S has a unique value of layer charge, 1.5 per $O_{20}(OH)_4$ (hereafter, all layer charge values indicated below are expressed in the same way) (Hower and Mowatt 1966; Inoue et al. 1978; Eslinger et al. 1979; Brusewitz 1986; Velde and Brusewitz 1986). Conversely, Srodon et al. (1986) have indicated the illite layers in I/S exhibit two different layer charges: 1.1 for I/S with more than 50% smectite and 2.0 for I/S with less than 50% smectite. Nadeau and Bain (1986) have pointed out the inaccuracy of expandability by X-ray diffraction (XRD) based upon the particle-thickness measurement by transmission electron microscopy (TEM). They have shown that illite layers in I/S do not have a unique value of layer charge, but values range from 1.0 to 1.8. The above two studies strongly suggest that it is not possible to determine the layer charge of smectite layers in I/S from overall chemical composition. Eberl and Srodon (1988) have pointed out the discrepancy of expandabilities between XRD and TEM and revised the value for illite-layer charge to 1.8. Srodon et al. (1992) have confirmed the unique value of illite-layer charge (1.78) by the precise

measurement of the maximum expandability and verified the different findings for the value of illite-layer charge. This unique value of the charge enables one to determine the layer charge of smectite layers in I/S, indirectly. The indirect determination method from overall chemical composition is very difficult to apply to samples containing impurities.

The layer charge characteristics of smectites have been examined by expansion behavior tests, which include ethylene glycol and glycerol solvation (Brindley 1966; Sato et al. 1992), Greene-Kelly test (Greene-Kelly 1953, 1955; Malla and Douglas 1987a, 1987b, 1987c) and alkylammonium method (Lagaly and Weiss 1969; Stul and Mortier 1974; Stanjek and Friedrich 1986; Hausler and Stanjek 1988; Olis et al. 1990). These tests, for I/S samples, provide information for only expandable smectite layers in I/S. Recently, the charge of the expandable interlayers in I/S has been determined by the alkylammonium ion exchange method (Cetin and Huff 1995). It is possible to estimate the smectite-layer charge directly when the above tests are appropriately applied.

We will show the changes in the amount and location of the layer charge of smectites before illitization, and of smectite layers in I/S during diagenetic processes. The layer charge changes will be discussed in relation to the mechanism of layer charge development for the tetrahedral sheets before illitization and during the early stage of illitization.

SAMPLES AND METHODS

Samples

The samples were collected from the Tertiary sandstones and shales exposed along the Nakanomata and Yachi Rivers in Niigata, Japan (Figure 1). The sedimentary fill of the basin has been divided into four major lithostratigraphic units: the Nishihiyama, Nodani, Kawazume and Nadachi Formations (Nishida et al. 1966). Most of the basin-fill materials are black shale, whereas, the Nishihiyama Formation and part of the Nodani Formation consist of deep-water shales and intercalated sandstone turbidites. The clay mineralogy of the sediments represent typical zoning of the authigenic minerals montmorillonite-clinoptilolite, montmorillonite and I/S, and a continuous decrease of smectite percentage in I/S with increasing stratigraphic depth (Sato and Watanabe 1989).

Methods

All experiments were carried out on $<2 \mu\text{m}$ fractions. To obtain the fractions, the sandstone and shale rocks were gently ground in a mortar. The powdered samples were mixed with distilled water and then ultrasonified. The $<2 \mu\text{m}$ fractions from each lithology were separated from bulk samples by centrifugation. If the samples were flocculated, they were washed sev-

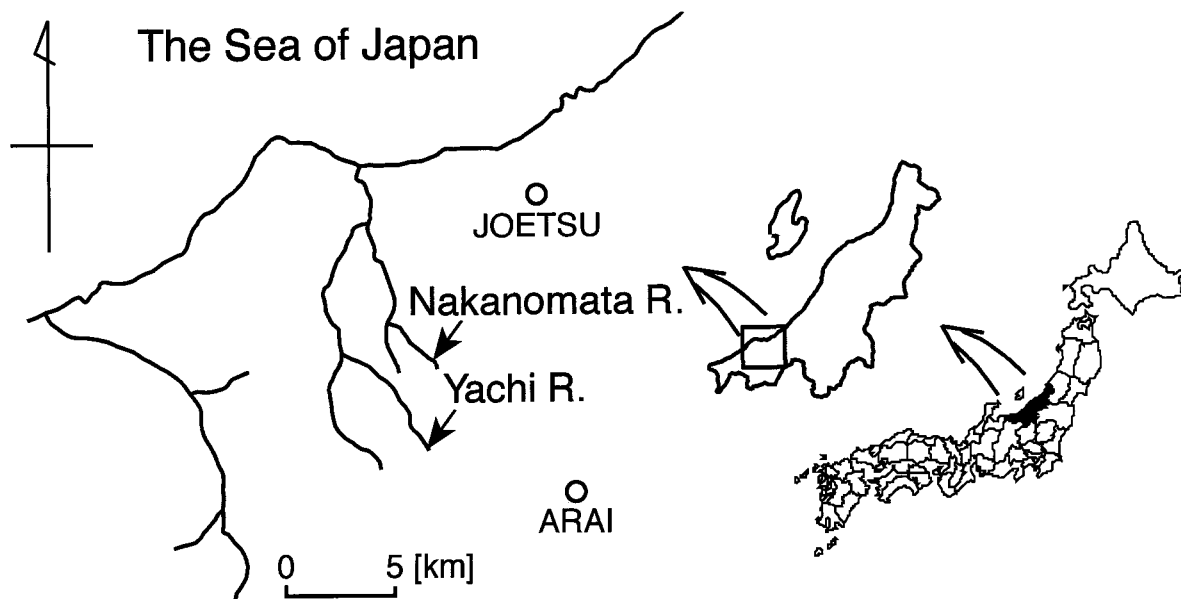


Figure 1. Locality map. The samples used were collected from the Nakanomata and Yachi districts.

eral times with distilled water until they dispersed. After drying, a small portion of each $<2 \mu\text{m}$ sample was resuspended with distilled water and transferred onto a glass or silica slide. The samples were examined with a Rigaku powder diffractometer with a graphite-monochromatized $\text{CuK}\alpha$ radiation at 40 kV and 20 mA. The diffractometer was controlled by a MAC Science software system (MAC Science Co. Ltd.). The XRD data were recorded from 2° to $50^\circ 2\theta$ with a data resolution of $0.05^\circ 2\theta$. The samples contain X-ray detectable impurities such as detrital illite, chlorite and quartz.

After solvation with ethylene glycol (EG) vapor (60°C for up to 24 h), the ordering type (Reichweite) and the percentage of expandable layers (smectite) of the I/S samples were determined using the $\Delta 2\theta_1 - \Delta 2\theta_2$ diagram by Watanabe (1988). The accuracy of the percentage of expandable layers was approximately 5% for most I/S samples. When a sample consists of a mixture of $g = 0$ and $g = 1$ interstratifications, the percent smectite of the sample was obtained from the peaks attributed to the $g = 0$ interstratification for convenience. The accuracy was approximately 10%.

A Greene-Kelly (GK) test was carried out for all samples except for ordered I/S. For the GK test, a portion of the $<2 \mu\text{m}$ fraction of each sample was immersed three times in 1 M LiCl solution for 24 h. They were subsequently washed three times with 80% ethanol and several times with deionized water until the samples were chloride free (by AgNO_3 test). The Li-saturated samples were spread with water onto silica slides to avoid the exchange of Li in the samples for Na in a soda-lime glass (Byström-Brusewitz 1975).

The Li-saturated samples were dried slowly at room temperature and then heated at 250°C for 24 h in a muffle furnace. Afterwards, the samples were saturated with glycerol (GLY) vapor at 110°C for up to 24 h before XRD measurements.

Another portion of the $<2 \mu\text{m}$ fractions, except for the ordered I/S, was saturated with 1 M KCl solution by the same method as that of Li-saturation. The K-saturated samples were solvated with EG and then X-rayed. The behavior of expandable smectite layers after K saturation gives information on the amount of layer charge (Harward and Brindley 1965; Sato et al. 1992); the expandable layers with high negative charge do not reexpand to 18 \AA when K is introduced into the interlayers.

Mean layer charges of the smectite samples were estimated using a single alkylchain of $n_c = 12$ or $n_c = 18$ according to the convenient alkylammonium ion-exchange method presented by Olis et al. (1990). The alkylamines of $n_c = 12$ is commercially available as dodecyl- and $n_c = 18$ is octadecylammonium chlorides and it is not necessary to prepare them from their respective amines. Thus, the method is particularly useful when we deal with a large number of geological samples. Alkylammonium chloride solutions were added to the smectite samples and then heated at 65°C for 2 d, with 1 change of solutions. The excess alkylamine and chloride were removed by washing the samples 10 times with 80% ethanol and twice with pure ethanol. The obtained samples were spread onto glass slides, dried at room temperature and examined by XRD. A 0.1 M aqueous alkylammonium complex was used for $n_c = 12$ and 0.05 M for the $n_c = 18$. The

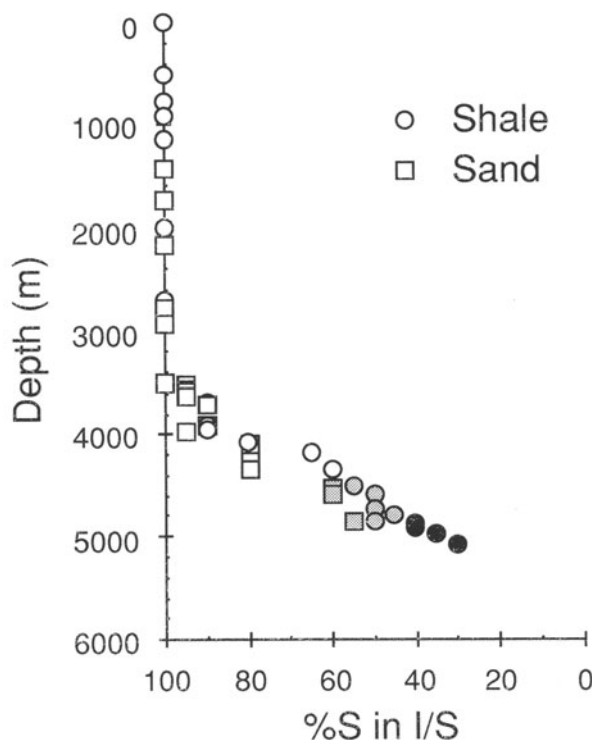


Figure 2. Variation in smectite percentage in I/S with depth. Key: Open symbols = samples of random interstratification; Solid symbols = ordered interstratification; Shaded symbols = mixture of random and ordered interstratifications.

average layer charges of a smectite obtained by the $n_c = 12$ and $n_c = 18$ alkylammonium ion-exchange method was determined to be the mean layer charge of smectites.

RESULTS

Structural Change of I/S

The variation of smectite percentage in I/S is shown as a function of stratigraphic depth in Figure 2. The smectite percentage in I/S decreases continuously from 100% to 30% with increased stratigraphic depth beginning at 3500 m. This decrease is accompanied by the structural change from random to ordered interstratification. The samples with <60% smectite display superlattice-like peaks at approximately $3^\circ 2\theta$ (approximately 27 Å) with the 17 Å reflection (Figure 3). When I/S evolves from random ($g = 0$) to ordered ($g = 1$) interstratification, the 17 Å peak shifts to higher $^\circ 2\theta$ (Reynolds and Hower 1970; Watanabe 1988). However, no obvious peak-shift was observed for the 17 Å peak. These observations indicate that the samples with <60% smectite consist of a mixture of $g = 0$ and $g = 1$ interstratifications. The existence of such an intermediate stage in the transition from $g = 0$ to $g = 1$ has been reported (Bethke and Altaner 1986; Bethke et al. 1986; Brusewitz 1986). The typical pat-

terns (Figure 3) also show weak reflections or shoulder peaks near 13.5 Å, which is the second-order reflections of the superlattice reflections.

Change in Mean Layer Charge

The alkylammonium ion-exchange method (Olis et al. 1990) applied to the samples with 100% smectite revealed that the smectite samples at shallow burial depths (< about 1000 m) have similar layer charges of approximately 0.56. The layer charge of smectites continuously increases from approximately 0.56 to 0.73 with increasing stratigraphic depth (Figure 4). The illitization of this basin begins at 3500 m depth. These data show that the development of layer charge in smectites begins before illitization.

Semi-quantitative estimation of the amount of layer charge of the smectite layers in I/S was obtained by an expansion behavior test using K-saturated and EG samples. Figure 5 shows the changes in peak position around at $5^\circ 2\theta$ obtained from observed and calculated XRD patterns of the K-saturated I/S with EG as a function of percentage of smectite layers. As a proportion of smectite layers decreases, the observed peak positions shifted to higher degrees for the early illitization. Conversely, for the calculated data, no obvious peak shift is observed for the 16.9 Å peak (two-EG layers complex) of I/S containing 100% to 50% smectite layers (Figure 5). Therefore, the observed peak shift for the early illitization is not due to the decrease of percentage of smectite layers by K-saturation.

Machajdik and Ciel (1981) have reported that for K-exchanged smectites with high net layer charge, a part of the layers fails to form two-EG layers complex. Rather, a randomly interstratified structure is formed with 2- and 1-EG layers complexes (d-spacing of 13.8 Å). The smectite layers of I/S probably have the same property as mentioned above. The observed peak shift for the region between 1- and 2-EG layers complex lines (Figure 5) indicate that the smectite layers in I/S have a randomly interstratified structure of both complexes. Consequently, the observed peak shift during early illitization is due to that part of the smectite layers in which I/S contains 1-EG layer complexes. This suggests that the smectite layers with higher layer charge than that of precursor smectites are formed in I/S.

Change in Charge Location

A GK test was performed to estimate the location of charge for all samples except for the ordered I/S. Figure 6 shows XRD patterns of the Li-saturated samples after heating and GLY solvation, and the sampling positions. The peak positions and intensities are markedly different between the samples of 100% smectite. Smectite before illitization has a d-spacing of 18 Å (KA05S in Figure 6). The 18 Å reflection indicates that most of the smectite layers of sample

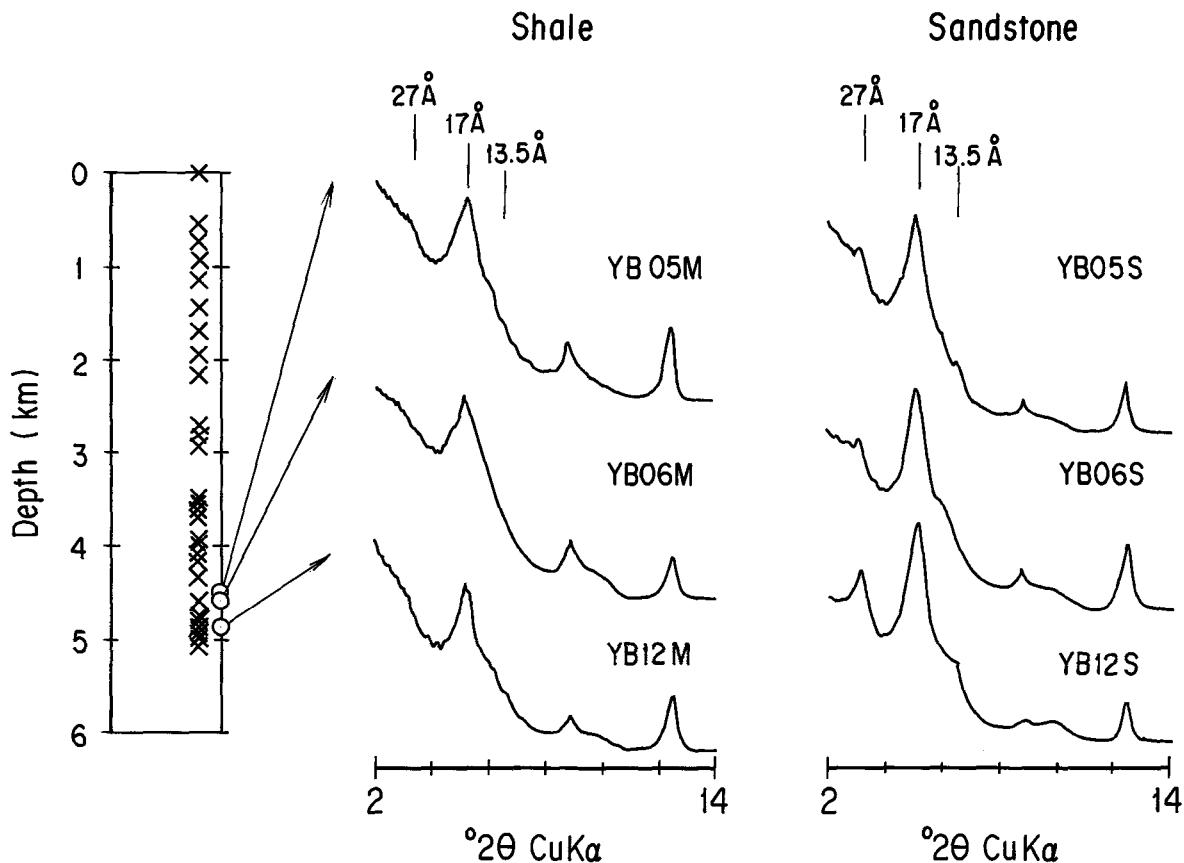


Figure 3. XRD patterns of glycolated samples of shales (left) and sandstones (right) with their sampling positions (circles). The samples have both random ($g = 0$) and ordered ($g = 1$) structures. Crosses = the remaining sampling positions.

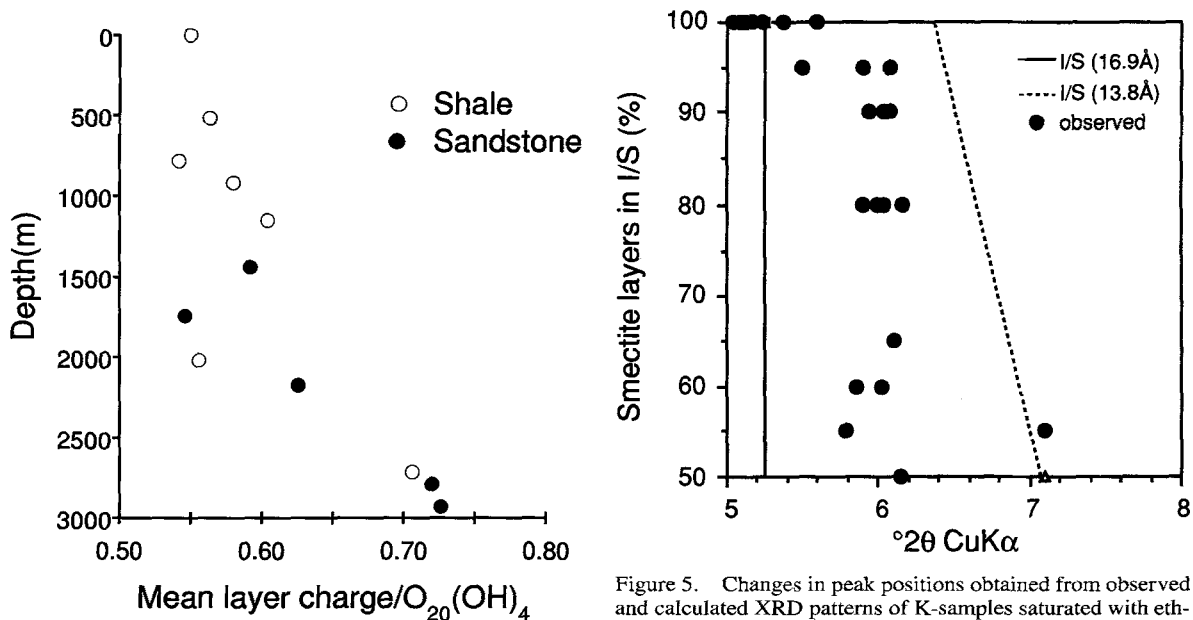


Figure 4. Variation in mean layer charge of smectites with depth.

Figure 5. Changes in peak positions obtained from observed and calculated XRD patterns of K-samples saturated with ethylene glycol. The calculation carried out for I/S samples with different d-spacing of expandable layers (16.9 Å: two-EG layers complex; 13.8 Å: one-EG layer complex).

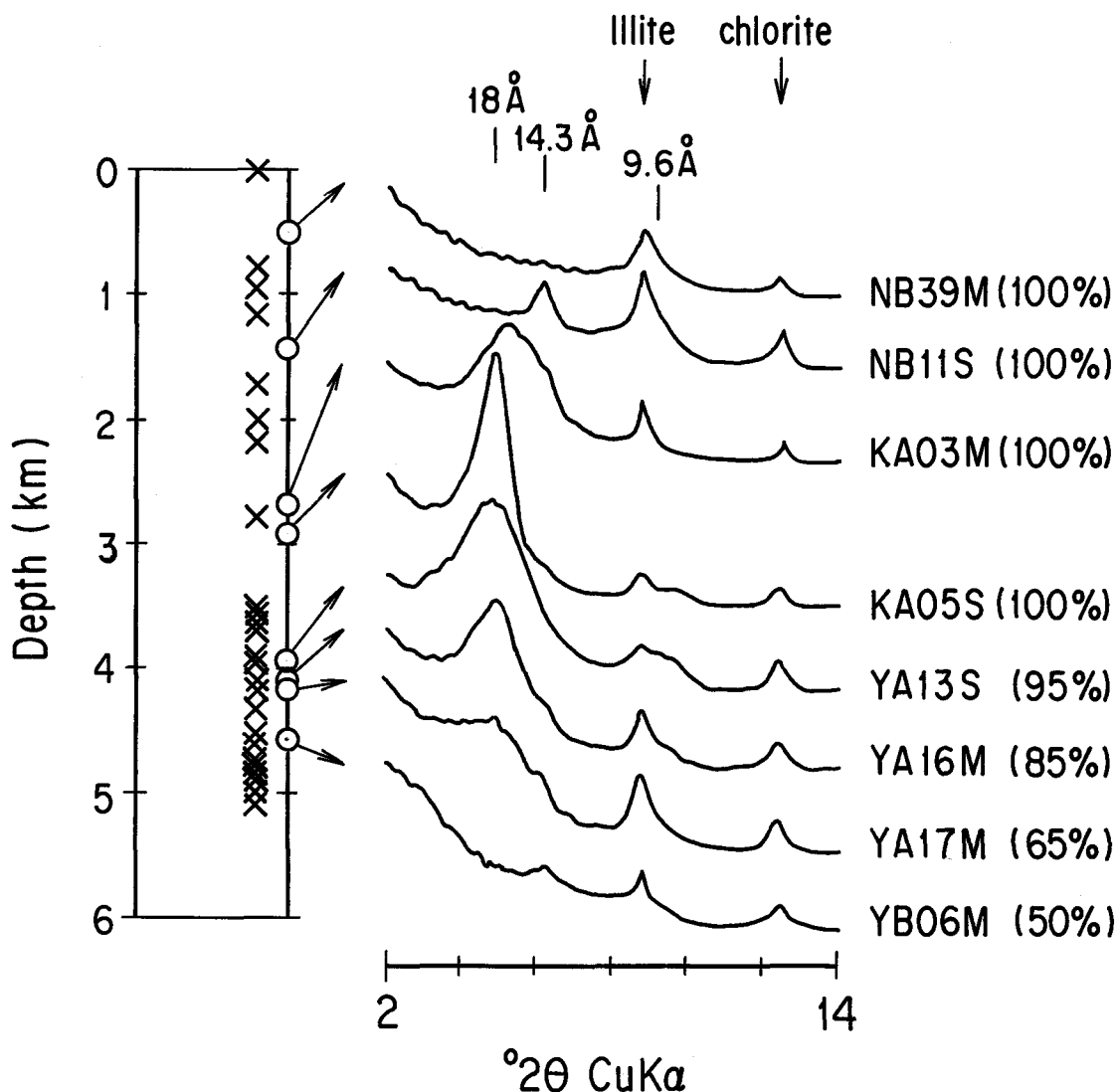


Figure 6. XRD patterns of Li-saturated samples after heating and glycerol solvation with their sampling positions (circles) and percentage smectite layer in illite/smectite. Crosses = the remaining sampling positions.

KA05S have a beidellite-like character. Conversely, smectite from the younger sediment (NB39M in Figure 6) does not show the reflection with a d-spacing of 18 Å, which indicates that most of the smectite layers have a montmorillonite-like character. The XRD pattern of sample NB39M after the treatments for GK test with EG solvation shows a weak reflection of an expanded 17 Å peak (Figure 7), suggesting that NB39M contains a small amount of beidellite-like layers. For sample NB11S, the peak with a d-spacing of 14.3 Å clearly appears after GLY solvation (Figure 7). The 14.3 Å peak is mainly attributed to 1 GLY layer complex, although a small portion of the 14.3 Å peak is attributed to chlorite. After EG solvation, the peak position shifts to 17 Å (2 EG layers complexes) and the intensity of the peak increases (Figure 7). The shift

of the peak after EG solvation indicates the formation of 2 EG layers complexes. This difference in expansion behavior between EG and GLY solvations is a result of more EG penetrating into collapsed layers than GLY (Calvet and Prost 1971). The continuous peak shift of the expanded phase (NB39M, NB11S, KA03M and KA05S; Figure 6) suggests that a proportion of the tetrahedrally charged layers in smectite layers continuously increases prior to illitization.

The 18 Å reflections remain for the samples from the early stage of illitization (YA13S, YA16M and YA17M; Figure 6). This suggests that beidellite-like layers exist in the I/S. However, as a proportion of illite layers in I/S increases, the 18 Å reflection becomes weaker and then disappears from the XRD profile of YB06M without obvious peak shift (Figure 6).

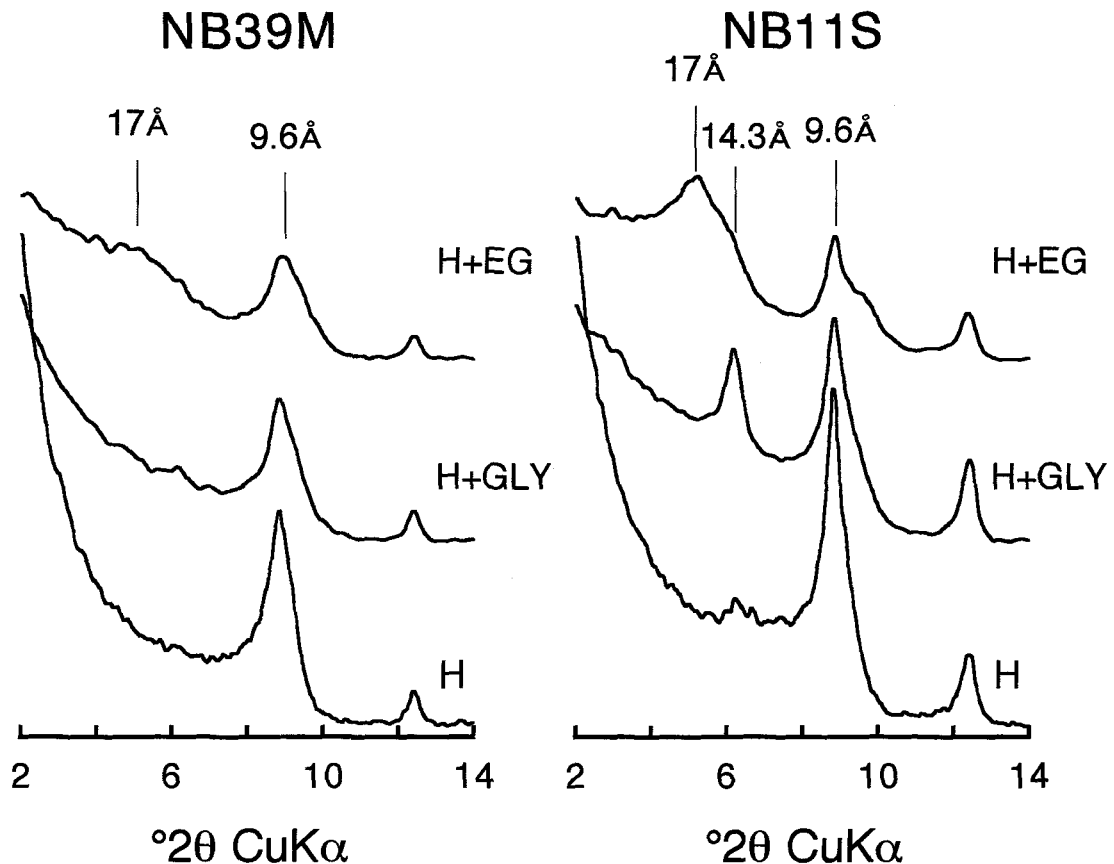


Figure 7. XRD patterns of Li-saturated samples after heating (H), heating and glycerolation (H + GLY), and heating and glycolation (H + EG).

Contrary to this, the XRD pattern of YB06M with EG solvation shows a 17 Å reflection (Figure 3). If the layers with d-spacing of 18 Å remain in YB06M, the 18 Å reflection undoubtedly retains the same way of the sample with EG solvation. This disappearance of a 18 Å reflection within the profile suggests that almost all of the expandable layers in YB06M have montmorillonite-like character.

DISCUSSION

This study emphasizes the expansion behavior of smectites before illitization and for the early stage of illitization. Before illitization, the (001) reflection of smectite samples shows peak a shift from 9.6 Å to 18 Å, and the intensity increases with increasing depth (peaks at approximately 5°; Figure 6) when the treatments for the GK test are carried out on the samples. The peak shift and the intensity increase are accompanied by an increase in mean layer charge (Figure 4), resulting from the increase in layer charge of the tetrahedral sheets (beidellitization). After illitization, beidellite-like layers exist in the I/S as expandable elementary layers at the early stage of illitization, where-

as a proportion of beidellite-like layers decreases with increasing proportion of illite layers.

Meunier and Velde (1989) have concluded that the smectite component of I/S is montmorillonite with a layer charge of 0.66 to 1.32 without tetrahedral charge, and no beidellite component exists in most natural I/S minerals. Their conclusion is inconsistent with ours. Both the precursor smectites and smectite layers in I/S investigated from the present study indicate beidellitic behavior. Bruce (1984) and Eslinger et al. (1979) reported that the smectites of Mississippi River shales consist of beidellite and montmorillonite, and that the smectites within Cretaceous bentonites before illitization have a tetrahedral charge of 0.6 and an octahedral charge of 0.2. Since natural smectites in the montmorillonite-beidellite series generally possess negative charge for either the tetrahedral and octahedral sheets (Lagaly et al. 1976; Nadeau et al. 1985b; Malla and Douglas 1987b; Christidis and Dunham 1993), it is possible that a component with tetrahedral charge exists as a precursor smectite and smectite layers in I/S.

Layer charge of natural dioctahedral smectites is distributed over tetrahedral and octahedral sheets. The

Table 1. Relationship between XRD characteristics and the layer charge of smectite (Data from Calvet and Prost 1971).

Solvent	Layer charge/ $O_{20}(OH)_4$				
	0.08	0.15	0.23	0.30	0.38
Glycerol	C	C	C	I	R
Ethylene glycol		I	I	R	R

Key: R = expanded with a rational series; I = interstratified; C = collapsed.

octahedral charge is neutralized by the GK test and the tetrahedral charge remains (Hofmann and Klemen 1950). Therefore, all of the remaining layer charge after the treatment for the GK test is located in tetrahedral sheets. According to Calvet and Prost (1971), when the remaining tetrahedral charge of a smectite is more than 0.38, the smectite expands to 18 Å with rational series (Table 1). Conversely, a smectite with a tetrahedral charge less than 0.38 does not expand to 18 Å, but has a random interstratified structure with collapsed, expanded to 14 Å, and expanded to 18 Å layers.

The reflection with a d-spacing of approximately 14 Å in sample NB11S (Figure 6) suggests that the remaining tetrahedral charge is less than 0.38. Conversely, sample KA05S, which is the sample just before illitization that has a net layer charge of 0.73, seems to have a tetrahedral charge of 0.38 because it shows the rational reflections with a 18 Å basal spacing. Thus, its octahedral charge is 0.35. If the octahedral layer charge was stable and did not change during the diagenesis, the tetrahedral charge of the parent smectite (NB39M) with a net layer charge of 0.56 takes a value of 0.21. If the tetrahedral charge is 0.21, the smectite partially expands with EG, but not with GLY (Table 1). This interpretation is supported by the XRD patterns after GK test. The XRD pattern of NB39M after the GK test and EG treatments shows a weak reflection of expanded phase with a d-spacing of approximately 17 Å, but does not show it with GLY (Figure 7). Consequently, 0.21 is a reasonable value for a tetrahedral charge of the parent smectite (NB39M). This also indicates the octahedral charge is stable during the increase in tetrahedral charge. During diagenesis within this basin, the tetrahedral charge of smectite possibly increases from approximately 0.21 to 0.38 and the octahedral charge is probably kept constant at approximately 0.35 in advance to illitization.

The K-test further documented an increase of smectic charge in I/S. This change in layer charge of smectites and smectite layers in I/S is represented by the arrow in Figure 8. This diagram shows the relationship between charge characteristics and expanding behavior of K-saturated smectites with EG solvation, and is modified from Sato et al. (1992). The charge increase ends at the point of the arrow as the expanded phases of smectite layers in I/S show an intermediate spacing

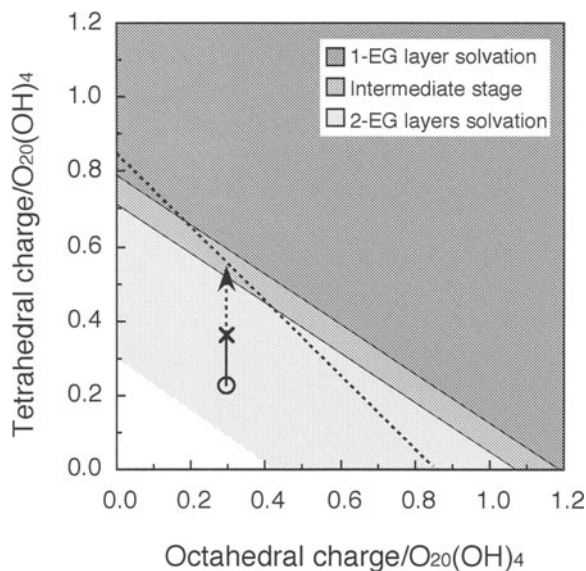


Figure 8. Change in layer charge of smectites and smectite layers in I/S shown by the arrow on diagram presenting the expanding behavior of K-saturated smectites with ethylene glycol solvation (modified from Sato et al. 1992). The parent smectite (sample NB39M) indicated by a circle and the precursor (KA05S) indicated by a cross. The dotted line shows the isoquant of net layer charge 0.85.

between 1 and 2 EG solvation with K-saturation (Figure 5). We concluded that the mean layer charge of expandable layers in I/S increases to approximately 0.85, but does not increase beyond this value. Srodon et al. (1992) indicated a stable layer charge for smectite in I/S from volcanic materials was about 0.80. Cetin and Huff (1995) have shown the average charge of smectite layers in I/S with expandability from 70% to 15% is 0.76, which is estimated by an alkylammonium ion exchange method. These values are similar to the ones we present.

Both continuous solid-state transformation (Hower et al. 1976) and stepwise dissolution-precipitation mechanisms (Boles and Franks 1979; Nadeau et al. 1985a) have been proposed for the formation of illite. The transformation model explains that the tetrahedral charge is developed through solid-state Al for Si substitution while the 2:1 layer structure of the reactant smectite was retained. The dissolution-precipitation model explains that low charged smectite dissolves and tetrahedrally high charged illite crystallizes from solution. However, the formation of beidellite-like layers from low charged montmorillonite-like layers shown for the present study is similar to the formation of illite in terms of the formation of a tetrahedrally charged mineral. Therefore, it is possible that the beidellitization for this study occurs either by transformation or dissolution-precipitation.

The formation of beidellite-like layers from low charged montmorillonite-like layers occurs with a con-

tinuous increase of the tetrahedral charge before illitization during the present diagenetic alteration. Another important feature is that the octahedral charge is probably kept constant during the continuous increase of tetrahedral charge. Furthermore, no obvious change of peak intensity and shape is observed for the (00 l) reflection of the smectites with EG solvation during the beidellitization. If the low charge smectite would dissolve partially and then tetrahedrally high charged smectite would form from a solution, the number of particles and X-ray scattering domain thickness would probably have a minimum at the halfway of this dissolution-precipitation process. This process would cause peak broadening and decreased intensity of the (00 l) reflections. Thus, the observed changes in tetrahedral and octahedral charges and peak profile of the (00 l) reflection are more consistent with the transformation through solid-state Al for Si substitution than with that by dissolution-precipitation.

After illitization, the content of the beidellite-like layers continuously decreases, while the layer charge of the expandable layers and the content of illite layers increases. For the I/S sample with 50% smectite, almost all of the smectite layers are montmorillonite-like as a result of a decrease in the content of beidellite-like layers. This suggests that the conversion of a precursor beidellite-like layer to an illite layer preferably occurs during the early stage of illitization. Our results agree with those of Eberl (1978) and Boles and Franks (1979), who have shown that Al-rich smectite reacts more easily to form illite than Al-poor smectite. Thus, beidellite-like layers are formed from precursor smectite before illitization, and beidellite-like layers are preferably consumed to form illite layers during the early stage of illitization.

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