

## Mineralogy of Illite/smectite Mixed-Layer Clays from the Beaufort-Mackenzie Basin, Arctic Canada

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**ABSTRACT:** Illite/smectite (I/S) in the Beaufort-Mackenzie Basin, Arctic Canada has been scrutinized on the basis of mineralogical analysis of 215 core and drill-cutting samples from 22 exploratory wells onshore and offshore. I/S in the Beaufort-Mackenzie Basin includes the following four types: random, a mixture of random and ordered, R1-ordered, and R>1-ordered I/S. A mixture of random and ordered I/S occurs in the transitional interval between random and R>1-ordered I/S, and may represent a metastable state in the ordering reaction. A widespread occurrence of the mixture in natural environments suggests that the ordering reaction may be a slow process that results in co-existence of reactants and products. K-saturation experiments show that layer charges of expandable layers in I/S are variable. High-charge expandable layers transform into illite-like layers upon simple K-saturation. K-saturation alters the composition and/or the degree of ordering in I/S, suggesting that illitization in nature can be transformational.

### INTRODUCTION

Illite/smectite (I/S) has been known as a mixed-layer clay mineral consisting of randomly or regularly interstratified smectite- and illite-layers (Perry and Hower, 1970; Lee *et al.*, 1985; Ahn and Peacor, 1986). This notion has been challenged by Nadeau *et al.* (1984a-c) who suggested, based on transmission electron microscopic (TEM) observations of finely dispersed I/S, that mixed-layering could be an artifact of interparticle diffraction between thin illite and smectite particles that are known as fundamental particles. The fundamental particles occur independently from one another in nature, and coherent stacking may take place upon sample preparation such as the parallel orientation method that is routinely used in X-ray diffraction (XRD) studies of clay minerals.

The interpretation of I/S clays as fundamental particles had far-reaching consequences. Conventionally, the smectite-to-illite reaction is considered to involve an increase of illite layers and ordering in a sequence of I/S crystallites made up of 5-15 layers (Perry and Hower, 1970). Instead, Nadeau *et al.* suggest that illitization is simply a process of disappearance of fundamental smectite particles through dissolution, and precipitation and growth of fundamental illite particles. It appears that the fundamental particle hypothesis becomes a mainstream thought in I/S clay-mineralogical studies (e.g.

Inoue *et al.*, 1988; Eberl and Srodon, 1988; Eberl *et al.*, 1990).

The present paper describes XRD patterns of I/S clays from the Beaufort-Mackenzie Basin, Arctic Canada, characterizes the various types of I/S, and discusses the identity of I/S as to mixed-layer crystallites versus fundamental particles.

### MATERIALS AND METHODS

The Beaufort-Mackenzie Basin is located in north-western Canada (Fig. 1). The Basin is one of the largest hydrocarbon reservoirs in Canada (estimated recoverable reserves: 1.5-2.0 billion bbl oil, 10.9-12.6 tcf gas; Dixon *et al.*, 1988).

The Basin is filled with thick progradational deltaic sequences of Tertiary age (Dixon *et al.*, 1986).

A total of 215 samples (110 core samples, 105 drill cuttings) were collected from 22 wells onshore and offshore for detailed mineralogical analysis. Drill-cutting samples were combined with appropriate intervals in order to obtain a sufficient amount of the fine-grained fraction (<1  $\mu\text{m}$ ). Preliminary washing for removal of drilling mud was carried out at the facilities of the Core Research Centre of the Energy Resources Conservation Board (Calgary, Canada) where the washed samples were vacuum-dried at room temperature. These samples were screened through a 10 mesh sieve for removal of cavings, and from the sieved material only shale chips were hand-picked. Repeated washings were done prior to further preparation for X-ray diffraction.

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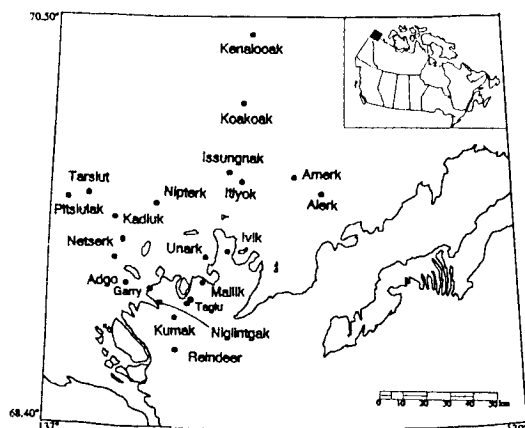


Fig. 1. Location map and wells used in this study.

Drill-cuttings and crushed core-samples of about 50g were shaken for >8 hours, and soaked in Na-acetate solution (pH 6) to remove carbonates and soluble salts (Jackson, 1969). Organic matter was removed using 30%  $H_2O_2$ . Samples were Na-saturated, and excess salts were removed by repeated washing and dialysis until no chloride was detected with  $AgNO_3$ . For better dispersion, 10% Na-metaphosphate (calgon) solution was added to the suspension (20ml calgon/350ml suspension). To maximize the amount of fine fractions, suspensions were ultrasonified briefly before size fractionation. Centrifugation was used to obtain a <1  $\mu m$  fraction that consists mainly of I/S clays. Suspensions of the <1  $\mu m$  fraction were freeze-dried to avoid artifacts

of oven-drying.

Slides of oriented particles were prepared following the membrane-filter transfer method (Moore and Reynolds, 1989; modified after Drever, 1973). Each slide was made from 100 mg of dried powder. Air-dried slides were kept in a desiccator ( $\sim 0\%$  relative humidity) until the registration of XRD patterns in order to obtain a single-layer state for interlayer water in expandable layers of I/S. Glycol treatment was done by keeping samples in a desiccator containing ethylene glycol at the bottom at  $60^\circ C$  for 72 hours which appear to be an adequate period to obtain a constant and maximum glycol-layer thickness for Beaufort-Mackenzie I/S. Prior to X-ray diffraction, these samples were transferred to an air-tight box containing a beaker with ethylene glycol.

Some selected samples were heat-treated at 400 and  $550^\circ C$  to ensure proper identification of components in mixed-layer clays, and distinction between discrete kaolinite and chlorite. About 60 samples from three wells (Reindeer D-27, TagluC-42, Taglu G-33) were K-saturated to estimate the proportion of high-charge expandable layers. K-saturation was done by keeping samples of the <1  $\mu m$  fraction in 1N KCl solution overnight, followed by washing with a fresh solution. Desalination was done by dialysis to avoid loss of ultra-fine particles.

X-ray diffraction was conducted with a Siemens D-500 x-ray diffractometer equipped with a graphite diffracted-beam monochromator. The X-ray source was  $CuK\alpha$  radiation generated at 40 kV and 20 mA. The slit conditions were  $1^\circ$  for the divergent slit and  $.15^\circ$  for the receiving slit. An automated data collection system

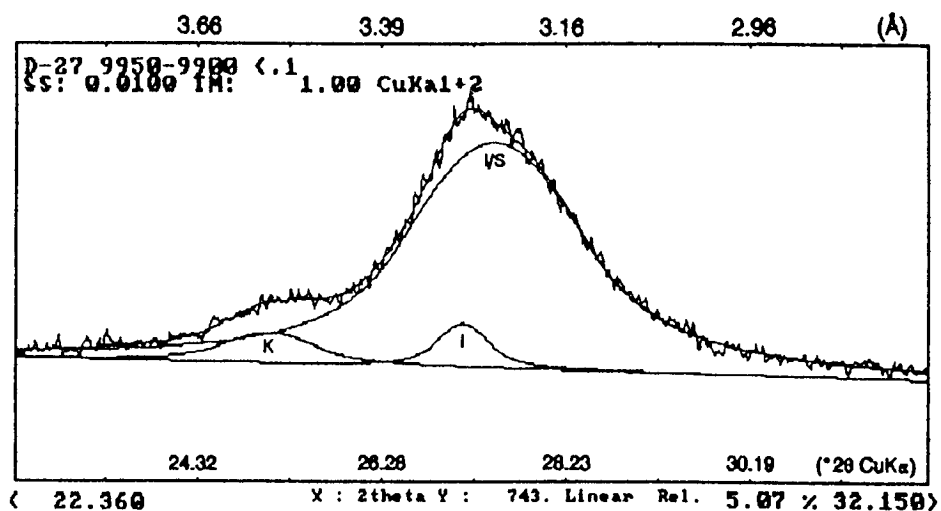


Fig. 2. Decomposition of a XRD curve in the  $3.3\text{\AA}$  region. Air-dried. A smooth curve on the diffraction pattern is the sum of three curves corresponding to I/S, kaolinite (K) and illite (I). Pseudo-Voigt function is used.

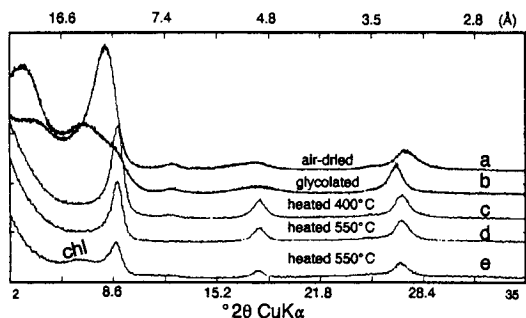


Fig. 3. X-ray diffraction patterns of (a) air-dried, (b) glycolated, (c) heated at 400°C and (d, e) 550°C specimens. <math>< 1 \mu\text{m}</math> fractions (a-d: Reindeer D-27 9250-9200, e: 11150-11100ft). Collapse to 10Å after heating indicates that mixed-layers consist of 2:1 layer-silicates, i.e. illite and smectite. 7Å series reflections disappear after heating at 550°C (d), indicating they correspond to kaolinite. Chlorite in Reindeer deep sample persists even after heating at 550°C (e).

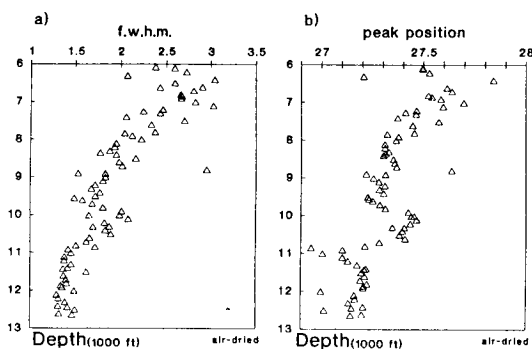


Fig. 4. Plot of 003/004<sub>s</sub> peak parameters with respect to depth. Air-dried. Reindeer D-27. a) f.w.h.m., b) Peak position (both in 2θ).

(DACO-MP) was used for step-scans carried out between 2 to 35° 2θ at 0.01° 2θ step size and 1s counting time.

#### Estimation of I/S Composition

Conventional methods to estimate the composition of I/S use peak positions or differential 2θ values on glycolated samples (Reynolds and Hower, 1970; Reynolds, 1980; Srodon, 1980, 1984; Watanabe, 1981). These methods, however, were not applicable for most Beaufort-Mackenzie samples due to weak intensities of the important peaks, especially (002)<sub>i</sub>/(003)<sub>s</sub>. For random I/S, the saddle/peak ratio of (001)<sub>10</sub>/(001)<sub>17</sub> peaks (subscripts denote the basal spacings) was used to estimate composition. A working curve similar to Inoue *et al.* (1989; modified after Rettke, 1981) was constructed ba-

sed on patterns generated by the Newmod2 program of Reynolds (1985). In calculating the patterns, default parameters given by the program were used because many parameters can not be determined with certainty. An error range of 10~15% was estimated for the method according to Inoue *et al.* (1989).

For ordered I/S, the addition of another variable, i.e. the degree of ordering, complicates the relationship between composition and peak parameters, i.e. peak position, intensity, full width at half-maximum intensity (f.w.h.m.), differential 2θ values, etc. In estimating the composition of ordered I/S, XRD patterns of air-dried samples were used. Peaks in the 3.3Å region were decomposed using the profile-fitting program FIT of So-cabim (1989) (Fig. 2). The peak at 3.5Å corresponds to kaolinite and/or chlorite, that at 3.3Å to illite, and that at <math>< 3.3\text{Å}</math> to I/S. A two-peak model was used for patterns with f.w.h.m. <math>< 1.5</math> because a relatively small f.w.h.m. did not permit reliable resolution of the peaks belonging to illite and I/S. The peak positions of air-dried I/S were compared to those obtained from calculated patterns of I/S-1 water (denoting a single interlayer-water) using the Newmod2 program. In general, the I/S composition estimated on air-dried samples agrees with that obtained from glycolated samples with better-defined peaks. The difference between the two does not exceed 10%.

#### X-RAY DIFFRACTION CHARACTERISTICS OF <math>< 1 \mu\text{m}</math> FRACTIONS

The <math>< 1 \mu\text{m}</math> fractions of the Beaufort-Mackenzie material show reflections corresponding to I/S, discrete illite, kaolinite and/or chlorite. The results of glycolation and heating indicate that mixed-layer clays consist of 2:1 layer silicates, i.e. illite and smectite (Fig. 3). The 7Å peak and its {00l} series correspond to kaolinite except for some deep samples of the Reindeer D-27 well that contain chlorite. Variable amounts of discrete illite are always present, interfering with I/S reflections (see also Fig. 5). Peaks of illite occur as a shoulder or asymmetry on low-angle reflections of I/S at 10Å (001) and a small hump at 5Å (002). The (003) peak of illite is not separable from the (003)<sub>10</sub>/(005)<sub>17</sub> peak of I/S.

I/S shows three well-defined peaks regardless of interference with discrete illite peaks. These include the peak between 17 and 10Å on glycolated samples, and the peaks at 12.5~10Å and at 3.3~3.1Å on air-dried samples. The peak position of glycolated samples between 17 and 10Å defines the degree of ordering in terms of Reichweite values (Bethke *et al.*, 1986). The peak positions of air-dried samples suggest a single-layer state

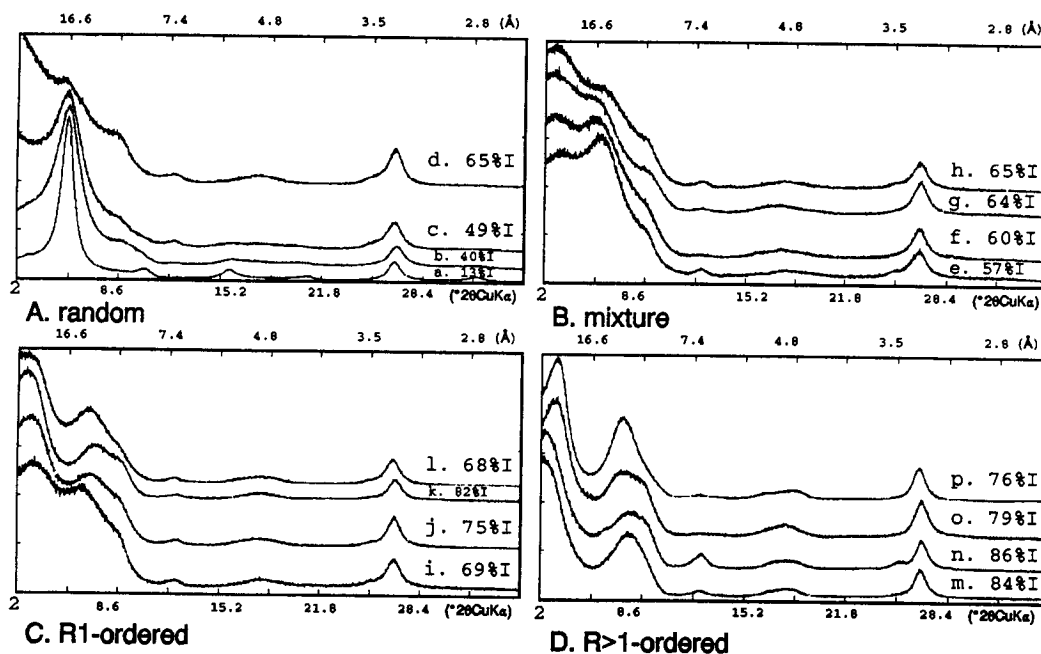


Fig. 5. X-ray diffraction patterns of typical Beaufort-Mackenzie clays ( $< 0.1 \mu\text{m}$  fraction). Glycolated. A. Random I/S, B. Mixture of random and ordered I/S, C. R1-ordered I/S, D. R $>$ 1-ordered I/S. (a- Taglu C-42 8468, b- Ivik J-26 10213, c- Taglu G-33 8279, d- Taglu G-33 5376, e- Reindeer D-27 6850-6800, f- Mallik A-069266, g- Taglu C-42 10430, h- Reindeer D-27 8250-8200, i- Reindeer D-27 8650-8600, j- Reindeer D-27 9250-9200, k- Reindeer D-27 9650-9600, l- Taglu C-42 13800-13700, m- Reindeer D-27 11443, n- Reindeer D-27 12650-12600, o- Taglu C-42 15800-15700ft, p- Amerk O-09 4866m). For description, see text.

for interlayer-water in most expandable layers of I/S. The peaks, especially the higher-order peak between 3.3 and 3.1 Å show depth-related variations (Fig. 4). Parameters of the peak, i.e. position and the f.w.h.m., change systematically with depth. The peak position moves towards 3.3 Å ( $26.8^\circ 2\theta$ ) and the f.w.h.m. decreases with increasing depth of burial. The f.w.h.m. ranges from  $>2^\circ$  for random,  $2\sim 1.5^\circ$  for R1-ordered, and  $<1.5^\circ$  for R $>$ 1-ordered I/S.

#### I/S Mineralogy

Fig. 5 shows typical XRD patterns of Beaufort-Mackenzie I/S in glycolated state. They can be grouped into 4 categories: random, a mixture of random and ordered, R1-ordered, and R $>$ 1-ordered I/S. Random mixed-layer I/S is characterized by the first peak  $[(001)_{10}/(001)_{17}]$  appearing at about  $5.2^\circ 2\theta$  (17 Å). With increasing proportion of I-layers, the saddle/peak ratio of  $(001)_{10}/(001)_{17}$  peaks decreases, and the intensity of higher-order peaks decreases. At about 40 %I, the precise position of higher-order peaks, especially  $(002)_{10}/(003)_{17}$ , cannot be determined.

A mixture of random and ordered I/S is identified by

two peaks, one at a very low angle ( $<4.2^\circ 2\theta$ ;  $>25\text{Å}$ ), indicative of a superlattice structure, and the other between 17 to 15 Å (Fig. 5B). The second peak for ordered I/S usually occurs at less than 14.5 Å (Bethke *et al.*, 1986). Contamination by drilling mud is highly unlikely, because samples were well consolidated and thoroughly washed. Note that two of the diffractograms shown in Fig. 5 (f, g) were obtained from core material. The mixture of random and ordered I/S is identified in  $>30$  core and drill-cutting samples. The mixture occurs at intermediate depths in the transitional interval between random and R1-ordered I/S. The relative abundance of ordered I/S in the mixture increases with depth. Intensities of the  $(001)_{27}$  peak increase while those of  $(001)_{10}/(001)_{17}$  decrease (cf. Fig. 5B). The composition of random I/S in the mixture ranges from about 55 to 65 %I based on saddle/peak ratios of the  $(001)_{10}/(001)_{17}$  peak. The composition of ordered I/S is probably similar to that of coexisting random I/S, though the weak intensity of the  $(002)_{10}/(003)_{17}$  peak at about  $16^\circ 2\theta$  (5 Å) and the presence of discrete illite make the estimation very difficult.

R1-ordered I/S shows two distinct peaks at low angles,  $(001)_{27}$  and  $(001)_{10}/(002)_{27}$  (Fig. 5C). The R1-ordering is

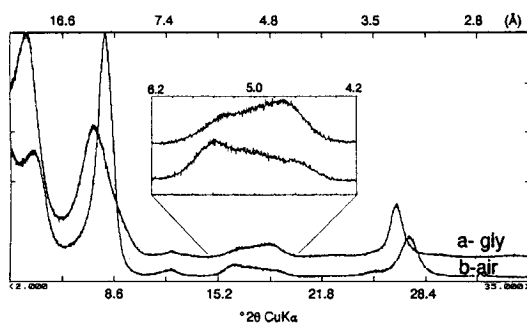


Fig. 6. X-ray diffraction pattern showing the abnormal glycol effect. Note that the glycol effect is pronounced in the high angle side of 5Å. a) glycolated, b) air-dried.

defined by the peak position of  $(001)_{10}/(002)_{27}$  that varies from 14.5 to 12.8Å (Hower, 1981; Bethke *et al.*, 1986).

In general, with increasing proportion of I-layers, the  $(001)_{27}$  peak shifts towards lower angles while  $(001)_{10}/(002)_{27}$  shifts towards higher angles. Positions of other peaks,  $(002)_{10}/(005)_{27}$  and  $(003)_{10}/(008)_{27}$ , were usually not measurable, either due to weak intensities or proximity to the peaks of discrete illite. Resolution, even with the efficient profile-fitting program, was rarely possible. Decomposition of peaks in the 5Å region (cf. Eberl *et al.*, 1987) did not provide reliable results to estimate composition. Decomposition results appear inconsistent among samples with similar X-ray diffraction patterns, and thus of similar composition. In many cases, the results did not bear any physical meaning, i.e. intensity, peak positions and the f.w.h.m. do not reflect the nature and relative abundance of phases present. Air-dried samples displayed better-defined and resolvable peaks (Fig. 5). Compositions of R1-ordered I/S based on peaks of air-dried samples range from 65 to 80 %I. I/S of 65~70 %I is characterized by a relatively high saddle at about 17Å (Fig. 5i) in glycolated patterns, probably due to the imperfection of ordering, i.e. the presence of smectite-to-smectite junctions (S.S). The difference between the  $2\theta$  angles (differential  $2\theta$ ) between  $(001)_{27}$  and  $(001)_{10}/(002)_{27}$  is usually less than  $3.5^\circ 2\theta$ . I/S of about 75 %I shows well-defined peaks of  $(001)_{27}$  and  $(001)_{10}/(002)_{27}$  (Fig. 5j), and the differential  $2\theta$  between the two peaks ranges from 3.5 to  $4.0^\circ 2\theta$ . Position of the  $(001)_{27}$  peak varies between 29 and 34Å, while that of the  $(001)_{10}/(002)_{27}$  peak between 14 and 13Å. As the I-layer content of I/S approaches 80 %I, the  $(001)_{27}$  peak disappears. Nevertheless, the convexity of X-ray traces near  $2^\circ 2\theta$  indicates the presence of a superlattice structure of increased spacing ( $R > 1$ ).

$R > 1$ -ordered I/S usually shows a single peak at d-values of <12.8Å (Fig. 5D). Peak positions suggest Rei-

chweite values greater than 1, but less than 3. Compositions based on the peak of air-dried samples cluster at 84~88 %I. Some deep samples of Reindeer D-27 register values as high as 92 %I.

## DISCUSSION

### Mixture of Random and Ordered I/S

A mixture of random and ordered I/S has rarely been reported in diagenetic studies. Previously, the mixture of random and ordered I/S has been identified in hydrothermal experiments of Whitney and Northrop (1988). In fact, the mixture should hardly exist according to Nadeau *et al.* (1984a) who showed that the mixture of smectite and R1-ordered I/S (rectorite) would produce a X-ray diffraction pattern corresponding to random I/S.

The mixture of random and ordered I/S is widespread in the Beaufort-Mackenzie Basin. The mixture is identified in a transitional interval between random and R1-ordered I/S. The occurrence of the mixture suggests that the transition from random to ordered I/S is a more complicated process than Nadeau *et al.* thought.

Nadeau *et al.* suggested that the smectite-to-illite process consists of a progressive dissolution of smectite, and precipitation and growth of illite. Random I/S becomes ordered I/S when smectite particles disappeared completely. In this scheme, the transition does not exist because I/S would assume either a random or ordered form. On the contrary, the conventional view is that the ordered I/S develops as the result of structural adjustment of random I/S that attained at a certain composition (~60%I). The random to ordered I/S transition, i.e. ordering, involves large-scale mass transfer, because it requires re-sequencing of randomly arranged I- and S-layers into an orderly form. Therefore, the reaction would be very sluggish. The mixture may represent a metastable state in the ordering reaction. In slow reactions, metastable co-existence of reactants and products is not unusual.

### Peak Broadness and Intensity

The broadness and weak intensities of Beaufort-Mackenzie I/S are attributed to turbostratic effects and  $\{00l\}$  stacking defects (Reynolds, 1989), and probably to varying thicknesses of glycol layers. Srodon (1980) showed that the thickness of smectite-glycol complexes can vary from 16.5 to 17.3Å. The same thickness variations may be characteristic of smectite-layers in I/S. Differences in glycol-layer thickness within a sequence of individual crystallites are analogous to the displacement of adjacent

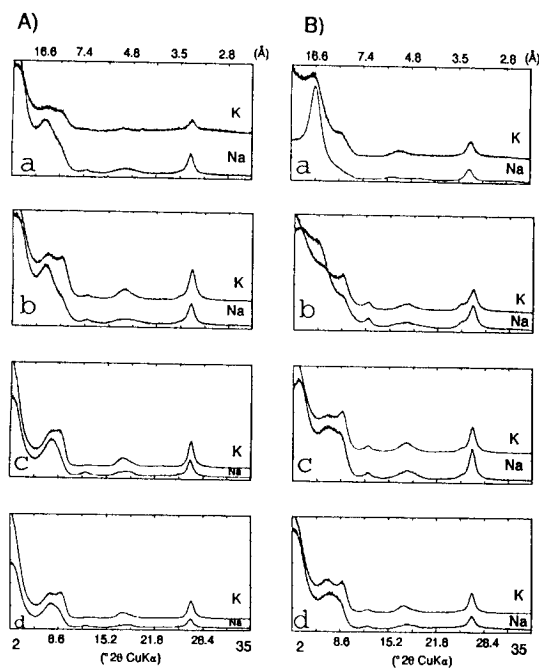


Fig. 7. X-ray diffraction patterns showing the effect of K-saturation for various types of I/S. Glycolated. A) Reindeer D-27 [a- 8375, b- 10329, c- 11443, d- 12462ft]. B) Taglu C-42 [a- 9738, b- 11508, c- 13000-12950, d- 16030-16000ft]. For explanation, see text.

unit-cells in strain broadening. In strain-broadening, the displacement of a lattice (lattice strain) may be infinitesimal; however, the effect can be very profound on diffraction patterns (Warren and Averbach, 1950; Reynolds, 1989). In general, broadening increases and intensity decreases with increasing  $2\theta$  angles. With increasing displacement of the lattice, all high-angle peaks disappear and only a first-order peak that represents the unit-cell itself may be seen.

The glycol-layer thickness appears to depend on layer charges, and types of interlayer cations. In mixed-layer I/S, expandable layers display a wide range of layer charges (Lagaly, 1979; Howard, 1981; Vali *et al.*, 1991). Expandable layers with relatively low-charge would have spacings between 16.5 and  $>17\text{\AA}$ . High-charge expandable layers may form double-layer complexes with ethylene glycol, but give spacings of 16.2 $\text{\AA}$  similar to vermiculite (Brindley, 1966). Diverse spacings of expandable layers would result in broadness and weak intensities of I/S peaks.

#### Abnormal Glycol Behavior

The overall XRD patterns of Beaufort-Mackenzie I/S

can be reasonably assessed on the basis of a two-component mixed-layer model, 10 $\text{\AA}$  and 17 $\text{\AA}$ . However, some high-charge expandable layers appear to form single-layer complexes with glycol. The presence of a single-layer complex (14 $\text{\AA}$ ), is identified in the  $2\theta$  region where the position of 14 $\text{\AA}$  series reflections lies between those of the 17 $\text{\AA}$  and 10 $\text{\AA}$  series [e.g.  $(001)_{14}$ ,  $(003)_{14}$ ]. The peak of I/S between 17 and 10 $\text{\AA}$  is broader than that which can be obtained with Newmod2 based on a two-component model. The peak in the 5 $\text{\AA}$  region does not show an appreciable effect of glycolation between 5.7 $\text{\AA}$  [ $(003)_{17}$ ] and 5 $\text{\AA}$  [ $(002)_{10}$ ] (Fig. 5). In some cases, the glycol effect is even reversed (Fig. 6). Normally, the glycolation effect on I/S is more pronounced on the lower-angle side of 5 $\text{\AA}$  than on the higher-angle side because of the proximity of the third order peak (003) of 17 $\text{\AA}$  to the second order peak (002) of 10 $\text{\AA}$  compared to (004) of 17 $\text{\AA}$ . Upon K-saturation, the glycol effect becomes normal, i.e. a stronger  $(002)_{10}/(003)_{17}$  and a weaker  $(002)_{10}/(004)_{17}$  peak (Fig. 7). In general, K-saturated samples show better-defined reflections at the low-angle side of 5 $\text{\AA}$ . The 14 $\text{\AA}$  component appears to collapse to form illite-like layers and, thus, no longer exists.

#### Implications of X-ray Diffraction Patterns of K-saturated Samples

K-saturation experiments indicate that expandable layers in I/S consist of low- and high-charge layers. Expandable layers with high charge collapse to form illite-like layers upon K-saturation. With sodium as an interlayer cation, these layers formed 1- or 2-layer glycol-complexes depending on layer charge (see discussion above).

Upon K-saturation, the saddle/peak ratio of the  $(001)_{17}$  peak of random I/S increases compared to Na-saturated samples (Fig. 7B-a), suggesting that the proportion of I-layers increased. In Reindeer D-27, the proportion of I-layers increases by 2~28 %I (Fig. 8). A mixture of random and ordered I/S, upon K-saturation, loses the peak representing random I/S (Fig. 7B-b). Random I/S in the mixture may have acquired an ordered layer-structure, i.e. a structure of alternating expandable layers with high- and low-charge.

For ordered I/S, K-saturation alters the composition as well as the degree of ordering. R1-ordered I/S shows a gain of about 5~10 %I (Fig. 8). In addition, some I/S particles appears to have transformed into illite. In general, peaks representing illite, especially (001), are more prominent than those in Na-saturated samples (Fig. 7A-b, 7B-c). The response of the  $(001)_{10}/(002)_{17}$  peak that defines the nature of ordering is more complicated. In most cases, it moves towards higher angles (Fig. 7A-a,

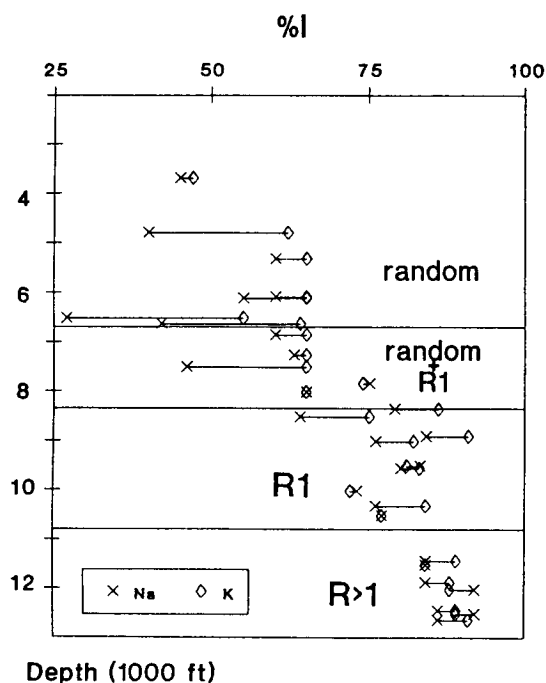


Fig. 8. Plot of I-content versus depth for K-saturated specimens in comparison to Na-saturated specimens of Reindeer D-27.

b), suggesting that the degree of ordering is improved. In some cases, the peak is broader and has an almost flat top (Fig. 7B-c), indicating that K-saturated samples consist of I/S mixed-layers displaying various degrees of ordering.

R>1-ordered I/S of Reindeer D-27 shows little change in XRD patterns upon K-saturation except for producing more prominent peaks corresponding to illite (Fig. 7A-c, d). On the other hand, K-saturated R>1-ordered I/S of Taglu C-42 displays a pattern similar to K-saturated R1-ordered I/S (Fig. 7B-d). The  $(001)_{10}/(002)_{27}$  peak and the equivalent peak of R>1-ordered I/S shift towards lower angles. Unlike Reindeer samples, K-saturation altered the nature of ordering in Taglu C-42.

Upon simple K-saturation, the proportion of I-layers in random I/S increased, while higher-order I/S as well as illite developed from R1-ordered I/S, by transforming high-charge expandable layers into I-layers. This suggests that the illitization reaction can be transformational. Random I/S appears to share a common structure in the composition range of <60 %I, while R>1-ordered I/S and probably also illite with R1-ordered I/S. The development of I-layers in the R1-ordered structure would result in odd numbers of I's between smectite-layers, i.e.

SISIS  $\rightarrow$  SIIS. Reichweite values greater than 1, but less than 3 for R>1-ordered I/S determined from X-ray diffraction patterns, are probably due to mixed stacking of R1- and R3-structures in the crystallite.

#### Discrete Illite or Elementary Illite Particles

The intensity of peaks corresponding to discrete illite increases with increasing I-content in I/S, as shown by increasing shoulder heights on the first order peak  $[(001)_{10}/(001)_{17}]$  of I/S at about  $10\text{\AA}$  (Fig. 5A). Most discrete illite is probably an artifact of dispersion. I/S crystallites are expected to dissociate into thin illite- and smectite-particles in a liquid according to the DLVO theory (van Olphen, 1977). Some illite particles may not associate back into I/S upon drying. Therefore, dissociation of I/S would increase the illite population, and thus contribute to the intensity of discrete illite peaks. As shown in Fig. 5A, the shoulder heights on the first order peak of random I/S at  $\sim 10\text{\AA}$  increase, as the intensity of  $(001)_{17}$  decreases. The increased intensity of the illite peaks is not due to newly-formed elementary illite particles that may have precipitate with increasing degree of diagenesis (for a geochemical point of view, see Ko *et al.*, 1995). Rather, the increase is due to the increased number of potential illite-particles in I/S, as I-contents increase. However, no systematic change in intensities of the illite peak was observed in the composition range of ordered I/S. This could be due to a greater proportion of high-charge expandable layers that may have developed in ordered I/S than in random I/S. High layer-charge would have prevented dissociation in ordered I/S.

#### CONCLUSION

Illite/smectite in the Beaufort-Mackenzie Basin includes the following four types: random, a mixture of random and ordered, R1-ordered, and R>1-ordered I/S. XRD patterns consisting of both random and ordered I/S signifies that mixed-layering in I/S may not be an artifact of interparticle diffraction between the 'fundamental' particles. The mixture of random and ordered I/S probably represents a metastable state in the ordering reaction.

Ordering has been considered an essential part of the illitization process by conventional viewers. However, the ordering reaction is disregarded, since the Ostwald ripening mechanism was introduced as an alternative for the illitization process to support the fundamental particle hypothesis (Inoue *et al.*, 1988; Eberl and Srodon, 1988; Eberl *et al.*, 1990). Ostwald ripening is a process

of crystal growth by which small particles dissolve due to high surface free energy, while large particles grow as matter is transferred from the former to the latter through dissolution and reprecipitation (Baronnet, 1984). However, clay minerals including I/S appear to be stabilized in terms of size by lateral growth rather than along the C-axis, as evidenced by face development and spacings ( $c > a, b$ ). The effect of layer thickness on the particle size would be negligible considering the dimensions of length and width.

K-saturation experiments indicate that layer charges of expandable layers in I/S are variable. Expandable layers in I/S consist of low- and high-charge layers. Upon K-saturation, expandable layers with high charge collapsed to form illite-like layers. K-saturation altered the composition and/or the degree of ordering in I/S. Upon K-saturation, random I/S gained I-layers by transforming high-charge expandable layers to illite-like layers. R1-ordered I/S became  $R \geq 1$ -ordered.  $R > 1$ -ordered I/S showed little change in the composition and the degree of ordering, but produced discrete peaks corresponding to illite. These observations suggest that the illitization reaction in nature can be transformational. Neof ormation probably operates while ordering of random I/S takes place.

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## 캐나다 보포트-맥켄지 분지의 일라이트/스멕타이트 혼합층 점토광물 연구

고재홍 · R. Hesse

**요약**: 캐나다 극지의 보포트-맥켄지 (Beaufort-Mackenzie) 분지에 분포하는 일라이트/스멕타이트 (illite/smectite)에 대한 광물학적 특성 연구가 육상 및 대륙붕의 석유시추공으로부터의 215개 코아와 파쇄시료를 대상으로 수행되었다. 보포트-맥켄지 분지의 일라이트/스멕타이트는 구성층의 배열 양상에 따라 불규칙, R1-배열, R>1-배열, 불규칙과 R1-배열의 혼합으로 구분된다. 불규칙과 규칙적인 배열의 혼합 양상을 보이는 일라이트/스멕타이트는 불규칙으로부터 R1-배열로 변화하는 전이대에서 나타나는데 혼합층의 배열이 규칙화하는 과정에서 불안정하게 나타나는 준안정상으로 해석된다. 불규칙과 규칙 배열을 갖는 일라이트/스멕타이트가 함께 나타나는 현상은 느린 화학반응에서 흔히 관찰되는 반응물과 생성물이 공존하는 현상과 일맥 상통한다.

K-포화 실험결과는 일라이트/스멕타이트 내의 스멕타이트층의 충전하가 다양함을 보여준다. 높은 충전하의 스멕타이트층은 K-포화시 준 일라이트층으로 변한다. K-포화는 일라이트/스멕타이트의 구성비와 배열을 변화시키는데 이는 자연에서의 일라이트화 현상도 기존 격자결합의 교란이 없이 일어날 수 있다는 것을 의미한다.