ASPECTS ON THE ILLITIZATION OF THE KINNEKULLE BENTONITES

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Abstract—Earlier interpretations of the conversion of the virgin smectite of the Ordovician Kinnekulle K-bentonites into the present mixed-layer illite/smectite imply that it took place through charge increase of the smectite with subsequent uptake and fixation of potassium. Recent analyses show that the layer charge of the smectite component of the I/S is in fact low and they suggest that neoformation of a separate illite phase took place. Pytte's kinetic model gives good agreement with the actual conversion rate for an activation energy of about 25–27 kcal/mole, depending on the adopted rate parameters, temperature history and assumed potassium source. In the Kinnekulle case the rate-controlling factor appears to have been the supply of potassium, which is concluded to have required large-scale, heat-induced groundwater convection.

Key words—Bentonite, Illitization, Smectites.

INTRODUCTION

The Chasmops series of Kinnekulle contains bentonite layers that have been the subject of several mineralogical investigations (Thorslund 1945, Byström 1956, Velde and Brusewitz 1982, Brusewitz 1986, Inoue *et al* 1990), and of studies for evaluating the physical properties of the clay material in conjunction with research on the longevity of smectitic clays in repositories for highly radioactive waste products (Pusch 1983, Müller-Vonmoos *et al* 1990, 1994). The report includes some new findings concerning the mechanisms of conversion from smectite (S) to illite (I), focusing on the rate-controlling function of the potassium uptake.

It is currently assumed that illite in bentonites results from two processes: 1) collapse around selectively adsorbed K^+ of smectite layers with tetrahedral Si^{4+} replaced by Al^{3+}, or 2) by a neoformation mechanism that involves dissolution of smectite and precipitation/growth of illite particles within populations of thin phyllosilicate particles (Nadeau *et al* 1985). This latter mechanism is akin to the generally accepted process of diagenetically precipitated illite in the voids of sandstones, by which regularly shaped illite laths grow. Thus, for bentonites and deeply located smectite clays with very limited pore space it can be imagined that precipitation of 20 Å illite in close association with smectite particles yields randomly interstratified I/S with the XRD-recorded percent illite layers increasing until the smectite fraction has dropped to 20%, when ordering is observed. Dominance of homogeneously distributed 20 Å illite particles yields a rectorite-like pattern and when the illite particles have grown to larger thickness than about 50 Å by successive precipitation, the typical 10 Å spacing is observed. Applying this model of smectite-to-illite conversion, Nadeau *et al* (1985) explained the XRD patterns of apparent I/S mixed-layer minerals as an interparticle diffraction effect at hydrated smectite-like interfaces within aggregates (stacks) of thin phyllosilicate crystallites.

Layer-by-layer transition through simple lattice reorganization is not probable because of the misfit of I and S crystal lattices and the low probability of replacement of interlamellar Ca^{2+} by K^+ at normal Ca/K concentration ratios in the porewater. A further reason is the difficulty in explaining the mechanism by which tetrahedral Si is replaced by Al, and all this makes neoformation of illite a more conceivable process.

GEOLOGY

Stratigraphy

Figure 1 shows a general picture of the stratigraphy of the Kinnekulle hill area with diabase of Permian age forming the top and covering an about 200 m high series of shales, limestones and sandstones, that rests on crystalline bedrock. At about 95 m depth below the diabase cap bentonite layers are present, among which there is an approximately 2 m thick major bed that is of particular interest in the present context.

Figure 2 shows the build-up of sediments at the stratigraphic level where the major bentonite bed appears. The map was worked out on the basis of a drillcore taken in 1982 for mineralogical and physical testing by the University of Luleå under the heading of the senior author and for mineralogical characterization by the Swedish Geological Survey. Undisturbed box samples were extracted a couple of years later from the major bentonite bed for investigation at ETH, Switzerland.
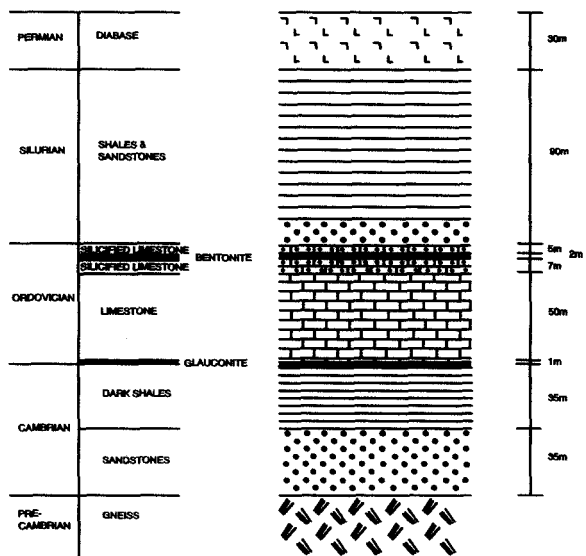
Figure 1. The Kinnekulle strata. Scale denotes approximate stratigraphic thickness in meters.

Formation

Volcanic ash was deposited in seawater on top of about 120 m of muds and calcareous sediments in the Kinnekulle area in southwestern Sweden about 450 M years ago. Additional sediments of similar type and also silty and sandy sediments were deposited on top of the ash beds, yielding a series of marine sediments with a total thickness of several hundred meters. The ash, which originated from rhyolite or dacite lava, was converted to smectitic bentonite layers, which were consolidated under an estimated effective overburden pressure of 5–10 MPa, yielding a density of about 2.0–2.2 g/cm^3 and a water content of 15–25%. The porosity was about 30–40%. About 300 M years ago, magma moved up and penetrated laterally into the sediment series at about 250 m height over the crystalline bedrock, forming a diabase layer with a thickness of several tens of meters and exposing the sediments to high temperatures. Pressures, precipitation of dissolved substances, and the heat pulse in Permian time transformed the clastic strata to sedimentary rock. The top part of the diabase is more coarse-grained than its lower part, which suggests that the present upper surface represents the central portion of the diabase layer (Johansson *et al* 1943), implying that its total thickness was on the order of 60 m.

Prequaternary erosion and Quaternary glaciation removed the sediments covering the diabase and its upper part, leaving about 30 m diabase over the sedimentary rock sequence. The maximum overburden pressure, which acted in Quaternary glacial time, is estimated at 30 MPa and it should have reduced the water content to about 10%, provided that the interstitial water was not frozen.
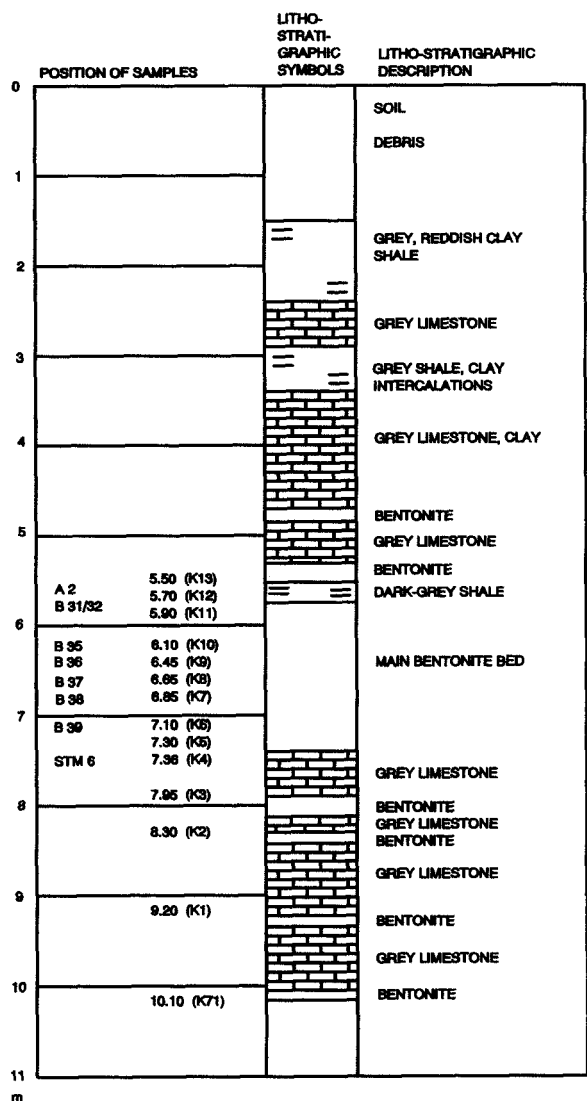

Figure 2. Detailed stratigraphy of the about 2 m thick bentonite bed and adjacent strata. Scale denotes stratigraphic distance in meters from top of exposure.

Where samples have been extracted through core drilling and excavation (Mossen bentonite quarry), the effective overburden presure has only been about 0.1 MPa in postglacial time, which means that the strongly overconsolidated, largely plastic bentonite layers have undergone expansion and an increase in water content to the present 22–35% in the 2 m thick central bentonite bed (Pusch 1983). The expansion and softening would have proceeded beyond this if cementation had not taken place.

Temperature history

The temperature history is not known in detail but a number of indications combine to give a highly prob-

Table 1. Thermal data.

Rock type	Heat conductivity, W/m, K	Heat capacity, J/kg, K
Diabase	2.5	800
Sedimentary rocks	2.0	800
Shale	2.0	800
Bentonite	1.0	1600

able picture of the peak temperature and heat decay induced by the magma intrusion. Since the overburden hardly exceeded 500–1000 m before this event, the temperature cannot have been higher than 20°–30°C if normal geothermal conditions prevailed. Hence, the heat pulse caused by the Permian magma intrusion is concluded to have been responsible for possible mineral conversion in the bentonite.

Two methods of estimating the temperature have been applied, namely thermal calculation of the heat evolution induced by the magma intrusion using a numerical finite difference code, and conodont analysis. The first approach was made by assuming "symmetric" conditions with respect to the stratigraphy, i.e., taking the diabase to have been 60 m thick and with several hundred meters thick sediments covering the diabase. The initial temperature of the intrusive magma forming the diabase was assumed to be 1100°C. The thermal properties of the various components have been summarized in Table 1 (Pusch 1994).

The calculated temperature increase was found to be as shown in Figure 3, from which one finds that the bentonite bed about 95 m below the base of the diabase would have reached a maximum temperature that was of about 140°C higher than before the heat pulse. Taking the initial temperature to have been 20°C the maximum temperature would thus have been about 160°C and the temperature would have been in the interval 140–160°C for 300 years, 120–140°C for another 300 years, and 100–120°C for an additional period of 500 years.

Conodonts, a group of widely distributed phospatic microfossils, turn out to be useful as a semiquantitative index of thermal metamorphism (Bergström 1980). The color changes exhibited by conodonts during gradually increased heating is diagnostic and can be used as indicators of temperatures in the interval 80°–500°C. Such analyses of the limestone located about 10 m above the bentonite bed have yielded values in the range of 110°–200°C, which fits well with the thermal calculation (Pusch 1983).

One concludes from the two ways of estimating the temperature history of the bentonite bed that it underwent heating to 150°C for about 300 years and that it was then exposed to about 130°C for 300 years and subsequently to 100°–130°C for 400 years. The temperature subsequently dropped back to the original 20°C in an approximately 2000 years long cooling period.
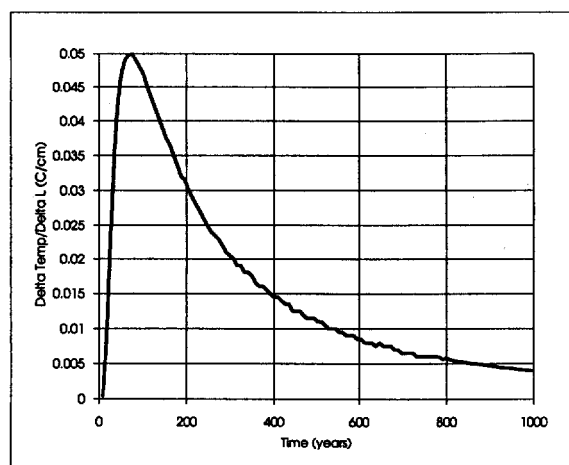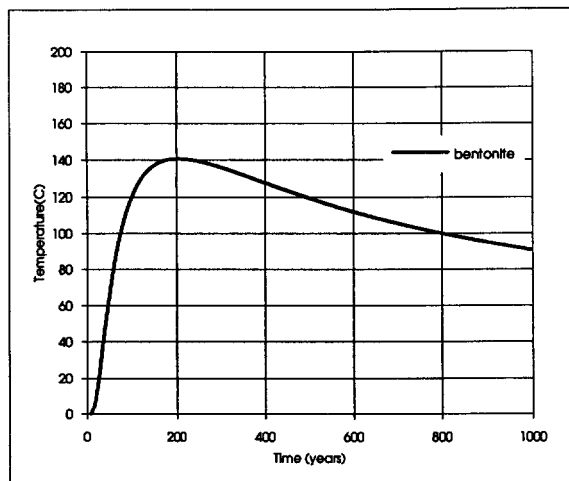

Figure 3. Temperature conditions. Upper: evolution in the main bentonite bed in the first 1000 years after the magma intrusion. Lower: Temperature gradient over the main bentonite bed as evaluated from the thermal calculations.

The temperature gradient over the main bed cannot have exceeded about 0.05°C/cm (Figure 3).

MINERALOGY

General

The mineralogy of the bentonite layers is complex and there are indications of significant variation in the composition of the originally deposited material. The mineral components vary in the different grain size fractions, the <1 μm fraction having been investigated most extensively.

Granulometry

The <2 μm fraction forms 35–40% of the main bed as determined by use of pipette sedimentation analyses after gentle crushing and ultrasonic treatment of the soil dispersed in sodium pyrophospate solution. The
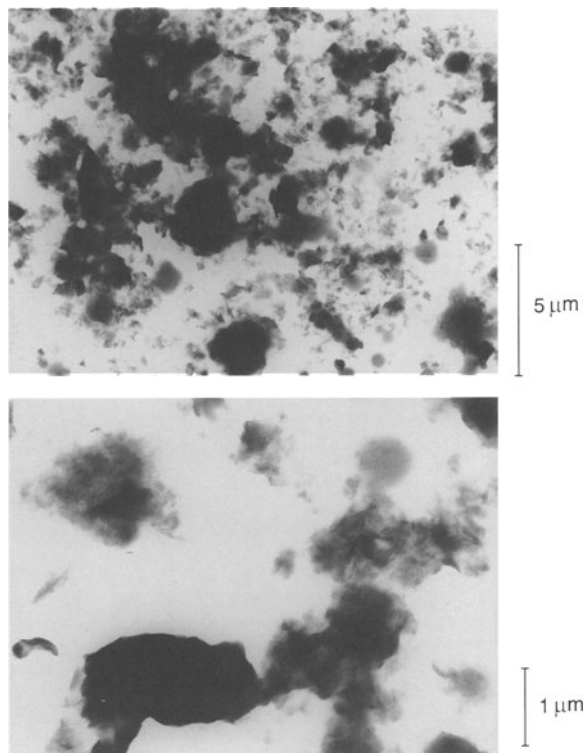
Figure 4. TEM micrographs of dispersed Kinnekulle material. Upper: 7800× magnification. Lower: 23,500× magnification showing "mossy" aggregates and minute crystallites with distinct boundaries.

grain size distribution is as follows: $<40 \ \mu m = 69\%$, $<20 \ \mu m = 64\%$, $<10 \ \mu m = 58\%$, $<6 \ \mu m = 52\%$ (Pusch 1971). In the electron microscope dispersed material appears as shown in Figure 4, which demonstrates the "mossy" character of smectite aggregates with a size of $1-5 \ \mu m$ and the presence of numerous particles with distinct boundaries and a size of $0.01-0.05 \ \mu m$. The latter give the same impression as minute illite particles in postglacial and glacial clays (Pusch 1962) and may well represent neoformed illite crystallies.

Microstructure

The microstructure is not characterized by strong orientation; in fact both transmission electron microscopy (TEM) of ultrathin sections cut from acrylate-embedded samples, and scanning electron microscopy (SEM) of freeze-dried samples, show that the phyllo-silicates form rather small curved stacks that are collected more or less randomly in bigger aggregates as illustrated by Figure 5 (Pusch 1971). This sort of microstructure does not form under high effective stress conditions; it is indicative of crystal growth in voids.

Rock-forming minerals

The upper part of the main bentonite bed has a lower content of pyrite, quartz and other phenocrysts and a
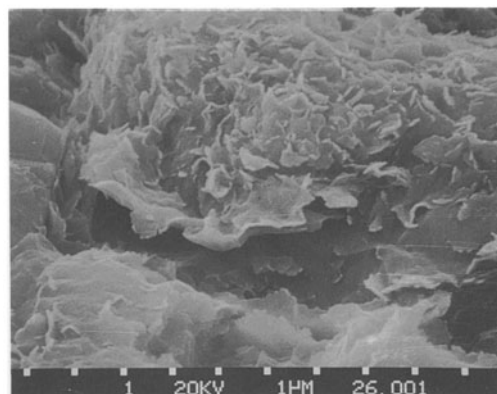

Figure 5. Microstructure of Kinnekulle bentonite showing random grouping and orientation of phyllosilicate stacks. Upper: TEM photo. Lower: SEM photo.

higher content of titanium than the central part and this suggests different original compositions of the magmas. In fact, it has been stated that there is a difference in age of 35 M years of the upper and lower parts, which may well imply significant differences in ash composition (Velde and Brusewitz 1982).

Biotite. This Fe-bearing mineral, which forms 2–3% of the total mineral mass, gives the Kinnekulle bentonites

their characteristic brownish color. Weathering may have produced chlorite.

Chlorite. This Fe-bearing mineral is present in about the same quantities as biotite.

Feldspars. Plagioclase in strongly kaolinized form makes up 5–10%. Sanidine, a K-feldspar, represents 2–5% and suggests that K-bearing feldspars were not the major source of potassium for conversion of smectite to illite.

Quartz, cristobalite and amorphous silica. Quartz in the form of thin, wavy or wedge-shaped microscopic plates, is the most frequent phenocryst species. The quartz grains are most abundant in the 2–6 μm fraction and locally make up 40% of the total mineral content (Velde and Brusewitz 1982). SEM studies have shown the presence of very fine quartz, cristobalite and amorphous silica, which may all serve as cementing agents (Müller-Vonmoos *et al* 1990). Amorphous silica amounts to about 0.5% of the total mineral content, partly in the form of precipitations at the rim of the stacks of flakes by which interlamellar hydration is retarded and expansion partly prevented.

Clay minerals

The clay mineral composition has been investigated and quantified in several comprehensive studies, which have given somewhat different results. Still, in general, they all indicate approximately the same composition of the about 2 m thick bentonite bed, namely that I/S mixed-layers dominate and that smectite (montmorillonite), kaolinite, illite and chlorite are also represented. Quartz and feldspars appear as well in the clay fraction (Byström 1956). Adjacent, thinner bentonite layers above and below the main bed have illite as major clay mineral.

Using the abbreviations S for smectite, I for illite, Q for quartz and K for kaolinite, the weight percentages given by Brusewitz (1986) for the minus 1 μm fraction are summarized in Table 2, along with I in I/S and relative K and Al contents. CEC values in meq/100 g are also given.

Table 2 shows that the average illite content in I/S decreases successively from about 60% at the upper boundary of the main bed to around 40% in its center, and that it again increases from the center of the bed to about 65% at 10 m depth. The K-data are in agreement with this and show that illitization started from outside the main bed and progressively moved towards its center from above as well as from below. Brusewitz (1986) concluded that the ordering of the I/S was R = 0 to R = 1, i.e., random to regular, in the uppermost part of the main bed and below it, while the larger part of the bed was said to have R = 0. Above the main bed the illite content in the I/S was stated to be as high as 90% and the ordering high (R = 3). Brusewitz claimed that the illite content in I/S is constantly 50% in the

Table 2. Mineral content in the <1 μm fraction (evaluated from Brusevitz 1986) and relative K- and Al contents of the <2 μm fraction from linear EDX analysis (Pusch 1983).

Sample no. [Fig. 2]	Distance [m] below level zero	Minerals in <1 μm fraction			CEC [meg/ 100]g	Rel. K- & Al counts/500	
		I% in I/S	Q and K [wt%]			K	Al
K13	5.50					3.1	3.9
K12	5.70					3.1	3.1
K11, B31	5.90	52–65	5	2	55	1.5	2.5
K10, B35	6.10	41–54	8	4	73	1.4	3.7
K9, B36	6.45	37–54	5	5	78	1.4	2.5
K8, B37	6.65	38–51	5	2	76	1.7	3.0
K7, B38	6.85	36–49	3	3	88	1.6	2.9
K6, B39	7.10	32–46	2	2	91	1.5	3.1
K5	7.30					1.8	3.0
K4	7.36					1.7	2.9
K3	7.95					3.8	4.0
K2	8.30					3.8	4.1
K1	9.20					3.5	4.0
K71	10.10	59–70			55		

lower part of the main bentonite bed, indicating that the conversion from smectite to illite is asymmetric in the main bed, which is contradicted by the K and the Al-distributions in Table 2.

The layer charge of the I/S was found by Brusewitz (1986) to be 0.65–0.67 charges per formula unit for samples B31 and B39, representing both the uppermost and central parts of the main bed. In contrast, Müller-Vonmoos *et al* (1994) found much lower layer charge of the I/S, i.e., 0.42 at the B31 level and 0.38 at the B39 level and they demonstrated that these data are correct. The present authors conclude that both low- and high-charge I/S are present and that a large part of the smectite has been preserved. The high-charge form represents illite that may well have been neoformed.

Recently, a more comprehensive and detailed investigation was made of the Kinnekulle bentonites by Inoue *et al* (1990) and it gave a more complete picture of their formation and of the conversion that they have undergone. This work comprised not only X-ray powder diffractometry and ordinary transmission electron microscopy, but also ordinary TEM of dispersed material and chemical analysis using EDX (AEM) technique for identifying possible differences between differently appearing particle assemblages. The comprehensive simulation of XRD spectra gave the conclusions and assumptions listed below.

1. The content of illite in I/S is 55–65% at the upper boundary (B31) of the main bed and in thinner layers (K71) below the main bed. It is 50% in the central and lower parts (B38 and STM6) of the main bed, while it is 100% higher up in the Silurian strata.

2. The K-content of the illite interlayers is assumed to be 0.75 ions per illite half unit cell.

3. The Fe content of both the smectite and the illite is zero.

4. The thickness of EG smectite complex layers is 16.9 Å.

5. The average number of flakes (layers) in diffracting crystallites is 10, assuming Gaussian distribution.

The TEM photography showed that all the I/S samples with 30–50% S were rather similar and dominated by flaky particles as illustrated also by the micrographs in Figure 5. However, they were also reported to contain a certain, small amount of laths with an average length/width ratio of 4, and a thickness of 30–100 Å regardless of the S content. The length/width ratio is two to three times as high as recorded for <1 μm particles in Swedish smectite-free glacial clays with illite as major clay mineral while the thickness is not very different; the median thickness value of the particles in the glacial clay being 50–200 Å, and the lower and upper quartiles being 40–100 Å and 80–600 Å, respectively (Pusch 1962). The preparation techniques and modes of determining the dimensions of the particles were similar and the results should therefore be comparable although the number of recordings was significantly higher in the Swedish study. The fact that the difference in particle thickness between the smectitic Kinnekulle clay and the smectite-free glacial clays is so small suggests that morphological data cannot be used as a safe indication of the nature and origin of the clay minerals. However, the presence of a certain fraction of lath-shaped crystallites in the Kinnekulle clays as well as the earlier mentioned content of minute particles with the characteristic morphology of illite crystallites do not contradict the hypothesis that neoformation of illite has taken place.

The AEM analyses performed by Inoue *et al* (1990) showed no significant difference in chemical composition between particles of different shape but the risk of escape of alkali ions like K from interlamellar and lattice positions in the course of the electron microscopy may have resulted in element distributions that were not relevant. A general observation was that the K and Al contents of the I/S increased and the Si and Mg decreased with decreasing S in the I/S.

Inoue *et al* (1990) concluded from their study that the dominant process of conversion of a smectite precursor in the Kinnekulle clay was cationic substitution described as a solid-state transformation mechanism, and not dissolution of smectite and neoformation of illite. They stated that the reason for this was the very limited space for supplying necessary elements like K during the conversion, referring to recent findings that the porosity and permeability significantly influence the morphology of I/S particles, the degree of illitization and the mode and mechanism of smectite-to-illite conversion. Thus, these investigators claimed that while the relatively large void space in tuffs and sandstones exposed to hydrothermal conditions yields growth of I/S crystals and formation of a separate I phase, this may not take place in bentonites and shales since solutions do not circulate freely by which S-to-I conversion is retarded and hindered. We do not find support of this hypothesis in the case of the Kinnekulle bentonites as will be outlined below.

MAJOR ALTERATION PROCESS

Recent research demonstrates that the porosity of smectite-rich clays resembling the Kinnekulle clays at the time when the diabase intrusion took place was sufficiently high to permit free growth of illite crystals in wider voids (Güven *et al* 1987). This fact and the illite-like morphology of the minute particles suggest that neoformation of illite was the most probable S-to-I mechanism. This mechanism requires a certain activation energy for the involved dissolution and lattice formation and also access to potassium in dissolved form.

RATE MODELING

The conversion model proposed by Pytte (Pytte and Reynolds 1989) is based on the assumption that the conversion from smectite to illite is an Arrhenius-type process, which—in addition to the access to potassium—makes the rate of conversion a function of temperature. Assuming that it applies to the conversion mechanism proposed by Nadeau *et al* (1985) we will use this semi-empirical S-to-I model for estimating the conversion rate of the Kinnekulle bentonites. The major variables are the activation energy, the ratio of K^+/Na^+ and the smectite concentration as expressed by Eq. (1).

$$-dS/dt = Ae^{-U/RT}f(K^+/Na^+)g(S) \qquad (1)$$

where

A = Constant
U = Activation energy
K^+ and Na^+ = Concentration of potassium and sodium, respectively
S = Mole fraction of smectite in I/S assemblages
f = function of K/Na ratio
g = function of smectite concentration in I/S
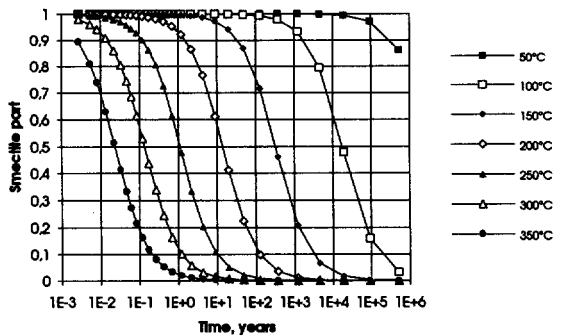R = universal gas constant
T = temperature

The model has been applied by several investigators who used various different parameter values depending on the assumed hydrothermal conditions (Pusch *et al* 1988a and b, Altaner 1989, Kamei *et al* 1990, Huang *et al* 1993). We will make the following assumptions:

1. The conversion of smectite to illite took place only in the heating period.

2. The f- and g-functions are the same as those applied by Huang *et al* (1993).

3. The K/Na ratio is maintained constant throughout the conversion period.

smectite fraction at start	SO		0	1
time	t	s	0	
frequence factor	A	1/s	80800	
activation energy	Ea	cal/mol	25000	
gas constant	R	cal/(deg*mol)	1,987	
temperature	T	K	323	623
K+ concentration	(K+)	mole/l	0,01	

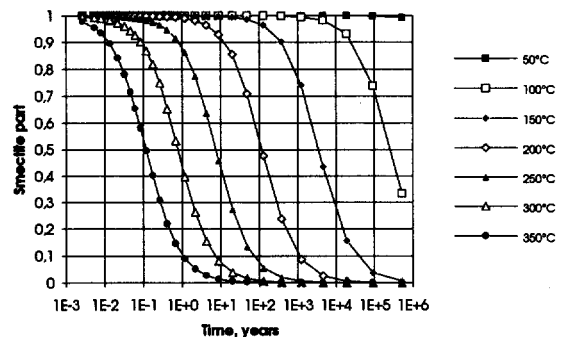| smectite fraction at start	SO		0	1
time	t	s	0	
frequence factor	A	1/s	80800	
activation energy	Ea	cal/mol	27000	
gas constant	R	cal/(deg*mol)	1,987	
temperature	T	K	323	
K+ concentration	(K+)	mole/l	0,01	

Figure 6.   Rate of conversion of smectite at a K^+ concentration of 0.01 moles/liter in the porewater according to Pytte's model for various temperatures. Scale: Vertical = proportion of smectite (1 = 100%), Horizontal = log time from 0.001 (1E − 3) to 1 million (1E + 6) years. Upper: Activation energy 25 kcal/mole. Lower: Activation energy 27 kcal/mole.

4. The K^+ content in the porewater was 0.01 moles per liter porewater, corresponding to about 400 ppm, i.e., the potassium concentration in seawater.

5. The Ca-concentration is not important.

Using the activation energies 25 and 27 kcal/mole, the remaining smectite content for different temperatures and periods of time is given by the diagrams in Figure 6. The one referring to 25 kcal/mole shows that the 300 years long period with 150°C should have led to a reduction from 100% (smectite part = 1) to 50–60% (smectite part = 0.5–0.6), while the subsequent 300 years long period with an average temperature of 130°C would have reduced it further to around 35%.
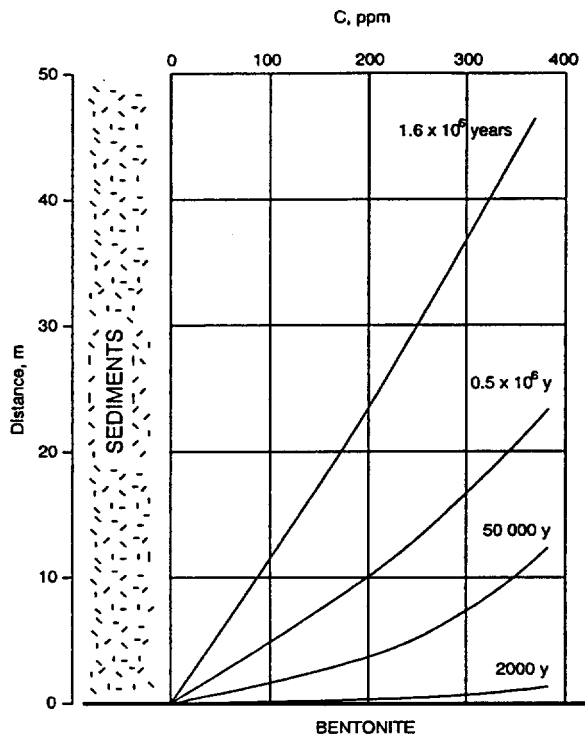

Figure 7.   Theoretical change in K^+ concentration in the porewater of the sediments adjacent to the 0.3 m bentonite bed at Hamra on southern Gotland (Pusch and Karnland 1988b). Potassium dissolved in the porewater migrates towards the bed in which the S > I reaction creates a K-sink that drives potassium in from the overlying sediment, which becomes depleted at successively larger distance with increasing time.

The latest phase with an average temperature of 110°C lasting for 500 years would have led to a drop of the smectite part to around 30–35%. This gives fair agreement with the finding that the actual smectite part is 30–50%. One finds, however, that also a very small change in activation energy gives quite different results. Hence, using the activation energy figure 27 kcal/mole the smectite part is as high as 85% at the end of the 1100 years long period with temperatures exceeding 110°C. Still, taking the temperature to have reached 185°C with the activation energy maintained at 27 kcal/mole one would also have obtained a good fit and such a temperature would in fact be reasonable with respect to all the recorded temperature indications. One concludes from this exercise that the degree of conversion evaluated from Pytte's model is very sensitive to the input data, particularly the activation energy and the temperature history, which hence have to be very accurately known in order to make meaningful calculations.

The other condition, i.e., that of access to potassium for the conversion, depends on how potassium was

transported and taken up in the smectite, and what the available amount of potassium was. Assuming that potassium was not moved in by groundwater flow, the transport mechanism must have been diffusion with the driving force being the concentration gradient induced by the illitization process. Thus, a sink should have been created in the converting bentonite due to the fixation of potassium irrespective of whether illite was created by neoformation of a new phase or whether I/S mixed-layers were formed. Earlier studies of practical cases of smectite alteration have indicated that the diffusion rate in fact controls the conversion (Pusch and Karnland 1988, Altaner 1989, Pusch 1992). In these studies it was assumed that potassium was supplied only by the porewater of the marine sediments adjacent to the smectite clay layers, yielding partial depletion of potassium from the initial concentration 400 ppm as illustrated by Figure 7, which refers to a 0.3 m bentonite bed located at about 500 m depths on the island Gotland in the Baltic Sea. For this particular case the apparent diffusion coefficient was concluded to have been between 10^{-11} m²/s and 10^{-10} m²/s, assuming that the conversion was limited to the 10^6–10^7 years period during which the temperature was 100°–120°C.

The fact that the thinner bentonite layers close to the main bed at Kinnekulle have undergone the strongest illitization and that there is a very obvious I/S profile in the main bed with minimum conversion in its center, clearly indicates that the conversion was controlled by the transport of potassium from the surroundings.

Making the same assumption for Kinnekulle as for the Gotland cases, i.e., that associated smectite conversion and diffusive transport of potassium into the bentonite layers took place in the approximately 1000–1500 years long period of significant heating, one finds that the change in potassium content in the porewater can have been noticeable only within the next few meters or possibly a few tens of meters from the main bentonite bed. A first and major question is then whether the available amount of potassium was sufficient to produce the recorded reduction of the smectite content by 50–70%, and it can be answered by considering the stoichiometrically required amount of about 5 percent by weight. Taking the initial content of smectite of the bentonite to have been 100% and estimating the density of the bentonite layers at 2.1 g/cm³ and the porosity of the adjacent sediments at 30% in Permian time, one finds that even if all the potassium in the porewater of the sediments located between the diabase and the bentonite and between the bentonite and the crystalline bedrock would have been used up it could only have produced conversion of about 10–15% of the smectite. In fact, in order to yield the present 50–70% conversion one has to make either of the following assumptions:

1. The initial smectite content was only 10–20% of the total mineral mass.

2. The conversion to illite proceeded long after the heating period.

3. The access to potassium in the heating period was much higher than assumed, requiring dissolving reactant phases.

The first alternative would imply that the bentonite was not autochtonous but strongly contaminated by non-smectite detrital material in an erosion/redeposition process, a possibility that can be ruled out on the ground that the microstructure is typical of smectite-rich material in bentonites formed from volcanic ash.

The second alternative would require transformation of the precursor smectite to a high-charge form in the heating period and subsequent conversion to illite solely controlled by the access to potassium. This implies lattice conversion through replacement of tetrahedral silica by aluminum in a solid-solution process as proposed by Brusewitz (1986) and Inoue *et al* (1990) and conversion to illite over the entire 400 million years that have passed since this event. This would have allowed for migration of potassium from larger distances like in the Gotland cases, leading to the observed high degre of illitization.

The third alternative would imply that the potassium concentration was maintained high in the sediment series in the heating period, requiring comprehensive dissolution of K-bearing minerals and/or groundwater flow to bring the potassium-rich solution to the bentonite layers. This condition may well have been caused by the heat pulse at the magma intrusion, since it could have generated a sufficiently high porewater pressure to cause hydraulic fracturing and an increase in porosity, yielding comprehensive groundwater convection. This possibility is considered to be plausible also since the assymmetric K-distribution with much less illitization in the lower part of the main bed would fit with the smaller impact of heating deeper down in the sediment series. Assuming Pytte's model to be valid, one finds that the actual I/S ratios in the main bed are obtained for a constant K-concentration of about 0.05 moles per liter (Figure 8).

Mechanisms of dissolution and precipitation

The current view is that silica is released from smectite undergoing transformation from low to high charge, but neoformation of illite may also have yielded free silica. Thus, the increased solubility of silicate minerals and thereby the enhanced concentration of dissolved silica and aluminum caused by the heating of the Kinnekulle limestone-embedded bentonites led to release of both Si and Al and diffusion of these elements from the bentonite layers into the adjacent limestone sediments. Silica was transported out while complexation of aluminum caused retainment of this element in the

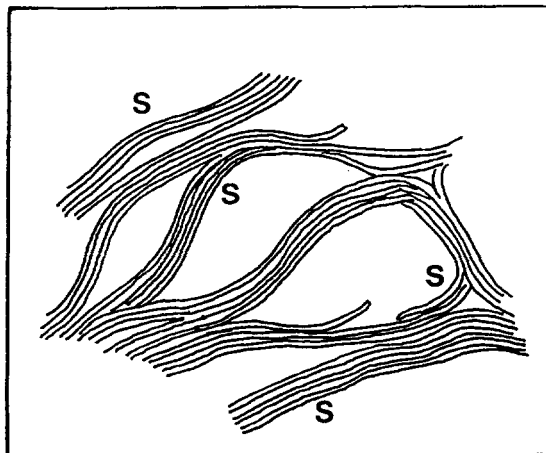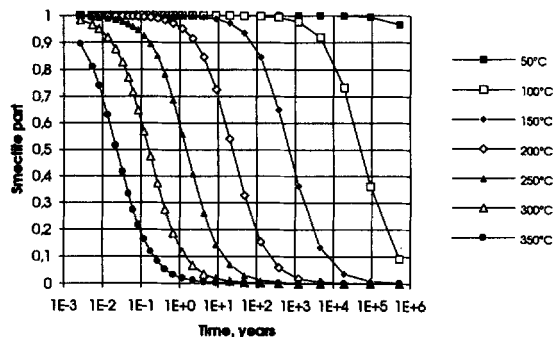|			
smectite fraction at start	S0	0	1
time	t	s	0
frequence factor	A	1/s	80800
activation energy	Ea	cal/mol	27000
gas constant	R	cal/(deg*mol)	1.987
temperature	T	K	323
K+ concentration	(K+)	mole/l	0.05

Figure 8. Rate of conversion of smectite at a K^+ concentration of 0.05 moles per liter according to Pytte's model. Compare with lower diagram in Figure 6.

bentonite. The bentonite layers, and particularly the main bed, may thus have caused enrichment of silica in the surrounding limestone, yielding precipitation of silica compounds and cementation when the temperature dropped (Figure 1). It is in fact probable that the precipitated illite layers made up part of the cement by connecting smectite aggregates in the fashion indicated schematically in Figure 9, which implies that neoformation of illite took place in either of the processes proposed by Nadeau.

CONCLUSIONS

The conversion of the smectite to illite in the Kinnekulle bentonites has been interpreted earlier as replacement of tetrahedral silica by aluminum and coalescence around interlamellar K^+ yielding high charge I/S, while the present report suggests that neoformation of illite took place in the fashions proposed by Nadeau. This is primarily because the heating led to an average charge of the I/S that is not much higher than that of smectite (Müller-Vonmoos *et al* 1994), indicating that a large part of the smectite remained intact and that high-charge illite layers were formed in close association of the smectite stacks. Secondly, the particle morphology does not speak against neoformation of illite. Thirdly, the uniform heating of the main bed should have led to the same degree of cementation of all parts of the bed if released tetrahedral silica had formed the cement, while in fact the peripheral parts were much more affected. This shows that illitization is strongly associated with the cementation and that neoformation of illite with a cementing function may have taken place.

Assuming the illitization to have taken place in the heating period, it is found that the access to potassium
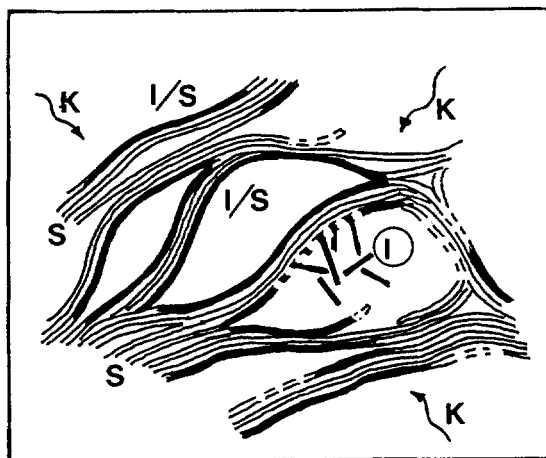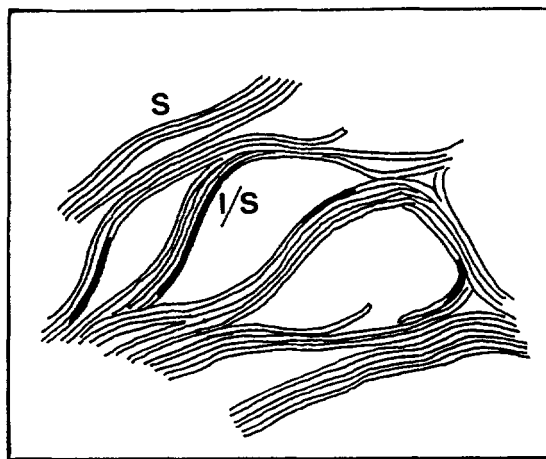

Figure 9. Congruent dissolution of smectite (upper) and formation of I/S by precipitation of illite layers using up available potassium from accessory minerals (central), and formation of a separate illite phase (lower) (Pusch and Karnland 1988a).

must have been much greater than offered by diffusion of potassium in the porewater of the adjacent sediments, which calls for verification of the processes proposed here.

Pytte's model is a practical tool for estimating the rate of conversion of smectite to illite provided that the temperature evolution can be determined and that the condition for access to potassium is really fulfilled.

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