ASYMMETRIC ZONATION OF A THICK ORDOVICIAN K-BENTONITE BED AT KINNEKULLE, SWEDEN

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Abstract—The clay fraction of a ~2-m-thick K-bentonite at Kinnekulle in southwestern Sweden has been studied by X-ray powder diffraction, chemical analyses, and cation-exchange capacity determinations. Previous investigations of the upper half of this bed (B-bed) have shown the clay mineral to be illite/ smectite (I/S), containing about 50% illite layers at the center of the bed and 65% illite layers at the upper contact. New data on six samples from the lower part of the bed show no zonation, the I/S containing about 50% illite layers in all samples. The bentonite occurs in limestones and shales overlying a 40-m-thick limestone bed and is overlain by limestones, marls, and shales (~90 m), which in turn are overlain by a 40-m-thick diabase. The limestones are silicified in contact with the bentonite, particularly beneath the B-bed. The increased K content towards the upper contact may therefore have resulted from diffusion of K-bearing solutions from overlying shales, a process that was impeded in the lower part of the bed, probably by the silicification.

Key Words—Bentonite, Diagenesis, Illite/smectite, Potassium, Shale, X-ray powder diffraction.

INTRODUCTION

In 1956, Byström showed the principal clay mineral in Ordovician K-bentonites at Kinnekulle, southwest Sweden, to be mixed-layer illite/smectite (I/S). Two types of I/S were identified; one type found in thinner beds (A beds, each about 20 cm thick) had 60% illite layers, whereas that in a thick bed (B bed, about 2 m thick) had fewer illite layers. Later studies on the Kinnekulle bentonites gave a more detailed picture of the B bed and showed a successive increase of potassium and illite layers in the I/S from the center of the bed to its upper contact (Velde and Brusewitz, 1982; Brusewitz, 1986). No samples were then available from the lower part of the B bed.

In a study of K-bentonites from the Marias River Formation in the Montana disturbed belt, Altaner *et al.* (1984) also found chemical and mineralogical zonation, especially in a thick (2.5 m) bed of comparable size to the Kinnekulle B bed. They reported an increase of potassium and of the proportion of illite layers in I/S from the center of the bed towards both the upper and lower contacts, from about 50% to 65–70%. The K-bentonites in the Montana area are enclosed in an Upper Cretaceous marine shale, which has been subjected to metamorphism by burial beneath Precambrian and Paleozoic thrust sheets during the Laramide orogeny (Mudge, 1972). Potassium for the illite formation was considered to have been derived from a breakdown of potassium-bearing minerals in the surrounding shale and subsequent diffusion into the bentonite (Altaner *et al.,* 1984).

In 1982, new drilling was undertaken at Kinnekulle by the Swedish Nuclear Fuel and Waste Management Company near the spot at Stora Mossen where sam-

pling had been carried out in the earlier studies (Thorslund, 1948; Velde and Brusewitz, 1982; Brusewitz, 1986). The availability of samples from the lower part of the Kinnekulle B bed prompted the present study to see whether the zonation continued towards the lower contact of this bed, as was found for the Montana bentonite.

GEOLOGICAL SETTING

A comparison of the geological settings of the two localities shows some differences. The Kinnekulle bentonites occur in limestones and shales overlying a ~40-m-thick limestone (Jaanusson, 1964; Thorslund, 1948), whereas the Montana bentonites are surrounded by shale (Altaner *et al.,* 1984). The sedimentary rocks at Kinnekulle were not subjected to major tectonic activity and may never have been overlain by more than 2–3 km of strata. They are flat-lying and have been shielded from erosion by a diabase cap (Johansson *et al.,* 1943). The Montana sediments were subjected to metamorphism by burial beneath thrust sheets and are tilted (Mudge, 1972). There is also a difference in age; the Kinnekulle bentonites were derived from ash falls dated at about 450 Ma (Byström-Asklund *et al.,* 1961; Kunk *et al.,* 1984). The volcanic glass devitrified to smectite and the further reaction to K-bentonite probably occurred during the Carboniferous age (340–300 Ma, Brusewitz, 1984; Williams *et al.,* 1982). The Montana bentonites are younger (Upper Cretaceous), and the change to K-bentonite occurred at 76–50 Ma (Hoffman, 1976).

The major part of the Kinnekulle section, which contains the bentonite beds, was described by Thorslund (1948) as mostly grey to dark-grey, fine-grained lime-

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stone, intercalated by grey to dark-grey calcareous mudstone. A 1-m-thick bituminous shale containing illite and chlorite (Mossen Formation, Skoglund, 1963) overlies the ~20-m-thick bentonite-bearing limestones and shales and is itself overlain by ~85 m of late Ordovician and Silurian mudstones and marls. The bentonite (B-bed) studied here occurs 3.3 m below the Mossen shale. The limestone layers in contact with the bentonites are typically siliceous, e.g., below the B bed the upper 0.7 m of rock is hard or flinty, the uppermost 10 cm consisting mainly of dark chert (Thorslund, 1948). Also, between the B bed and the A beds, a 35-cm-thick layer of dark, hard, siliceous limestone exists, which becomes increasingly flinty towards the base. Thorslund (1948) further described long lenses of aragonite at the upper contact with the B bed; these were later identified by the present author as calcite. The calcite lenses seem to have crystallized as fissure fillings. The siliceous environment was considered by Bramlette (1946) to have been derived by devitrification of volcanic glass, the silica having been leached out, but the smectite-to-illite reaction may also have contributed to this environment (Byström, 1956).

The B bed was found to contain no admixed material of nonvolcanic origin; no fossils were noted, although they are abundant in the surrounding strata. The bed is not homogeneous with respect to the phenocrysts present, as can be judged from the variations in quartz content and the size of biotite flakes at different levels. The variation may be due to repeated ash falls or redeposition in water (Thorslund, 1948; Jaanusson, 1964).

EXPERIMENTAL

From the new core six samples were collected from the 50-cm-thick zone nearest the lower contact of the B bed, corresponding to 130–180 cm beneath the upper contact. The cherty layer at the lower contact was also sampled. The samples were disintegrated without a dispersing agent in deionized water by mechanical stirring. The <0.5-μm fraction was collected by repeated decantations, centrifuged to reduce the volume of the suspension, and freeze dried. The cherty sample was ground for X-ray powder diffraction analysis.

The samples were dissolved for chemical analyses by the "single" dissolution technique of Shapiro (1975); Si, Al, and Ti were determined by spectrophotometric methods, and Fe, Ca, Mg, Na, and K were determined by atomic absorption spectroscopy, using a Varian 975 atomic absorption apparatus. A few controls of Si and Al were run by the "double" dissolution method of Shapiro (1975). The precision of the determinations was ±2 relative %. Ferrous iron was determined by the Shapiro (1960) method, a useful procedure if the amount of available material is limited. Sr was determined by X-ray fluorescence (XRF) with an estimated precision of ±10 ppm.
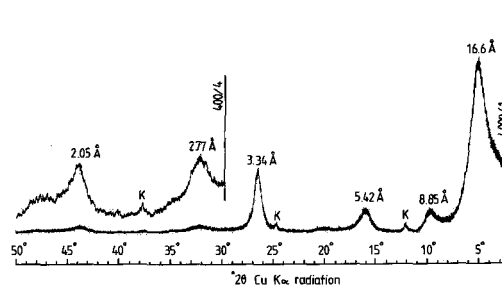
Cation-exchange capacities (CEC) were determined

Figure 1. X-ray powder diffraction curves of sample StM5 (<0.05 μm) from the lower part of the Kinnekulle B-bed, 10–15 cm from the bottom boundary; curve A = non-oriented mount of air-dried sample, curve B = ethylene glycol-saturated oriented mount (curve from 300$2\theta$ run with 10 times higher sensitivity). Cu$K\alpha$ radiation.

by saturating the sample with 0.5 M SrCl$_2$. The retained Sr was analyzed by XRF. Values of CEC are listed in Table 1. Structural formulae were calculated from the chemical analyses on the basis of O$_{10}$(OH)$_2$, using the procedure outlined by Brusewitz (1986).

X-ray powder diffraction (XRD) curves were made of oriented mounts, prepared by the peel-off technique (Drever, 1973; Brusewitz, 1982). In Figure 1 the XRD curve of an oriented mount of sample STMX5 after treatment with ethylene glycol vapor is shown. It is considered to be representative of the whole set of samples, STMX1–STMX6. The percentage of smectite layers in the I/S was determined by the method of Šrodoń (1980). Several curves were run; a few mounts were duplicated. The kaolinite peaks present in the curves were used as internal standards to obtain uniform determinations. The precise position of the peak at 44°2θ was difficult to measure; however, the data listed in Table 1 are considered to have a precision of ±5%. All samples showed random stratification (R=0) (Reynolds, 1980).

RESULTS AND DISCUSSION

The structural formulae in Table 1 of the six samples are similar. The slight variation among these formulae is probably insignificant. No marked trend of an increase of potassium towards the lower contact of the bed was noted in contrast with that found towards the upper contact (Brusewitz, 1986). A comparison of the present data with those given in the earlier paper shows some discrepancies, especially in total layer charge (−0.56 vs. an earlier mean of −0.67). One reason could be that the coarser size fraction (<1 μm) analyzed previously required greater corrections for impurities. Regarding interlayer potassium (K$_{fix}$), however, the new set of samples have values of 0.22–0.23, which match well with the K$_{fix}$ value of 0.23 found earlier for the nearest overlying sample (B39, 15 cm above).

Table 1. Chemical and mineralogical data for the <0.5-μm fraction of samples from the lower part of the B bed in a K-bentonite from Kinnekulle, Sweden.

	Sample					
	STMX1	STMX2	STMX3	STMX4	STMX5	STMX6
Depth from upper contact (cm)	125–130	130–140	140–150	150–160	165–170	175–180
	Structural formula[1]					
Tetrahedral						
Si	3.84	3.81	3.82	3.80	3.83	3.80
Al	0.16	0.19	0.18	0.20	0.17	0.20
Octahedral						
Al	1.48	1.47	1.47	1.47	1.46	1.46
Fe^{3+}	0.11	0.10	0.10	0.11	0.11	0.12
Fe^{2+}	0.04	0.05	0.05	0.04	0.04	0.04
Mg	0.39	0.41	0.41	0.40	0.41	(0.41)
Sum	2.02	2.03	2.03	2.02	2.02	(2.03)
Charge	−0.38	−0.37	−0.37	−0.38	−0.39	(−0.36)
Total layer						
Charge	−0.54	−0.56	−0.55	−0.58	−0.56	(−0.56)
Interlayer						
K_{fix}	0.22	0.22	0.22	0.23	0.23	(0.25)
M^+ = sum exchangeables	0.32	0.32	0.32	0.35	0.32	(0.33)
Charge	0.54	0.54	0.54	0.58	0.56	(0.58)
	Composition					
CEC^2 (meq/100 g)	82	81	81	88	83	n.d
K (%)[3]	2.14	2.21	2.23	2.27	2.32	2.30
Sr (ppm)[3]	211	213	234	219	226	217
K:Sr	102	104	95	104	103	106
Smectite layers in illite/smectite[4] (%)	50	52	52	50	51	52

[1] Per $O_{10}(OH_2)$.
[2] Cation-exchange capacity.
[3] Values refer to sample dried at 140°C.
[4] Percentage of smectite layers was derived from X-ray powder diffraction curves by the method of Środoń (1980). All samples showed random stratification, R=0 (Reynolds, 1980).
Prior to the calculation of structural formulae, the chemical analyses were corrected for 2% kaolinite, estimated from X-ray powder diffraction.
No cation-exchange capacity value was available for sample STMX6; exchangeable Mg was estimated in accordance with the other samples; values are given in parentheses.

In Figure 2a the percentage of illite layers in the I/S is plotted against sample depth in the B bed. The data from Brusewitz (1986) are included. The proportion of illite layers in the I/S does not increase in the lower part of the bed, in contrast with the trend reported for the Montana K-bentonites (Altaner *et al.,* 1984) and with the trend reported earlier for the upper part of the Kinnekulle B bed (Brusewitz, 1986). A plot of K:Sr ratios, considered to be a measure of I/S proportions, was given in Brusewitz (1986) for samples from the upper half of the B bed. In Figure 2b of the present paper this plot has been extended to include the lower part of the bed. The K:Sr ratios for the newly analyzed samples connect smoothly with the old curve, but show almost invariable values (102 ± 4) throughout the lower half of the bed, in contrast with the increase from about 100 to 400 noted for samples from the upper half of the bed. This plot, as well as that of the percentage of illite layers in the I/S (see Figure 2a, left)

indicate that the zonation of potassium is not symmetrical, but exists only towards the upper contact of this bed.

The XRD pattern of the sample from the lower "cherty" contact of the B bed showed chiefly quartz and small amounts of illite had chlorite. Postulating that the potassium was not available from underlying layers, a systematic decrease in the percentage of illite layers in the I/S should have been expected approaching the lower contact. As is evident from Figure 2a, however, no such decrease was found, the percentage of illite layers in the I/S remaining almost constant at about 50%.

Inoue *et al.* (1987) put forward a hypothesis for the conversion of smectite to illite from studies of the morphology and chemistry of individual particles. They noted that pure smectite (i.e., 100% expandable layers) occurred as flaky particles, but that as the amount of potassium fixation increased, lathlike particles became

more prevalent, and that both flakes and laths were present in I/S samples containing 100–50% smectite layers. They suggested that for I/S containing fewer than 50% illite layers no great structural rearrangement of the initial smectite was required, potassium being bound by ion exchange, forming some type of unstable illite layers in the I/S. Further conversion of smectite to illite causes the unstable layers to dissolve, and "stable" illite layers to form in the I/S by precipitation. The flaky particles disappear, and XRD patterns begin to show ordered stratification (Inoue *et al.,* 1987).

With regard to the Kinnekulle bentonites, homogenization probably occurred at the level of least structural rearrangement, before the next step to an ordered structure began, a reaction that probably involved a greater potassium potential and greater energy. In the upper part of the B bed, the supply of potassium was greater than in the lower part, perhaps being derived from the overlying shales and mudstones, and the second phase of the smectite-to-illite conversion could begin, as is indicated by the partial ordering of the I/S layers and the appearance of a superstructure. At this point, diagenetic activity ceased in the bentonite.

SUMMARY AND CONCLUSIONS

The results of this and the previous (Brusewitz, 1986) study indicate that potassium diffused downwards from the upper contact of the B bed and reacted with smectite in the bentonite to produce I/S. The lower half of the B bed, however, shows a constant 50% illite layers in the I/S, in contrast with the thick bed of the Montana bentonites in which the percentage of illite layers in the I/S increases towards both contacts (Altaner *et al.,* 1984). Differences in the geological settings is the most plausible reason for these disparate results: the Kinnekulle bed is flat-lying; it has a particularly siliceous (and probably impervious) layer beneath its lower contact, and it occurs in a calcareous environment having a low potassium potential as compared with the tilted nature of the Montana bed which is enclosed in shale. The presence of calcite lenses immediately above the B-bed suggest that at some time solutions did indeed circulate at this level, promoting illite crystallization in the upper part.

It is nevertheless surprising that the percentage of illite layers in the I/S is nearly constant at about 50% throughout the lower half of the B-bed, but according to Inoue *et al.* (1987), 50% illite layers is a critical composition in the conversion of smectite to illite. For I/S containing fewer than 50% illite layers, potassium fixation requires no major structural rearrangement of the smectite layers; this is a low-energy reaction. With further increase in potassium, dissolution and precipitation produced "stable" illite layers; these reactions were probably more energy-intensive. Thus, at Kinnekulle an equilibrium was probably approached with-
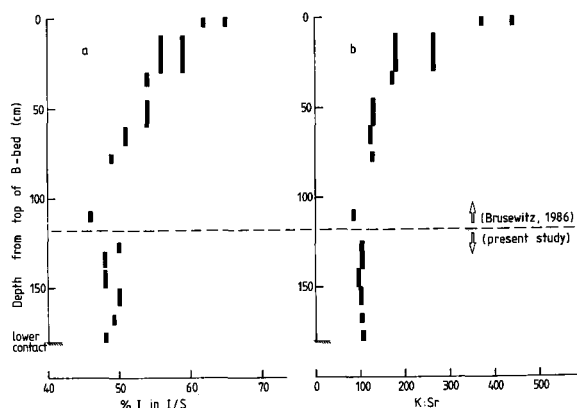

Figure 2. Plot of K:Sr and K:Rb ratios in relation to level within the Kinnekulle B-bed. Scale at left shows distance in centimeters from upper contact of the B-bed. Open bars = K:Sr ratio, solid bars = K:Rb ratio. Length of bar indicates sampling interval (point B35 corrected) (cf. Figure 3 in Brusewitz, 1986).

in the B bed initially at the lower energy level, before the next reaction step began. At the upper contact, however, where potassium must have been more available, the I/S shows a slight ordering. Before this reaction propagated very far down the bed, diagenetic activity subsided and the reaction stopped.

ACKNOWLEDGMENTS

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