

NOTE

Detailed X-ray diffraction characterization of illite-smectite from an Ordovician K-bentonite, Walker County, Georgia, USA

Outcrop samples of Ordovician K-bentonite from northeast Georgia were studied with X-ray diffraction (XRD) using different cation saturations to look for possible redistribution in layer charge. It was noted that XRD patterns of the samples responded uniquely to each cation treatment. The purpose of this note is to demonstrate a refinement to the method of Środoń (1980) for the precise identification of mixed-layer illite-smectite (I-S) and to note the importance of using several homoionic saturations in the interpretation of the XRD patterns.

Materials and methods

Samples were collected near Davis Crossroads, Walker County, Georgia, USA, from the Deicke K-bentonite bed found in the Middle Ordovician Chickamauga Group (Haynes, 1995). The initial intention was to note potential mineralogical differences due to weathering. Two samples were collected; one on a talus slope and the other ~30 cm into freshly exposed outcrop. The <2 µm fraction for each sample was extracted using a high-speed centrifuge. Six aliquots were saturated with 1 M NaCl, KCl and NH₄Cl and 0.1 M CaCl₂, MgCl₂ and BaCl₂ solutions, respectively. Oriented mounts were prepared by ultrasonically dispersing 200 mg of clay, slurried onto petrographic slides. Each slide was placed in a 65°C ethylene glycol (EG) atmosphere for 24 h.

One-dimensional XRD modelling was performed using NEWMOD[®] (Reynolds, 1985). Appropriate NEWMOD instrument-sensitive parameters were tuned to best-fit the Scintag[®] diffractometer optics (Hurst *et al.*, 1997). Sample-sensitive NEWMOD parameters held constant in the final calculations were: coherent scattering domains (N) = 2 to 10; K^+ = 0.9, Fe^{3+} = 0.2 for illite; Fe^{3+} = 0.2 for EG-saturated dioctahedral smectite. All calculations performed in the range 42–50°2θ

included the effects of $Cu-K\alpha_1$ and $Cu-K\alpha_2$ radiation by co-adding in a 2:1 ratio.

Results and discussion

As the XRD differences between the two samples under similar saturation states were negligible, the initial intention of this work was deemed inconclusive. However, the differences amongst the various cation saturations were significant. Figure 1 shows the observed diffraction data for the outcrop sample. The two reflections are the result of $R = 3$ type mixed-layering, which can be viewed as interference between the ISII superstructure or tarasovite ($d_{001} \approx 47 \text{ Å}$) and discrete illite ($d_{001} \approx 10 \text{ Å}$). The low-angle and high-angle peaks are modulations of the 0023₄₇/005₁₀ and 0024₄₇/005₁₀ reflections, respectively.

The complexities of decomposing neighbouring peaks due to $K\alpha_1$ and $K\alpha_2$ radiation necessitated a simplification of the method for measuring calculated and observed peak intensities. Modelling revealed slight negative shifts of ~0.1°2θ in the absolute positions of the peak maxima 0023₄₇/005₁₀ and 0024₄₇/005₁₀ with a 0.2 Å increase in d_{s001} . The difference in peak locations (Δ_{ds}) however, is relatively constant (1.15°2θ). The intensity ratio of the 0023₄₇/005₁₀ and 0024₄₇/005₁₀ was, therefore, measured directly from patterns at the positions of 45.00° and 46.15°2θ (herein defined as $R_{23/24}$). Given that all samples were prepared with the same thickness and run under the same experimental conditions, this assumption is reasonable.

The systematic variation in relative peak height intensity is illustrated in Fig. 2, where the triangular data points show the ratios of the calculated 0023₄₇/005₁₀ and 0024₄₇/005₁₀ peak intensities plotted vs. d_{s001} . The solid line in Fig. 2 is a linear least-squares best fit of $R_{23/24}$ vs. d_{s001} using calculated data. The equation:

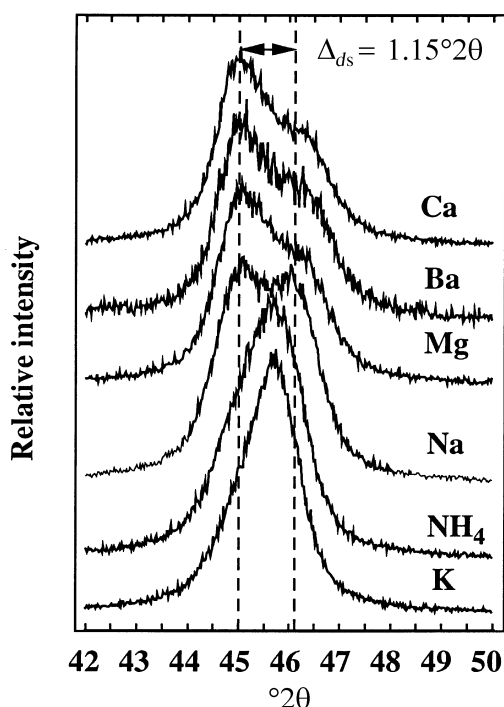


FIG. 1. X-ray diffraction patterns for the $<2 \mu\text{m}$ K-bentonite fraction, saturated with EG and various cations. The dashed lines represent the difference ($1.15^\circ 2\theta$) between the $0023_{47}/005_{10}$ and $0024_{47}/005_{10}$ peak maxima positions (Δd_s), as calculated for I-S with 87.5% illite type layers and a range of smectite thickness (d_{s001}).

$$d_{s001} (\text{\AA}) = 17.29 - 2.9 R_{23/24} \quad (1)$$

provides a means to measure the average thickness of smectite layers in I-S assuming 87.5% illite-type layers. The dashed lines show graphically the d_{s001} for each saturated sample using $R_{23/24}$ values measured from Fig. 1.

Środoń (1980) has shown the importance of variations in the EG-complex thickness on the diffraction patterns of dioctahedral smectites. Increasing thickness of the smectite complex is manifested in decreasing 2θ positions of the 003 and 005 peaks. Środoń (1980) also demonstrated with NEWMOD the relative insensitivity of the 003 and 005 peak locations to domain size effects. Our data indicate that for highly-ordered I-S (ISII), relative peak intensities of $0023_{47}/005_{10}$ and $0024_{47}/005_{10}$ reflections are also insensitive to

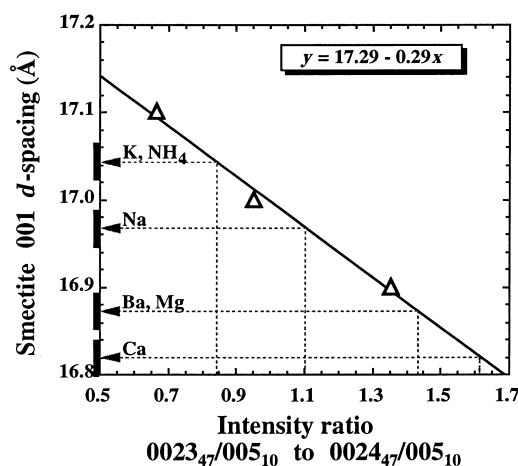


FIG. 2. Relative intensities of calculated $0023_{47}/005_{10}$ and $0024_{47}/005_{10}$ peak maxima vs. thickness of smectite (triangles). The solid line is a least-squares linear regression ($r^2 = 0.99$). The dashed lines originate from the measured $R_{23/24}$ values from the observed data and point to the expected smectite 001 d -spacing. The black bars show the range of values expected from instrumental errors.

domain size effects, if the range of coherent scattering domains includes values >8 . The relative peak intensities of $0023_{47}/005_{10}$ and $0024_{47}/005_{10}$ are, however, sensitive to d_{s001} changes.

A comparison of the observed data (Fig. 1) and calculated data assuming only variation in the thickness of the smectite d_{s001} (Fig. 3), reveals that not all of the observed response can be attributed to changing dimensions of d_{s001} . The data observed are explained better by changing the percentage of I in I-S for each cation saturation state. Figure 4 shows the 'best fit' results based on trial-and-error testing of the % of I in I-S and the dimension of d_{s001} .

Mixed-layering ranged from 87% I in I-S, with a d_{001} of 16.8 Å for the Ca, EG-saturated sample to 95% I in I-S, with a d_{001} of 17.1 Å for the K, EG-saturated sample. These results independently support the observation of Cetin & Huff (1995) that I-S in K-bentonites have heterogeneous layer-charge distributions. The difference between 87% and 95% I in I-S seen in our sample shows that about half of the smectite layers have sufficient layer charge to dehydrate the K-saturated layers, indicating that half the smectite layers are actually vermiculitic.

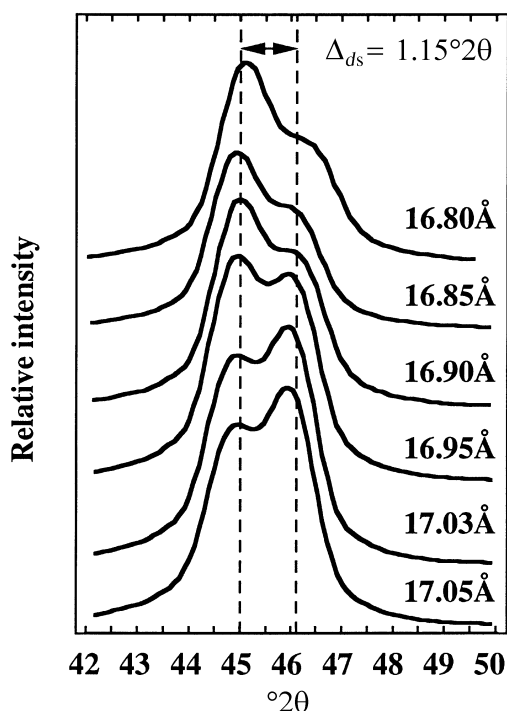


FIG. 3. Model XRD patterns showing 0023₄₇/005₁₀ and 0024₄₇/005₁₀ peak maxima positions using a constant 87.5% I in I-S and variable ds_{001} thickness to simulate best the observed relative intensities as measured by $R_{23/24}$.

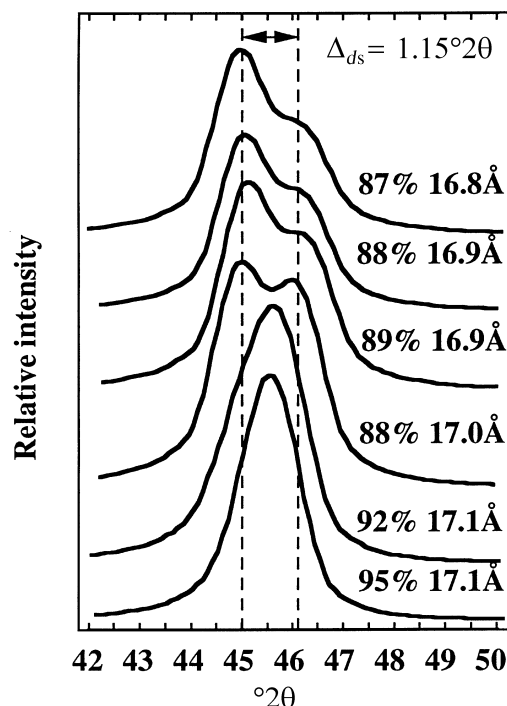


FIG. 4. Optimized model XRD patterns showing 0023₄₇/005₁₀ and 0024₄₇/005₁₀ peak positions using different percentages of I in I-S and ds_{001} thickness to simulate best the observed relative intensities.

The ds_{001} response to cation saturation state is explained by Reynolds (1965) who noted that water molecules and exchangeable cations most likely occupy spaces near the centre of the double-layer EG-complex. The Ca^{2+} - and EG-saturated smectite XRD data agree best with an arrangement of four water molecules (radius ≈ 1.4 Å) per interlayer cation. Monovalent cations Na^+ , K^+ and NH_4^+ have atomic radii of 1.02, 1.33 and 1.43 Å and the divalent cations Mg^{2+} , Ca^{2+} and Ba^{2+} have radii of 0.72, 1.00 and 1.35 Å, respectively when in 6-fold coordination with O. The size of the monovalent complex thickness can be viewed as a function of ionic radius (r) which, in turn, is related to cation coordination state and the inverse of cation charge density ($c = \sqrt{z/m}$). Figure 2 shows this for monovalent cations, with K^+ having the thickest EG-complex and Na^+ smaller. Also K^+ , NH_4^+ and Na^+ , have r/c values ≈ 8 , 6 and 5, respectively, which correlate positively with ds_{001} .

Divalent cations result in thinner EG complexes due to their greater charge density (i.e. stronger ionic forces with tetrahedral and octahedral negative layer charges). Reynolds (1965) noted the potential for stronger polarization effects of a divalent cation and hydrogen bonding, that would cause water molecules to depart from a more spherical symmetry. For Ba^{2+} , the large cation size minimizes polarization of the water molecules. The Ba^{2+} -saturated EG-complex is thicker than the Ca^{2+} -complex, however, by virtue of its larger radius. MacEwan & Wilson (1980) pointed out that the polarizing influence of cations decreases in the sequence $\text{Mg} > \text{Ca} > \text{Na} > \text{K}$. In the case of the Mg^{2+} -saturated EG-complex, the smaller radius and high charge density maximize polarization of water in the EG-complex, thus making the smectite layer slightly thicker than its Ca^{2+} counterpart. Eberl (1980) has also shown that the energy of adsorption for an ion in smectites is inversely related to its radius.

Conclusions

The XRD analysis of K-bentonite outcrop samples saturated with six different cations reveals a varied response of the smectite-EG-cation-water complex thickness and the percentage of illite in I-S. Values range from 87% I in I-S; $d_{s001} = 17.1 \text{ \AA}$ for K^+ samples to 95% I in I-S; $d_{s001} = 16.8 \text{ \AA}$ for Ca^{2+} samples. Calculated diffraction patterns using NEWMOD[®] show that the relative heights of the 0023₄₇/005₁₀ and 0024₄₇/005₁₀ reflections serve as a useful index of the d_{s001} in ISII ordered I-S. These results highlight the importance of using several homoionic cation saturations for the detailed characterization of K-bentonites.

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