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Bentonite as a Backfill Material in a High-Level Waste Repository

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Introduction

The concept for the disposal of high-level radioactive waste (HLW) in Switzerland is illustrated in Figure 1:[1] the waste, solidified in a borosilicate glass matrix, is encapsulated in a 25-cm-thick steel canister which has a minimum life expectancy of 1,000 years. After this time, the heat produced by ^{90}Sr and ^{137}Cs will have dissipated and the repository will have adjusted to the host rock ambient temperature of around 60°C.

The steel canisters will be placed in horizontal tunnels, 3.7 m in diameter, at a depth of around 1,000 m in the granite of northern Switzerland, and the tunnels then backfilled. The backfill material, an important link in the chain of engineered and natural safety barriers, satisfies both physical/mechanical and chemical requirements. The most important of these are:

- Low hydraulic conductivity compared to the host rock;
- Good swelling properties to seal construction-caused joints and rock fractures;
- Plasticity to absorb rock movements and to distribute pressure homogeneously;
- Good retention of radionuclides; and
- Stability over a period of at least 10^6 years.

Economic aspects and availability should also be considered: each canister requires 8 tons of backfill material, or of the order of 250,000 metric tons for the planned repository.

Natural bentonites mostly fulfill this set of requirements.[2,3] Named after their discovery locale at Fort Benton, Wyoming, bentonites are weathering products of volcanic ash. Their essential component is the clay mineral, montmorillonite, present in proportions of 65–99%. Depending on the composition of the volcanic starting material, bentonites also contain various proportions of quartz, mica, and feldspars as inert components.[4]

Structure of Three-Layer Silicates

Montmorillonite—along with illite which is also of interest here—belongs to the multifold group of three-layer silicates.[5] The structural elements of these minerals are SiO_4 tetrahedra [T] and MO_6 octahedra (O), where the metal cation M is usually Al or Mg. Pyrophyllite can be regarded as the structural prototype (Figure 2),

$$[Si_4](Al_2)O_{10}(OH)_2, \quad (1)$$

constructed from the T-O-T composite layers, which have a thickness of 1 nm. Montmorillonite varies from this structure with the isomorphic substitution of magnesium(II) for aluminum(III) in the octahedral layer. This results in a negative charge on the composite layers which is compensated for by the presence of interlayer alkali- or alkaline-earth cations. The ideal composition of sodium montmorillonite is:

$$Na_{0.33}[Si_4](Al_{1.67}Mg_{0.33})O_{10}(OH)_2. \quad (2)$$

Illite is similarly constructed except that the layer charge arises from the exchange of aluminum(III) for silicon(IV) in the tetrahedral layers and the interlayer sites contain potassium cations. The ideal composition is:

$$K_{0.67}[Si_{3.33}Al_{0.67}](Al_2)O_{10}(OH)_2. \quad (3)$$

The most important properties of the three-layer silicates—swelling capacity, plasticity, low permeability, and absorption behavior—are closely related to the structure, layer charge, and type of interlayer cation. Microcrystallinity is also important; the platelet diameter is less than 2 μm.

Swelling of the Three-Layer Silicates

The cohesion of the three-layer silicates is due to the electrostatic attraction between the charged layers and the interlayer cations. In addition to charge density, charge separation is also important because of the substitution in the octahedral layer; this is larger in montmorillonite than in illite, where the substitution takes place in the tetrahedral layer (Figure 2).

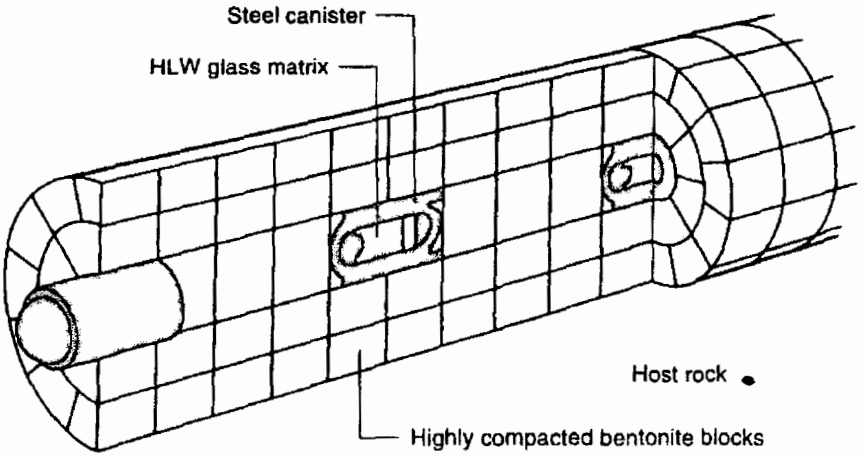

Figure 1. Sectional drawing of a disposal tunnel (diameter: 3.7 m) with emplaced high-level radioactive waste and the system of technical safety barriers. Courtesy of Nagra.

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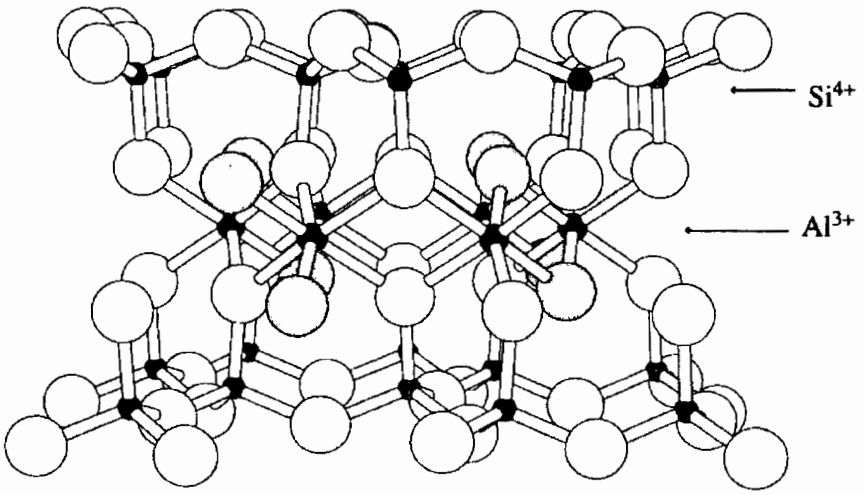

Figure 2. The structure of pyrophyllite with silicon in tetrahedral, and aluminum in octahedral coordination. Open circles, oxygen; shaded circles, OH-groups.

In water-free clay, the interlayer cations are coordinated by the Si-O surface. With water ingress, the Si-O surface, especially the interlayer cations, are hydrated. The larger the hydration energy of the interlayer cations, which increases at constant ionic charge with decreasing ionic radius, the greater the degree of hydration. The relative influence of these two coordination states determines the water absorption capacity of the clay. Qualitatively, it is understandable that a sodium-montmorillonite (small charge density, large charge separation, and large heat of hydration: -406 kJ mol^{-1}) swells on water absorption, whereas potassium-illite (high charge density, smaller charge separation, and small heat of hydration: -320 kJ mol^{-1}) does not. These relationships in the numerous clays with different interlayer cations have been thoroughly investigated (e.g., see References 2, 6, and 7).

The swelling of montmorillonite takes place stepwise: absorption of the first water layer, up to a water content of 10%, causes a 0.25 nm increase in the layer spacing. The interlayer cations are partly coordinated by the water, partly by the Si-O surface.[8] With uptake of a second water layer, the spacing increases 0.5 nm and the interlayer cations are now fully octahedrally coordinated by water. The second layer is complete with a water content of around 20%.[9] Further water absorption causes a maximum increase in the layer spacing of 1 nm in calcium-montmorillonite, whereas sodium-montmorillonite can completely disperse as elementary layers.

If montmorillonite swelling occurs in a restricted volume, water uptake generates a swelling pressure which, depending on the density of the material used, can reach several hundred bars and, thus, the range of lithostatic pressure in the repository. Experimental determination of the swelling pressure of Wyoming bentonite MX-80, for water contents in the range 10–30%, gives the empirical relationship,

$$\log p\,(\text{bar}) = 3.61 - 0.077\,w, \qquad (4)$$

where w is the percentage water content.[10] Thermodynamic considerations show that the swelling pressure can, in principle, also be derived from the water vapor adsorption isotherm of the clay;[11] agreement with the experimental values is satisfactory.

Cation Adsorption on Bentonite

An important property of bentonite for repository safety is its capacity to adsorb cations. This happens by two different mechanisms: ion exchange, and the binding of cations on the edge OH-groups. A distinction between the adsorption mechanisms is essential for predicting nuclide behavior since cation binding on the OH-groups is little influenced by water salinity, while adsorption by ion exchange decreases with increasing water salinity.

Cation Exchange

The hydrated interlayer cations in montmorillonite are exchangeable with other cations (mainly alkali- or alkaline-earth cations):

$$z\,NaX + M^{z+} \leftrightarrow MX_z + zNa^+, \qquad (5)$$

where X^- represents a fixed charge on the montmorillonite framework. Basically such equilibria can be treated quantitatively with mass action laws,[2] although that is outside the scope of this article. The expression shows qualitatively that the adsorption of M^{z+} from solution depends on the sodium concentration and hence on the water salinity. So, the partition coefficient of strontium in sodium-montmorillonite, for example, decreases from 0.9 to 2×10^{-3} m^3/kg if the sodium concentration is increased from 0.03 to 1 mol/l.[12] The partition coefficient is given by

$$K_d = \frac{Sr^{2+}\text{ in solid, mol/kg}}{Sr^{2+}\text{ in the solution, mol/m}^3} \qquad (6)$$

Although cation exchange plays only a secondary role in the retardation of radionuclides in the backfill, exchange of the interlayer cations for potassium is important for the long-term stability of montmorillonite, as shown in the next section.[3]

The Adsorption on Structural OH-Groups

The dependence of cation adsorption on solution salinity but not on solution pH is a consequence of the ion exchange model. However, investigations of heavy metal adsorption on three-layer silicates have shown a marked pH dependence but only a secondary influence from salinity. This behavior can be explained by reaction of the cation with the structural OH-groups (>SOH, where > represents the montmorillonite network and S is the surface) and the "broken bonds" on the crystal edges (Figure 2):

$$>SOH + M^{2+} \leftrightarrow >SOM^+ + H^+. \qquad (7)$$

This reaction type has been thoroughly investigated on fine-grained oxides and hydroxides. It was found that the equilibrium constant for adsorption is correlated with the hydrolysis constant of the homogeneous reaction

$$H_2O + M^{2+} \leftrightarrow MOH^+ + H^+. \qquad (8)$$

As hydrolysis constants are cataloged, predictions about the adsorption behavior of different cations are possible.

The surface complexation models subsequently developed for these materials have been well confirmed[13,14] and can be applied to real systems.[15] In comparison, the formation of surface complexes on the edges of sheet silicates has until now been investigated only patchily,[16] leaving a crucial gap.

At the Paul Scherrer Institute, progress

is being made on surface complexation. As an example, Figure 3 shows the pH dependence of nickel adsorption on sodium-montmorillonite.[17] At pH 5, the adsorption occurs by ion exchange while, at higher pH values, adsorption by surface complexation increasingly dominates. This drastically increases the partition coefficient in the pH range of natural waters and shows that, for the adsorption of heavy metals, ion exchange is of only secondary importance. Based on existing concepts, a model for heavy metal adsorption of montmorillonite has been developed and is currently being tested with other cations.

Bentonite as a Transport Barrier

The compacted and swollen bentonite has an extraordinarily low hydraulic conductivity, of the order of 10^{-13} to 10^{-14} m/s.[18] This means that the backfill is practically impermeable to water flow and that nuclide transport occurs only by diffusion. The diffusion coefficients (D_p) of nonsorbing nuclides in the porewater of compacted bentonite are around 2×10^{-10} m²/s. Because of adsorption on the bentonite, the rate of diffusion of most nuclides is further reduced and their effective diffusion coefficient is $D_a = D_p/R$, where R is the retardation factor. Then,

$$R = 1 + \rho_b K_d \frac{1}{\varepsilon} \qquad (9)$$

where ρ_b is the bulk density of the bentonite and ε is the porosity. The agreement between calculated and directly determined apparent diffusion coefficients is satisfactory for most cations; however, some differences were observed, most importantly for cesium and strontium.

Experimental values for the apparent diffusion coefficients for a number of weakly sorbing nuclides were measured in the range 10^{-11} to 10^{-12} m²/s. For technetium(IV), americium, and the tetravalent actinides, $D_a \leq 10^{-14}$ m²/s.[19,20] Using the approximation $t_b = 0.1 \times x^2/D_a$ and a diffusion distance x of 1 m, the breakthrough time is estimated to be more than 300,000 years. This means that the nuclides ^{243}Am ($t_{1/2}$ = 7,370 years), ^{240}Pu ($t_{1/2}$ = 6,550 years), and ^{239}Pu ($t_{1/2}$ = 24,110 years) decay within the backfill in an undisturbed repository (after 10 half-lives the radioactivity has fallen to 0.1% of the initial level).

For the retardation of technetium, neptunium, and plutonium, it is important that these elements remain in the tetravalent state. The reducing conditions essential to ensure this are provided by the corrosion products of the steel canisters. Earlier suggestions to include iron(II) minerals in the backfill[21] are consequently obsolete.

Anions are not adsorbed on montmorillonite, so it has been suggested that charcoal or heavy metal sulfides[21,22] be added to the bentonite to retard especially iodide. Because ^{129}I has a half-life of 1.6×10^7 years, however, only with an unrealistically high K_d could it decay within the backfill. Custom-made additions for the retardation of a particular radionuclide are today rarely considered.

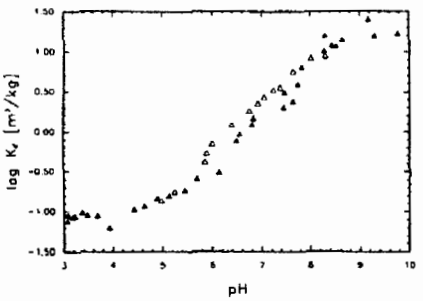

Figure 3. The sorption of nickel on montmorillonite as a function of pH ($[Ni]_{tot} = 2 \times 10^{-8}$ M, 1.5 g clay per liter). At pH below 5, sorption is controlled by ion exchange. The sorption on structural OH-groups and on "broken bonds" dominates at higher pH values.[17]

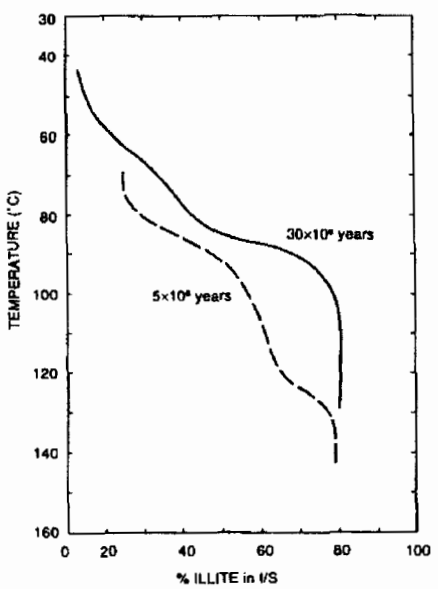

Figure 4. The proportion of illite in illite/smectite (I/S) interstratifications in bore cores from argillaceous sediments of different geologic age, Gulf of Mexico. Simplified from Reference 31.

The Stability of Bentonite

Because the barrier effect of the repository backfill is required to last for a long period, the diagenetic changes to montmorillonite during this time must be considered. Of the various possible reactions,[23] the most prominent is the transformation to illite. Such a reaction would impair the swelling capacity (and thus the hydraulic conductivity) and the ion exchange capacity of the backfill. For the formation of illite from montmorillonite, two requirements must be fulfilled simultaneously: the tetrahedral layer charge must increase to values greater than 0.6 per $O_{10}(OH)_2$-unit, and the interlayer cations must be replaced by potassium. In nature, the transformation of montmorillonite to illite proceeds through intermediate stages of mixed illite and montmorillonite layers. Increase in the layer charge alone does not reduce the swelling capacity, which is lost only if the interlayer cations are replaced by potassium.

For the hypothetical case where ingress of potassium into the repository controls illite formation, the transformation rate can be estimated: the cation exchange capacity of the bentonite is 0.76 mol/kg, so for an assumed water exchange rate of 1 l per canister per year and a potassium concentration in solution of 1 mmol/l, the full alteration of the montmorillonite in the repository layout shown in Figure 1 would require about 7×10^7 years.

If, on the other hand, it is assumed that the increase in the layer charge is the controlling factor, then kinetic data for the transformation of montmorillonite to illite are required. This reaction, occurring at a low water supply, forms approximately two illite layers and some silicic acid from three montmorillonite layers. The process takes place extremely slowly, so its kinetics can be investigated only in the laboratory under hydrothermal conditions ($T \geq$ 250°C). Eberl and Hower[24] have determined the activation energy for the conversion of a potassium-saturated clay to illite (82 ± 14.5 kJ/mol). Extrapolated to the repository temperature, this value leads to a life expectancy for the montmorillonite of about 10^6 years. Such extrapolations are problematic not only because of the uncertainty in the activation energy but also because the mechanism of the transformation is complex[2,3,25] and depends on numerous factors, particularly the clay-to-water ratio and the interlayer cation.[26] So, the results of the hydrother-

mal experiments should not be applied blindly to the situation in a repository.

Essential supporting evidence for the prediction of long-term stability comes from investigations of natural analogs which, in the form of clay sediments, are widely available.[27–29] For example, the clays of the Gulf of Mexico have been studied extensively because of their association with petroleum occurrences in the area. These sediments were deposited continuously over the course of 10^8 years. In a number of papers, the proportion of swelling clays in drill cores has been investigated (e.g., see References 30 and 31). Even in old sediments, significant illitization only appears at temperatures above 80°C (Figure 4) and, independent of the geological age, the maximum proportion of illite occurring is 80%. According to other authors,[32] illitization begins at a temperature in the range 60 to 90°C, while transformation to 70–80% illite occurs at temperatures of 90 to 140°C.

The interpretation of the numerous investigations of natural analogs leads to the conclusion that, for a repository temperature of 60°C, no drastic changes to the swelling, hydraulic conductivity, or cation exchange capacity are expected over more than 10^6 years. The formation of illite/montmorillonite interstratifications over the course of time is, of course, not discounted, only full-scale illitization. Calcium-montmorillonite behaves more favorably than the sodium form because it is less easily transformed to illite. This is demonstrated by hydrothermal experiments as well as by natural sediments.[2,3,25]

For assessing the long-term stability of the backfill, possible reactions between montmorillonite and the corrosion products from the steel overpacks (2 m^3 magnetite) must also be taken into account. For a basic assessment, however, thermodynamic data and suitable natural analogs are not available. So, possible reactions can only be assessed on chemical and crystal-chemical grounds.[3] Most probable is the formation of the iron-bearing clay minerals such as chamosite, greenalite, and nontronite. With the given amounts of steel and montmorillonite in the repository, complete reaction of the magnetite could convert 5–20% of the montmorillonite. The possible reaction products are only partly swelling, but the newly formed clay minerals would be microcrystalline; consequently, the sorption capacity of the backfill would not be greatly diminished. Besides, as with illitization, a very slow reaction can be expected.

Concluding Remarks

Natural bentonite offers a nearly ideal backfill material for a high-level radioactive waste (HLW) repository in deep-lying rocks. Through its swelling capacity, it prevents convective water movement through repository tunnels; due to good sorption characteristics, the diffusive transport of most radionuclides would be effectively retarded.

The occurrence of old bentonites in nature is an indication of their long-term stability. Numerous investigations in natural clays as well as laboratory findings can therefore be used to support the assessment of their stability. Though the extensive clay mineral literature is not always consistent, support from natural analogs is an important factor.

For safety considerations, illitization of montmorillonite is frequently identified as a worst-case scenario. But this concern overlooks the fact that illites also have favorable properties and were proposed in place of montmorillonite as repository backfill material,[22] particularly since they swell to a certain extent.[10] After the transformation of montmorillonite to illite, the hydraulic conductivity of the backfill would increase to a value of perhaps 10^{-11} m/s[18] and the cation exchange capacity would fall to 10–20% of the original value. For the adsorption of heavy metals, however, the important concentration of edge OH-groups is maintained. So it appears that, although the (improbable) complete illitization of montmorillonite would degrade the properties of the repository backfill, an acceptable barrier effect would still be ensured.

Acknowledgments

I am indebted to Fiona Neall (PSI) for her excellent translation of the German text and to Wolfgang Hummel (PSI), who designed the model of the pyrophyllite structure.

References

1. *Kristallin I: Safety Assessment Report*, Nagra Technical Report NTB 93-22E (Nagra, Wettingen, 1994).
2. R. Grauer, *Bentonite as a Backfill Material in the High-Level Waste Repository: Chemical Aspects*, Nagra Technical Report NTB 86-12E (Nagra, Baden, 1986).
3. R. Grauer, *The Chemical Behaviour of Montmorillonite in a Repository Backfill: Selected Aspects*, Nagra Technical Report NTB 88-24E (Nagra, Baden, 1988).
4. R.E. Grim and N. Güven, *Bentonites. Geology, Mineralogy and Uses* (Elsevier Science, New York, 1978).
5. R.E. Grim, *Clay Mineralogy*, 2nd ed. (McGraw-Hill, New York, 1968).
6. P.L. Hall and D.M. Astill, *Clays and Clay Minerals* 37 (1989) p. 355.
7. P.G. Slade and J.P. Quirk, *J. Coll. Interface Sci.* 144 (1991) p. 18.
8. G. Sposito and R. Prost, *Chem. Rev.* 82 (1982) p. 553.
9. F. Kraehenbuehl, H.F. Stoeckli, F. Brunner, G. Kahr, and M. Müller-Vonmoos, *Clay Minerals* 22 (1987) p. 1.
10. F. Bucher and U. Spiegel, *Quelldruck von hochverdichteten Bentoniten*, Nagra Technical Report NTB 84-18 (Nagra, Baden, 1984).
11. G. Kahr, F. Kraehenbuehl, H.F. Stoeckli, and M. Müller-Vonmoos, *Clay Minerals* 24 (1990) p. 499.
12. S-Y. Shiao, P. Rafferty, R.E. Meyer, and W.J. Rogers, in *Radioactive Waste in Geologic Storage*, edited by S. Fried (Am. Chem. Soc. Symp. Ser. 100, Washington, DC, 1979) p. 297.
13. P.W. Schindler and W. Stumm, in *Aquatic Surface Chemistry*, edited by W. Stumm (Wiley & Sons, New York, 1987) p. 83.
14. J.A. Davis and D.B. Kent, in *Mineral-Water Interface Geochemistry*, edited by M.F. Hochella and A.F. White (Mineralogical Society of America, Washington, DC, 1990) p. 177.
15. Y-H. Li, *Geochim. Cosmochim. Acta* 55 (1991) p. 3223.
16. R. Grauer, *Zur Chemie von Kolloiden. Verfügbare Sorptionsmodelle und zur Frage der Kolloidhaftung*, PSI-Bericht Nr. 65 (Paul Scherrer Institute, Villigen, 1990).
17. M. Bradbury, Paul Scherrer Institute, unpublished results.
18. R. Pusch, *Clay Minerals* 27 (1992) p. 353.
19. B. Torstenfelt, *Radiochim. Acta* 39 (1986) p. 105.
20. F. Brandberg and K. Skagius, *Porosity, Sorption and Diffusivity Data Compiled for the SKB 91 Study* (Swedish Nuclear Fuel and Waste Management Co., Stockholm, 1991).
21. G.W. Beall and B. Allard, *Nucl. Technol.* 59 (1982) p. 405.
22. D.G. Brookins, *Geochemical Aspects of Radioactive Waste Disposal* (Springer-Verlag, New York, 1984) p. 278.
23. D. Eberl, *Clays and Clay Minerals* 26 (1978) p. 327.
24. D. Eberl and J. Hower, *Geol. Soc. Am. Bull.* 87 (1976) p. 1326.
25. N. Güven, *Eng. Geol.* 28 (1990) p. 233.
26. D. Eberl, *Geochim. Cosmochim. Acta* 42 (1978) p. 1.
27. A.M. Brusewitz, *Clays and Clay Minerals* 34 (1986) p. 442; 36 (1988) p. 349.
28. R. Pusch and O. Karnland, *Geologic Evidence of Smectite Longevity. The Sardinian and Gotland Cases*, SKB Technical Report 88-26 (Swedish Nuclear Fuel and Waste Management Co., Stockholm, 1988).
29. B. Velde, *Clay Minerals* (Elsevier Science, New York, 1985).
30. J. Hower, E.V. Eslinger, M.E. Hower, and E.A. Perry, *Geol. Soc. Am. Bull.* 87 (1976) p. 725.
31. S.M. Couto Anjos, *Clays and Clay Minerals* 34 (1986) p. 424.
32. R.L. Freed and D.R. Peacor, *Clay Minerals* 24 (1989) p. 171. □