

SAPONITE AND VERMICULITE IN AMYGDALES OF THE GRANBY BASALTIC TUFF, CONNECTICUT VALLEY

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Abstract—Clay of apparent hydrothermal origin that fills amygdales in the Granby Basaltic Tuff (Lower Jurassic) of the Connecticut Valley was analyzed and found to consist of two exceptionally well-crystallized Fe-rich, trioctahedral 2:1 layer expandable phyllosilicates. Based on chemical and XRD analyses, the minerals were tentatively identified as saponite and vermiculite. The saponite exists predominately in the two-water hydration state, but also displays one- and three-water layer hydration states, which suggests heterogeneous layer charge distribution—a phenomenon not uncommon in smectites. The identity of the second clay remains equivocal, but XRD analyses, especially with regard to the swelling properties of the clay, indicate that it is a vermiculite. The well-crystallized nature of the Granby clay and the large size of the clay flakes (up to 1 mm) allowed us to use SEM/EDS X-ray imaging and spot analysis techniques in an attempt to detect chemical differences between the saponite and vermiculite. Results showed that the chemistry of individual crystals, within and among amygdales, was essentially uniform. This suggests that the saponite and vermiculite are chemically similar and that variations in their swelling properties result from other factors, such as crystal size, layer charge density, or charge localization within the unit layers. Crystal size differences in the Granby clay were observed with both the petrographic and scanning electron microscope. Changes in layer charge density or charge localization within unit layers could have been affected by the oxidation of Fe²⁺ to Fe³⁺, a transformation inferred from the green-to-brown color changes observed in the larger amygdales. The Granby clay is of special importance, because it is one of the few examples of a naturally occurring mixture of two well-crystallized, Fe-rich trioctahedral 2:1 layer expandable phyllosilicates with crystallochemical and swelling properties that appear to bridge the operational definitions for the smectite and vermiculite groups.

Key Words—Amygdales, Basalt, Fe-rich smectite, Saponite, Saponite-vermiculite intermediate, Smectite, Vermiculite.

INTRODUCTION

A zone of vesicular basalt in the Granby Basaltic Tuff (Lower Jurassic) of the Connecticut Valley contains amygdales filled with calcite and a dark-brown clay, the identity of which was unknown. Samples of the vesicular basalt were collected and the clay material was isolated, analyzed and found to consist of Fe-rich, trioctahedral 2:1 layer expandable clays displaying some unique properties with regard to ferrous-to-ferric iron ratios, layer charge, hydration states, crystallite size (or mean defect-free distance), and X-ray diffraction behavior.

The occurrence of Fe-rich smectite as an alteration product in basalts and other basic igneous rocks has been reported several times before (see the excellent comprehensive review given by Güven, 1988), but rarely has smectite been reported to occur in intimate association with vermiculite. For some reported occurrences of Fe-rich smectite it was difficult to determine with certainty the chemical composition and mineralogical properties of the clay because of the presence of impurities, such as oxide and other clay minerals (e.g., Kohyama *et al.*, 1973; Kodama *et al.*, 1988). Also, it has been suggested by a number of investigators

(e.g., Malla and Douglas, 1987; Suquet and Pezerat, 1988) that the distinction between a high-charge smectite and a low-charge vermiculite based on criteria such as total layer charge ($0.5 < \times \leq 0.6$), swelling properties, hydration states with various cations, and layer stacking, is quite arbitrary when, in fact, studies have indicated that there is no clear crystallochemical distinction between the two minerals. After compiling and summarizing available evidence on the properties of vermiculite and high-charge smectite, de la Calle and Suquet (1988) suggested that the two clays “should belong to a single family” considering that chemical and structural similarities seemed to outweigh any differences. As we report in this paper, the apparent intimate physical association of the two minerals within individual amygdales of the Granby Basaltic Tuff, and the mineralogical and chemical analyses obtained seem to offer further evidence in support of this idea.

MATERIALS AND METHODS

The Granby Basaltic Tuff, consisting of basalt flows, dikes, sills, and volcanic plugs, and well-bedded, gray-to-brown pyroclastic units is well exposed in the northern part of the Hartford Basin where the Connecticut

River passes through the Holyoke Range. Tuff deposits grade into and are interbedded with the underlying East Berlin Formation and are also intimately associated with the overlying Hampden Basalt flow. Samples of vesicular basalt were collected from an outcrop of the Granby Basaltic Tuff exposed at a scenic rest area in Massachusetts on Interstate 91 (southbound lane) at about 42°14'30"N and 72°38'00"W. Vesicles in the basalt, ranging in diameter from a few millimeters to about a centimeter across, were mostly round to elliptical indicating that some flow deformation of the gas-filled cavities occurred during extrusion of the basalt. Approximately 30–40% of the vesicles in the basalt sampled for this study were empty, 50–60% of the vesicles were filled with clay, and less than 10% of the vesicles contained crystals of calcite. About 4 g of the brown clay was removed from amygdalae using an assortment of dental picks and microspatulas.

One split of the clay was prepared for X-ray diffraction (XRD) analysis following the general techniques given by Brown and Brindley (1980) and Moore and Reynolds (1989). Both random and oriented powder mounts were prepared and analyzed with a Diano XRD-8000 diffractometer using Ni-filtered, $\text{CuK}\alpha$ radiation. For the oriented mounts, XRD patterns were obtained for the clay material treated as follows: (1) air-dried, (2) ethylene glycol solvated, and (3) Mg-saturated and glycerol solvated. In addition, oriented mounts of Ca-, Mg-, Na-, Li-, and K-saturated clay were prepared and analyzed after each was sequentially air-dried, heated to 90°C, and ethylene glycol solvated. The K-saturated clay was heated further to 300°C. Patterns were run at a scanning rate of 0.8° or 1.6°/min with the X-ray tube voltage and amperage adjusted accordingly for maximum intensity.

Chemical analyses of the bulk rock and a split of the clay material were obtained with a Diano XRF-8560 vacuum-path X-ray spectrometer. The samples were prepared using a modified version of the Norrish and Hutton (1969) method, which involves fusion of sample powder with lithium tetraborate to produce a silicate glass disc. Calibration curves for the major elements were prepared by multiple linear regression and matrix correction techniques using 40 rock, mineral and synthetic standards.

Small splits of the clay material (0.5 g each) were used to determine the amount of Fe^{2+} (ferrous iron) present following the $\text{HF-H}_2\text{SO}_4$ dissolution, dichromate titration method given by Shapiro (1975), and the cation exchange capacity (CEC) following the neutral salt-exchange method of Jackson (1974) and using a Perkin-Elmer model 3030B atomic absorption spectrophotometer.

Specimens for scanning electron microscopy (SEM) were mounted as chips on aluminum stubs or prepared as polished thin sections, then carbon- or gold-coated. A Cambridge SEM-5200 scanning electron microscope

fitted with a Tracor Northern energy dispersive X-ray analysis (EDS) system was used to determine the morphology and chemical characteristics of both the basalt and the clay material. Both secondary electron and Z-contrast, back-scattered electron imaging were employed, as well as quantification and Bence-Albee matrix correction programs for chemical analyses of the major elements in oxide weight percents.

Modeling of diffraction patterns was accomplished using NEWMOD, a computer program developed for the calculation of one-dimensional X-ray diffraction patterns for clay minerals (Reynolds, 1985; Moore and Reynolds, 1989).

RESULTS

Morphology and occurrence

At the outcrop, in hand specimen and on freshly broken surfaces of the basalt, the color of the clay is dark-brown to black. This is unlike the clay that coats and fills amygdalae in rhyolitic tuffs and basaltic pyroclastic rocks of Japan, for example, which is usually dark- to blue-green in color when freshly exposed, changing to black or gray in less than an hour, and then to brown in a few weeks (Kohyama *et al.*, 1973; Sudo and Shimoda, 1978). In rock chips viewed under a binocular microscope the clay appears dark-brown, but at the thin edges of clay-flakes the mineral takes on a golden- or honey-brown color. In amygdalae—especially in the larger amygdalae—inspected in thin section under plane polarized light, however, the clay sometimes displays two distinct colors with pale- to pistachio-green in the center and honey-brown near the outer edges of the cavity.

The clay filling the vesicles in the basalt displays a radiating texture with well-developed laths or flakes that may extend unbroken from the center of the cavity to its edge (Figures 1a, 1b). In some instances a narrow zone of clay comprised of substantially smaller-sized crystals lines the interior rim of the amygdale (Figure 1c). The contact between the clay and the surrounding basalt appears relatively sharp and unaltered. Figure 1d shows one of the few vesicles observed in thin section that was filled (partially) with calcite.

Mineralogy

Mineralogy of the basalt. The mineralogy of the host basalt was determined by XRD powder analysis, and by inspection of thin sections with the petrographic and scanning electron microscope. Major minerals present are plagioclase feldspar and pyroxene; minor amounts of ilmenite and sphene and a trace of olivine were also identified. Albite is the dominant feldspar in the basalt, but more abundant is an altered (sericitic) plagioclase with an average grain composition (expressed as a feldspar formula) of $\text{K}_{.17}\text{Ca}_{.06}\text{Na}_{.69}(\text{Al}_{1.28}\text{Si}_{2.76})_{4.04}\text{O}_8$ (plus trace amounts of Fe and Mg).

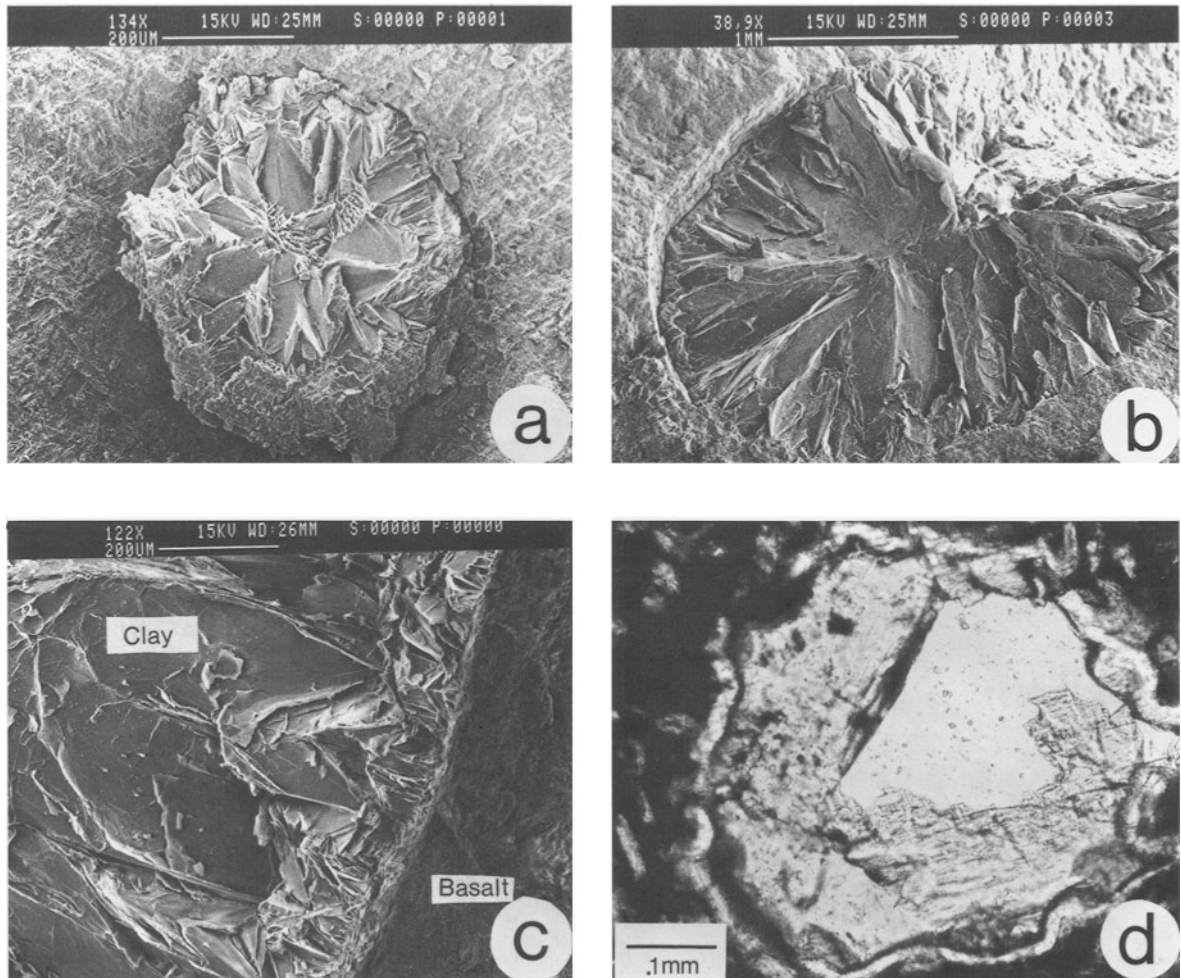


Figure 1. Photomicrographs showing clay- and calcite-filled amygdales in the Granby Basaltic Tuff: a) scanning electron micrograph showing the radial morphology of the clay laths and plates; b) scanning electron micrograph of a deformed amygdale filled with clay; c) higher magnification of (b) showing smaller crystal sizes at the rim of the amygdale; d) photomicrograph of an amygdale in thin section partially filled with calcite.

The pyroxene is an augite with an average composition of $(\text{Ca}_{.72}\text{Mg}_{.76}\text{Fe}_{.36}\text{Al}_{.06}\text{Ti}_{.02}\text{Na}_{.08})_{2.0}\text{Si}_2\text{O}_6$. The surface of the basalt weathers to a brown to buff-tan color in outcrop, and fracture surfaces exposed by a hammer blow are occasionally thinly coated with what appear to be dark- to reddish-brown precipitates of Fe oxides or hydroxides. Freshly-broken basalt is fine-grained, dense, and dark gray in color. Overall, observations with the petrographic microscope, especially the altered nature of the plagioclase and the habit and mode of occurrence of the clay crystals, suggest a hydrothermal origin for the clay material.

Mineralogy of the Granby clay. Figure 2 shows the results of the three standard XRD analyses of the clay mineral found filling the amygdales. The diffractogram of the air-dried sample (RH = 58%) shows an intense 001 reflection at about 14.8 Å, and higher order (00 l) reflections at 7.46 (002), 4.98 (003), 3.74 (004) and 3.0

Å (005). Upon glycol solvation of this same sample, the 001 reflection shifted to about 17.0 Å with weaker higher order reflections appearing at approximately 8.4 (002), 5.5 (003), and 3.3 Å (005). Mg-saturation + glycerol solvation of the sample produced an intense $d(001)$ at about 17.8 Å and a series of weaker rational order (00 l) reflections.

The series of diffractograms shown in Figure 2 indicates that the mineral is a relatively pure 2:1 layer expandable clay mineral, probably a smectite. A small, broad shoulder on the high-angle side of the 001 reflection at approximately 14 Å for the ethylene glycol- and glycerol-solvated samples suggests the presence of minor amounts of a nonexpandable phase, perhaps vermiculite. A small, but rather sharp reflection on the low angle side of the 001 reflection at about 16.3 Å for the air-dried sample, and again occurring (but barely discernible) at about 18 Å for the ethylene glycol-solvated sample, may result from heterogeneity in the

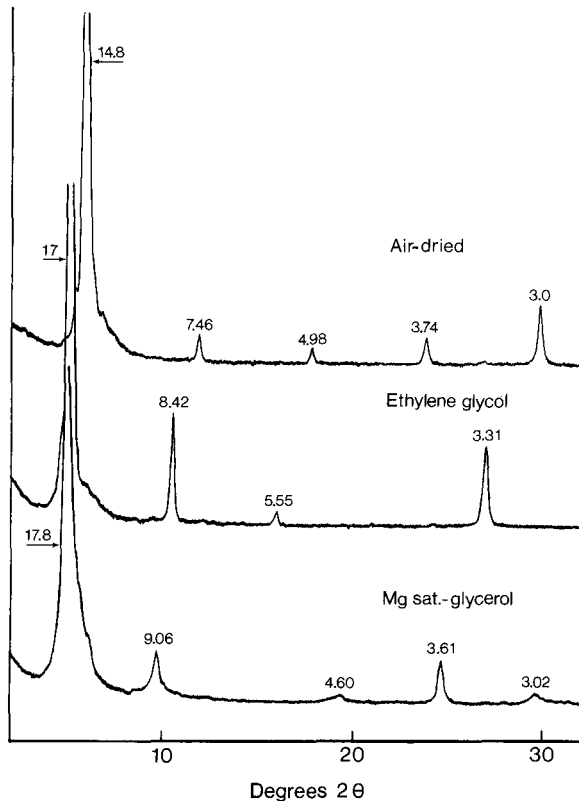


Figure 2. X-ray diffraction tracings of the air-dried (RH = 58%), ethylene glycol-solvated, and Mg-saturated, glycerol-solvated Granby clay. CuK α radiation. *d*-spacings in Ångströms.

swelling characteristics of this clay—a topic to be discussed later.

The intensity ratio of the 002 to the 003 reflections in the diffractogram of the ethylene glycol-solvated sample suggests that a substantial amount of Fe is present in octahedral sites, as might be expected for a nontronite (Moore and Reynolds, 1989). X-ray diffraction analysis of a randomly oriented powder mount, however, gave an 060 reflection at 1.538 Å and a calculated unit cell *b*-dimension of 9.23 Å, values more typical of a trioctahedral smectite (Brindley and Brown, 1980). Overall, the initial XRD analytical results suggest that the clay material is composed predominantly of an Fe-rich, trioctahedral smectite.

Chemistry

The chemistry of the clay material was obtained using several different methods. First, a split of the clay (0.5000 g) was analyzed by XRF for total oxide weight percentages of ten major elements. Second, the chemical homogeneity of the clay flakes was assessed using EDS X-ray mapping techniques on the amygdales, and spot-mode quantitative analysis on points within single clay flakes. H₂O⁻ and H₂O⁺ were determined by heating a separate split of the clay sample to 110°C and then

Table 1. X-ray fluorescence (XRF) and energy dispersive X-ray (EDS) analyses of the Granby clay and basalt.¹

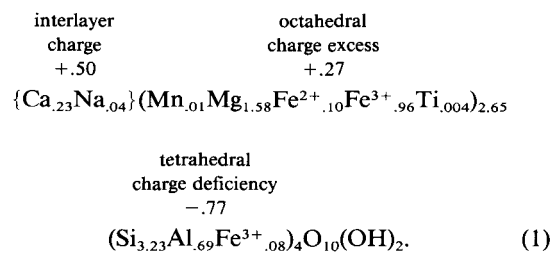
	XRF	EDS (mean) (n = 11)	Std. Dev. (EDS)	Range (EDS)	Basalt (XRF)
Na ₂ O	0.27	0.80	0.42	0.24–1.51	4.60
MgO	15.98	14.87	0.78	13.83–16.18	4.86
Al ₂ O ₃	8.80	8.46	0.60	7.23–9.59	13.51
SiO ₂	48.70	49.68	1.42	46.30–51.06	54.57
P ₂ O ₅	<0.01	0.00	—	—	0.26
K ₂ O	0.01	0.06	0.10	0.00–0.34	1.49
CaO	3.17	2.36	0.35	1.75–2.85	5.18
TiO ₂	0.08	0.02	0.04	0.00–0.14	1.50
MnO	0.21	0.11	0.07	0.00–0.22	0.29
FeO	1.85	—	—	—	—
Fe ₂ O ₃	20.71	23.72 ²	1.40	21.82–25.63	12.12 ²
Total	99.78	100.06	—	—	98.38
H ₂ O ⁺	8.02	—	—	—	2.64
H ₂ O ⁻	13.14	—	—	—	—

¹ All analyses given in weight percent on an ignited basis.

² Total Fe reported as Fe₂O₃.

to 950°C, and measuring the weight loss after each treatment. Finally, the amount of Fe²⁺ present was measured on a third split of the sample by the dichromate titration method previously described. Actual Fe³⁺ was calculated by difference, knowing both the amount of ferrous iron present in the sample and the total iron content from the XRF analysis. Results of these analytical procedures for the clay along with the XRF analysis of the surrounding basalt are given in Table 1.

Assuming the clay to be a single homogeneous phase, we recast the XRF chemical analysis of the clay material into a structural formula based on 22 negative charges (or O₁₀(OH)₂) with the following result:



According to this formula, 63% of the filled octahedral sites contain R²⁺ cations, most of which are Mg. The remainder contain predominantly Fe³⁺ cations resulting in an excess positive charge in the octahedral sheet and a total octahedral cation population of 2.65, a value intermediate between those for a dioctahedral and a trioctahedral clay mineral. The average total layer charge of $-.50$ compares well with the measured CEC value of 112 meq/100 g. These chemical results taken together with the XRD data suggest that the clay should be categorized as a saponite. In addition, the chemical data confirm the XRD results that indicated the clay was Fe-rich.

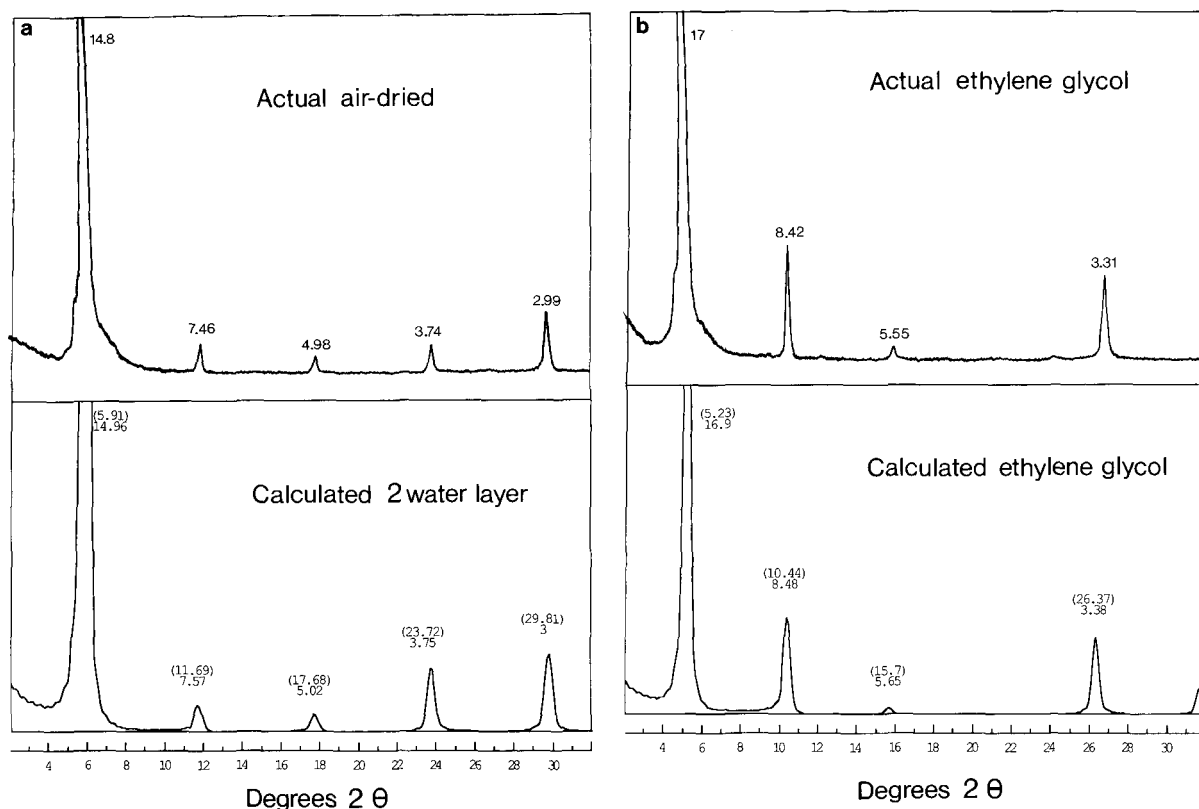


Figure 3. Actual and calculated diffractograms for the a) air-dried and b) ethylene glycol-solvated clay. Calculations in NEWMOD were based on a trioctahedral smectite containing 1.2 atoms of Fe. CuK α radiation. *d*-spacings in Ångströms.

X-ray diffraction modeling of the Granby clay

We used NEWMOD (Reynolds, 1985; Moore and Reynolds, 1989) to model the Granby clay, with trioctahedral smectite as the basic clay type and input variables as noted in Figure 3. All other chemical, structural, and sample variables were set to default values. As can be seen in Figure 3, the match between the calculated and actual diffraction patterns for both the air-dried clay (two-water layer hydrate) and the ethylene glycol-solvated clay are exceptionally good and reinforce the conclusion that the Granby clay should be categorized as a trioctahedral smectite. One important difference noted between the calculated and actual diffraction patterns, however, was in the breadth of the peaks. The actual patterns display much “sharper” reflections. The calculated patterns were produced using default values of $N = 3$ and $N = 14$, where the value for N refers to, respectively, the smallest and largest number of unit cells stacked in the Z crystallographic direction that comprise crystallites of the clay. After resetting the high N value from 14 to 20, the sharpness of the calculated peaks more closely approximated those in the actual diffraction pattern. [Although we did not attempt to model the effects of changing δ , the mean defect-free distance, or the average distance in the crystallite that is not interrupted by a stacking fault, in-

creasing the δ value will also lead to modifications in peak shape, including peak sharpness (Reynolds, 1989).] This result confirms the SEM observations depicting the well-crystallized nature of the Granby clay.

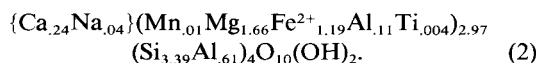
DISCUSSION

Precursor chemistry of the Fe-rich saponite

Fe-rich saponite is not uncommon in geologic environments, having been reported to occur in submarine and alkaline lake sediments, in altered volcanoclastics, and in weathered mafic and ultramafic rocks (Sudo, 1954; Miyamoto, 1957; Kohyama *et al.*, 1973; Sudo and Shimoda, 1978; Nahon and Colin, 1982; Cole and Shaw, 1983; Kodama *et al.*, 1988). In many of these reports the authors showed or suggested that some or all of the iron in the Fe-rich saponite was originally present in the ferrous form but was later oxidized to Fe³⁺, a reaction undoubtedly caused by the instability of ferrous iron in the smectite structure at surface conditions (see especially Badaut *et al.*, 1985). As a result of this conversion of Fe²⁺ to Fe³⁺, chemical analyses of Fe-rich saponites and subsequent calculations of structural formulae commonly deviate from what is expected for an ideal trioctahedral saponite containing three R²⁺ octahedrally-coordinated cations per O₁₀(OH)₂. Total octahedral occupancies with in-

intermediate values between di- and trioctahedral character are often reported and could result, for example, from site vacancies created by expulsion of octahedral iron to maintain unit layer charge balance after Fe^{2+} is oxidized to Fe^{3+} . Precise mechanisms for the oxidation of the Fe are not fully understood, but may involve deprotonation of structural hydroxyls and consumption of atmospheric oxygen, as demonstrated by Farmer *et al.* (1971) for biotites and vermiculites.

Considering the evidence that some Fe-rich saponites initially exist in *ferroan*-form and subsequently convert to *ferrian*-form following exposure to more oxidizing conditions, we first recalculated the structural formula for the Granby clay sample. We assumed that the clay was initially monomineralic and chemically homogeneous, and that *all* Fe was originally present as Fe^{2+} . The formula is:

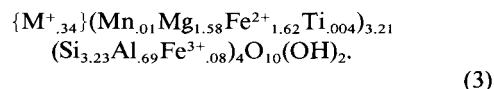


As shown, the total octahedral cation population is now close to the ideal value of 3.0 expected for a trioctahedral smectite. Also, a small amount of aluminum is present in octahedral coordination and no iron substitution is required in the structural formula calculation to fill completely all four tetrahedral sites.

As previously mentioned, there is evidence that the clay in the Granby Tuff originated in the *ferroan* form. Most convincing is the petrographic observation in which green-clay cores are seen surrounded by brown-clay rims (see Figure 1). This suggests, perhaps, that Fe presently exists in two oxidation states in the clay mineral and that the conversion of Fe^{2+} to Fe^{3+} occurred, or is presently occurring, from the outer edge of the clay-filled amygdale inward toward its center. The brown color of the clay in the oxidized rim may, in fact, result from tetrahedrally-coordinated Fe^{3+} (refer to structural formula 1), which has been shown to give rise to a strong absorption band in the optical spectrum near 2300 cm^{-1} in an Fe-rich saponite chemically similar to the clay in the Granby Tuff (Sherman and Vergo, 1988). Although the analytically determined Fe^{2+} content of the clay is quite low compared with Fe^{3+} (FeO vs Fe_2O_3 , Table 1), this result may be an artifact of the analytical method that required light grinding of the material in a mortar and pestle prior to the dissolution of the clay in acid. Exposure of the clay to the atmosphere for this short period of time may have caused oxidation of much of the octahedrally-coordinated Fe^{2+} .

Because small amounts of iron oxides/hydroxides were noted along fracture surfaces present in the basalt, we also considered the model that Kodama *et al.* (1988) proposed for the conversion of a *ferroan* to a *ferrian* saponite in a gabbro saprolite, which involves expulsion of iron from octahedral sites following conversion of Fe^{2+} to Fe^{3+} to account for octahedral vacancies.

This model assumes (1) no cationic changes in the octahedral sheet except for Fe, and (2) that the original Fe^{2+} content of the clay can be determined by layer-charge balancing after fixing the interlayer charge at 0.34, the theoretical value for an ideal saponite or iron saponite end-member composition. Using this model to recalculate the structural formula for the Granby clay we derived the following:



An immediate problem that arises in using this model is that layer-charge balancing requires 1.62 Fe^{2+} ions in the octahedral sheet bringing the total octahedral occupancy to 3.21, a value far from the ideal of 3.0. A second observation that seems to militate against the importance of the reaction proposed by Kodama *et al.* (1988) in the Granby Tuff is the virtual absence of iron oxide or hydroxide precipitates within, or in close proximity to, the amygdales themselves. The *ferrian* saponite in the gabbro saprolite was found intimately associated with substantial amounts of lepidocrocite and goethite, but this is not the case in the Granby Tuff. Oxidation of the *ferroan* saponite shown above (formula 3) to the observed *ferrian* saponite (formula 1) composition results in the release of 0.56 moles of $\text{FeO}(\text{OH})$ per mole of clay transformed, but whether or not this amount of iron oxide/hydroxide can reasonably account for the occasional iron staining observed in the fractures of the Granby Tuff could not be determined. Also, it is uncertain what role augite weathering played in supplying Fe for later precipitation as oxides or hydroxides in these fractures.

Saponite or saponite plus vermiculite?

As previously mentioned, diffraction tracings of random and standard oriented clay mounts, and modeling of the diffraction patterns using NEWMOD suggested that the Granby clay comprised a relatively pure trioctahedral, Fe-rich smectite (Figures 2, 3). In addition, the SEM/EDS chemical and X-ray mapping results showed that the chemistry of individual clay flakes was quite uniform, as was the distribution of elements in the clay material filling individual amygdales. This information seemed to leave little doubt that the clay was essentially monomineralic and, considered along with the XRF chemical data, likely a saponite. Additional chemical treatments, however, produced diffraction results indicating that the Granby clay is actually composed of an intimate mixture of saponite and a second clay with swelling properties, and an inferred layer charge more characteristic of vermiculite.

The case for the presence of a second mineral component in the Granby clay first becomes evident upon close inspection of the diffractogram for the Mg-saturated, glycerol-solvated mount. A broad shoulder on

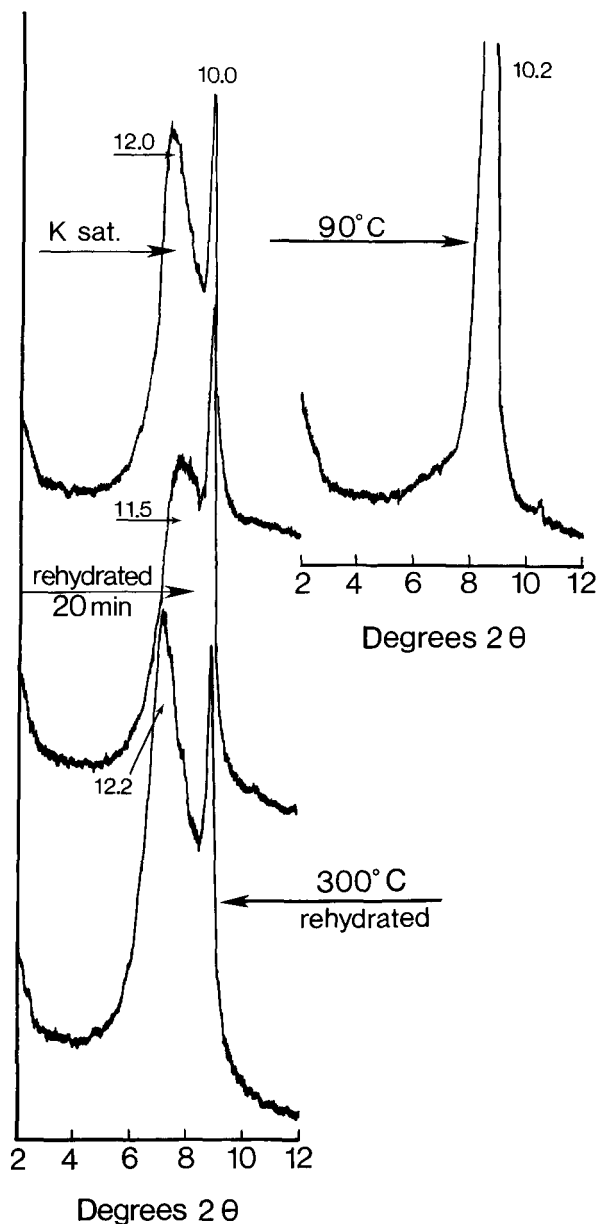


Figure 4. X-ray diffraction tracings of the K-saturated clay, the K-saturated clay heated to 90°C, and the rehydrated K-saturated clay after heat treatments at 90° and 300°C. CuK α radiation. *d*-spacings in Ångstroms.

the high-angle side of the 17.8 Å peak, extending to about 14.3 Å, indicates the presence of a nonswelling phase (Figure 2). A similarly placed, but smaller, shoulder can also be seen in the diffractogram for the ethylene glycol-solvated specimen. Upon K-saturation of the clay, two definitive peaks appear on the X-ray diffractogram; a sharp reflection with a basal spacing at 10 Å (typical of a vermiculite) and a broad reflection with a basal spacing at approximately 12 Å (typical of a smectite) (Figure 4). Heat treatment of the K-satu-

rated clay to 90°C for two hours caused the smectite layers that gave rise to the 12 Å peak to dehydrate and collapse to 10 Å. Rehydration to a one water-layer structure in air with a relative humidity of 57% took less than 20 minutes (Figure 4). The clay behaved similarly even after the K-saturated sample was heated to 300°C, although rehydration took days rather than minutes. The XRD results after saturating the clay with various other cations, heating the sample to 90°C for two hours, and solvating the clay with ethylene glycol are shown in Table 2. According to previous work on the swelling characteristics of expandable clay minerals saturated with various cations (e.g., Walker, 1961; Suquet *et al.*, 1975; MacEwan and Wilson, 1980; Kawano and Tomita, 1991), these data strongly suggest that in addition to saponite a vermiculite or, perhaps, a high-charge smectite constitutes a significant portion of the Granby clay.

The fact that the chemistry of the clay was found not to vary significantly within and among clay crystals and amygdales—at least at the resolution of the electron beam—suggests that the variations in swelling properties for the two clays may not be due to crystallochemical differences, that is, in the sense that two chemically discrete clay phases are present. Instead, as suggested by Suquet and Pezerat (1988), differences in swelling properties for clays of transitional character between saponite and vermiculite, such as appear to be present in amygdales of the Granby Basaltic Tuff, may result from heterogeneity in grain size, layer-charge density, or charge localization within the unit layers. Recall that grain size and color variations (with the latter presumably caused by changes in the oxidation

Table 2. Effect of cation solvation, heating to 90°C for 2 hours, and solvation with ethylene glycol on the basal spacings (Å) of the Granby clay.

Cation	Air-dried ¹	90°C	Ethylene glycol
Mg	12.8 (vw)	12.6 (vw)	14.4 (vw)
	14.7 (vs)	14.5 (vs)	16.7 (vs)
	16.2 (w)	15.9 (w)	18.4 (w)
	17.7 (vw)	17.5 (vw)	~20 (vw)
Ca	13.6 (vw)	—	14.7 (vw)
	15.5 (vs)	14.6 (vs)	16.8 (vs)
	17.2 (w)	—	18.4 (w)
	18.8 (vw)	—	~20 (vw)
K	10.1 (sh; s; A/hi)	10.0 (sh; s)	10.0 (sh; s)
	12.2 (b; s; A/hi)	12.2 (b; s) ²	16.7 (b; s)
Na	10.0 (vw)	9.9 (sh; vs)	10.0 (vw)
	12.4 (sh; vs; A/hi)	12.4 (b; vw)	16.5 (sh; vs)
Li	9.9 (sh; m)	10.0 (sh; s)	10.0 (sh; w)
	12.6 (b; s; A/hi)	12.6 (b; s)	16.8 (sh; vs)

¹ Relative humidity ranged from 65 to 69%.

² After rehydration at relative humidity = 57%.

sh = sharp; b = broad; v = very; w = weak; m = medium; s = strong; A/hi or A/lo = asymmetrical towards high/low spacings.

state of Fe) were the only significant differences observed for the clay material occupying the amygdales. Changes in unit layer charge or charge localization may have been brought about by the oxidation of octahedral Fe, as was discussed earlier. If this, in fact, is the case, then further characterization of this clay must include an attempt to separate the brown (oxidized?) clay from the green (unoxidized?) clay—a difficult task.

Therefore, in considering once again the structural formula calculated from the XRF chemical data, the assumption that the clay is comprised of a single homogeneous phase is no longer valid. Hence, structural formula 1 is more accurately a representation of the average composition of the two clays, regardless of the fact that the two clays appear to be chemically indistinguishable and may differ from one another only with respect to grain size, layer-charge density or charge distribution in octahedral and tetrahedral sheets. Figure 5 schematically illustrates how a mixture of the two clays can give rise to a calculated structural formula with an average total layer charge of -0.50 . The broad peak for the low-charge smectitic component in Figure 5 represents the possibility that the saponite in the Granby Basaltic Tuff displays greater heterogeneity in layer charge than the vermiculite (Lagaly and Weiss, 1976; Lagaly, 1982; Newman and Brown, 1987).

Evidence that the saponite in the Granby clay consists of layers with heterogeneous charge distribution comes from the apparent variety of hydration states displayed by the clay, as inferred from XRD results (Table 2). In the Mg- and Ca-saturated air-dried samples clay reflections at 12.8, 14.7, 17.7 Å and 13.6, 15.5, and 18.8 Å, respectively, suggest the presence of one-, two-, and three-water layer hydrates. Using peak height as a rough indicator, the two-water layer hydrate clearly constitutes the bulk of the Granby clay. Suquet *et al.* (1975) conducted a thorough study of the hydration states of smectites and vermiculites saturated with various cations and concluded that both the Mg- and Ca-saturated Kozakov saponite, when solvated with water, comprised two-water and three-water layer hydrates, and mixtures thereof.

In the Mg-saturated clay, a weak but sharp reflection at approximately 16.2 Å in the air-dried sample, which shifts to about 18.5 Å with ethylene glycol solvation could indicate the presence of crystallites containing randomly interstratified two- and three-water (and ethylene glycol) layer hydrates (Figure 6). Similar reflections (with d -spacings slightly shifted) were observed in diffractograms of the Ca-saturated clay, and in the untreated clay in which Ca is the predominant inter-layer cation. Interstratification between two hydration states is not uncommon in smectites, and random interlayering can produce a continuous variation of $d(001)$ as a function of the relative amount of each hydrate present (MacEwan and Wilson, 1980). It should be noted, however, that in this study the d -spacings for

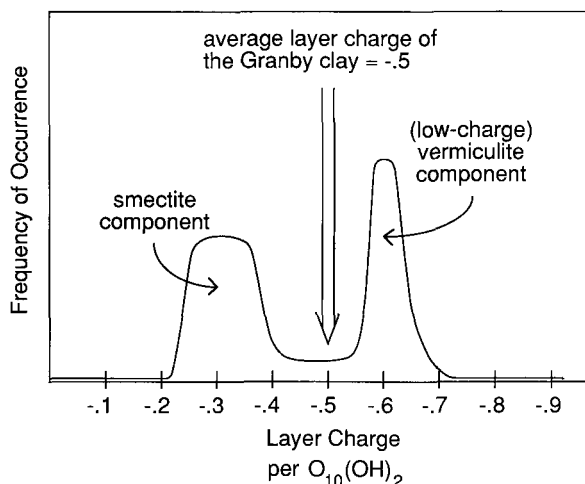


Figure 5. Schematic representation of the layer-charge distribution for clays in amygdales of the Granby Basaltic Tuff. Saponite with heterogeneous layer charge averaging about -0.3 , plus vermiculite (or a high-charge smectite) with an approximate layer charge of -0.6 gives rise to a "clay material" with an average layer charge of -0.5 , and an average CEC of 112 meq/100 g.

all the hydrates mentioned above varied significantly in replicate analyses with changes in relative humidity. Therefore, to document better the hydration states displayed by the Granby clay, and to determine whether or not interstratified hydrated phases actually do occur, a more detailed study of swelling properties should be undertaken in which conditions of relative humidity are carefully controlled.

To test the hypothesis that random interstratification between two hydration states in the Granby clay can generate $d(001)$ spacings intermediate or continuous in value between the d -spacing "steps" expected for integrally-hydrated (i.e., noninterstratified one-, two-, and three-water layer hydrates) structures, we took some untreated clay (which diffractograms had already shown existed predominately in the two-water layer state) and prepared an oriented glass slide mount from a clay-water suspension. During evaporation of the water, and for one hour afterward, the temperature of the slide was maintained at about 90°C with an infrared heat lamp to induce dehydration of some of the layers. The sample was immediately transferred to the XRD unit and a diffractogram was obtained. As shown in Figure 7, and based on subsequent modeling with NEWMOD, the reflection at about 13.2 Å results from a random interstratification of saponite hydrates with 70% of the layers containing one-water layer and 30% containing two-water layers.

CONCLUSIONS

Amygdales in the Granby Basaltic Tuff of the Connecticut Valley contain a dark-brown clay material that has been shown to consist of a mixture of Fe-rich,

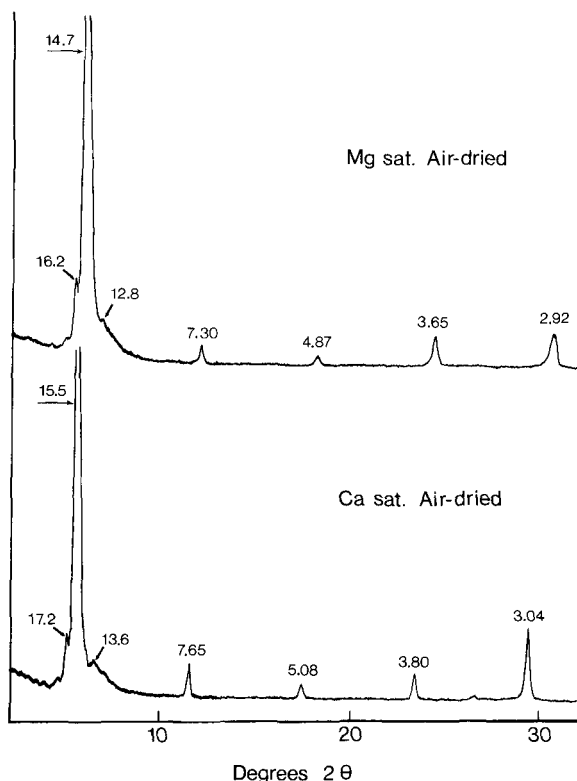


Figure 6. X-ray diffraction tracings of the Mg- and Ca-saturated, air-dried clay (RH = 65%). Reflections at 16.2, 14.7 and 12.8 Å for the Mg-saturated sample and at 17.2, 15.5 and 13.6 Å for the Ca-saturated sample suggest the presence of a number of hydration states. Also present in both diffractograms, but barely discernible, are reflections at about 18 Å. CuK α radiation.

trioctahedral 2:1 layer phyllosilicates. The clay appears to have precipitated in gas vesicles from solutions generated by the hydrothermal alteration of the basaltic tuff (timing unknown). Results from chemical and X-ray diffraction analyses performed on the clay thus far, demonstrate that it is composed of saponite and a second clay with swelling properties more characteristic of vermiculite. The actual identity of the second clay mineral remains equivocal, but based on available evidence it seems reasonable to suggest that it is a vermiculite or a high-charge saponite. A possible alternative, however, is that the second clay be categorized tentatively as a *saponite-vermiculite intermediate*, following the classification scheme for 2:1 trioctahedral phyllosilicates suggested by Suquet and Pezerat (1988).

The Granby clay is unique. It represents one of the few reported instances of an intimate association between two trioctahedral 2:1 layer expandable phyllosilicates, with crystallochemical characteristics and swelling properties that span the operational boundaries used to distinguish minerals belonging to either the smectite or vermiculite group. Although our study of the Granby clay provides some basic chemical and

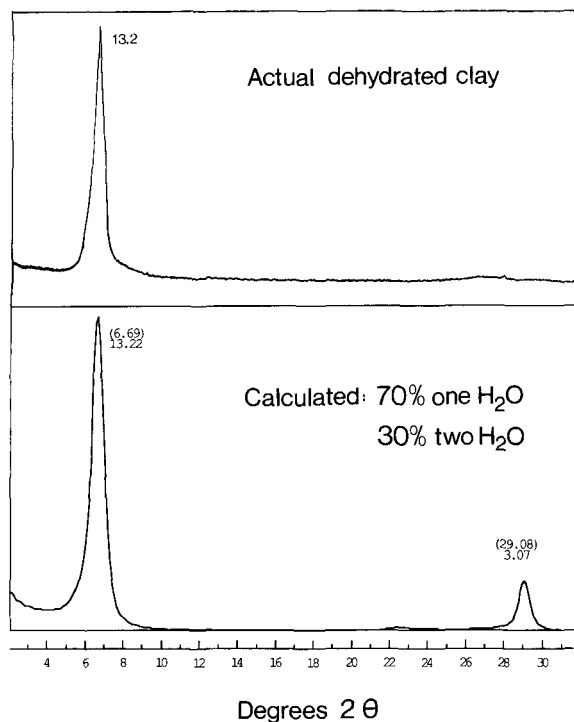


Figure 7. Actual and calculated diffractograms for the dehydrated Granby clay. The best fit occurred for a clay containing a random interstratification of unit layers with 70% containing one-water layer and 30% containing two-water layers. Calculations in NEWMOD were based on a trioctahedral smectite containing 1.2 atoms of Fe. CuK α radiation. *d*-spacings in Ångstroms.

mineralogical information, complete characterization of the properties of these minerals awaits further work. The large size of the crystallites may, for example, facilitate analytical techniques (e.g., single crystal X-ray diffraction) not practicable with the more common, fine-grained smectites. Also, we believe that an attempt should be made to define the physical nature of the clay mixture. Is the Granby clay composed of a true physical mixture of discrete saponite and vermiculite particles, do the minerals occur in composite crystallites, or does the transition from saponite to vermiculite take place within an individual crystallite or along a single unit layer? We plan to continue investigating the nature of the Granby clay and would gladly distribute samples of the mineral to interested parties, while supplies last.

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