

CONVERSION OF FERRUGINOUS ALLOPHANES TO FERRUGINOUS BEIDELLITES AT 95 °C UNDER ALKALINE CONDITIONS WITH ALTERNATING OXIDATION AND REDUCTION

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Abstract—Ferruginous beidellites with Al:Fe atomic ratios up to 2.36 were obtained when solutions containing Al, Fe²⁺ and H₂SiO₄ were adjusted to pH 8.5 with Ca(OH)₂ and incubated at 95 °C in the presence of CaCO₃ as a pH buffer. Incubation took place under cyclic reducing and oxidizing conditions achieved by adding 2 mM hydrazine at 14–15-d intervals over a period of 10–13 weeks. During the 14–15-d cycle, atmospheric oxygen slowly diffused through the high-density polyethylene bottles used, causing a slow oxidation of Fe(II) to Fe(III). The infrared (IR) spectra of the products approached that of natural beidellite, but indicated little change in octahedral Al:Fe ratio in the products for starting Al:Fe ratios from 2.5 up to 3.5, which was the highest Al:Fe ratio at which a well-crystallized product was obtained. Chemical analysis showed the presence of more Al+Fe in the products than could be incorporated into a dioctahedral formula. After the excess was assigned to a hydroxy-aluminium interlayer, the formula of the most Al-rich beidellite was calculated to be 0.575Ca(Si_{6.85}Al_{1.15})(Al_{2.47}Fe_{1.53})O₂₀(OH)₄. This composition lay within the range recorded for the ferruginous beidellites that form in Vertisols.

Key Words—Allophane, Beidellite, Infrared Spectra, Nontronite, Vertisols, X-ray Diffraction (XRD).

INTRODUCTION

Aluminium liberated by acidic weathering is, in the short term, usually precipitated not as crystalline clays, but as highly reactive allophanes and other amorphous species. These amorphous species readily absorb or react with phosphate and are readily remobilizable sources of toxic amounts of Al in soils and waters (Paterson et al. 1991). Such amorphous precipitates can persist in soils and weathered tephras for some thousands of years (Wada 1989; Farmer and Russell 1990). Ultimately, Al is incorporated either into crystalline clay minerals, or, in low-silica environments, into Al hydroxides. The aluminous clay minerals are, mostly, of low solubility even in acidic environments, so it is of potential importance to identify conditions that favor crystallization.

The widespread occurrence of ferruginous beidellites in Vertisols (Wilson 1987) suggests that the presence of ferrous Fe, cyclic oxidizing and reducing conditions and an alkaline pH promote the crystallization of such clays under Mediterranean and subtropical climates. Vertisols occur in basins that receive alkalies and silicic acid in drainage water from surrounding higher ground, and they experience oxidizing and reducing conditions because of a climate with marked wet and dry seasons (Duchaufaur 1982). In investigating this process, Farmer, Krishnamurti and Huang (1991) and Farmer et al. (1994) examined the products obtained when precipitates formed from solutions containing Al, Fe²⁺ and orthosilicic acid were digested in CaCO₃-buffered alkaline reducing conditions, initially maintained by the presence of hydrazine, and then in

alkaline oxidation conditions. They found that well-crystallized aluminous nontronites were rapidly formed at 90 °C with Al:Fe ratios up to about 1, but crystallization became progressively slower and more incomplete at higher Al:Fe ratios. The highest Al:Fe ratio giving a fully crystallized product was 1.66. They considered that this material probably lay in the nontronite composition range, that is, with an octahedral Al:Fe ratio less than or equal to 1, with few or no Al₂OH octahedral groupings.

In the course of that work it was noted that crystallization was promoted by repeating the reduction-oxidation cycle, so we have examined again the possibility of preparing products in the beidellite composition range by using multiple reduction-oxidation cycles. It was also realized that the hydrazine used in some of the previous work (Farmer et al. 1994) was only about 1/3 of its nominal strength, due to deterioration in storage.

METHODOLOGY

The experimental procedures were essentially those described by Farmer, Krishnamurti and Huang (1991); that is, solutions containing orthosilicic acid (1.45–1.50 mM) and various concentrations of Al(ClO₄)₃ (0.5–1.0 mM) and Fe^{II}(ClO₄)₂ (0.2–0.4 mM) plus 2 mM N₂H₄ were adjusted to pH 8.5, 60 mg CaCO₃ added as a buffer and the suspensions heated in an oven at 95 ± 1 °C with daily shaking. Care was taken to exclude oxygen by bubbling nitrogen through the solutions before and during pH adjustment. The initial gray-green color of the precipitates slowly changed to

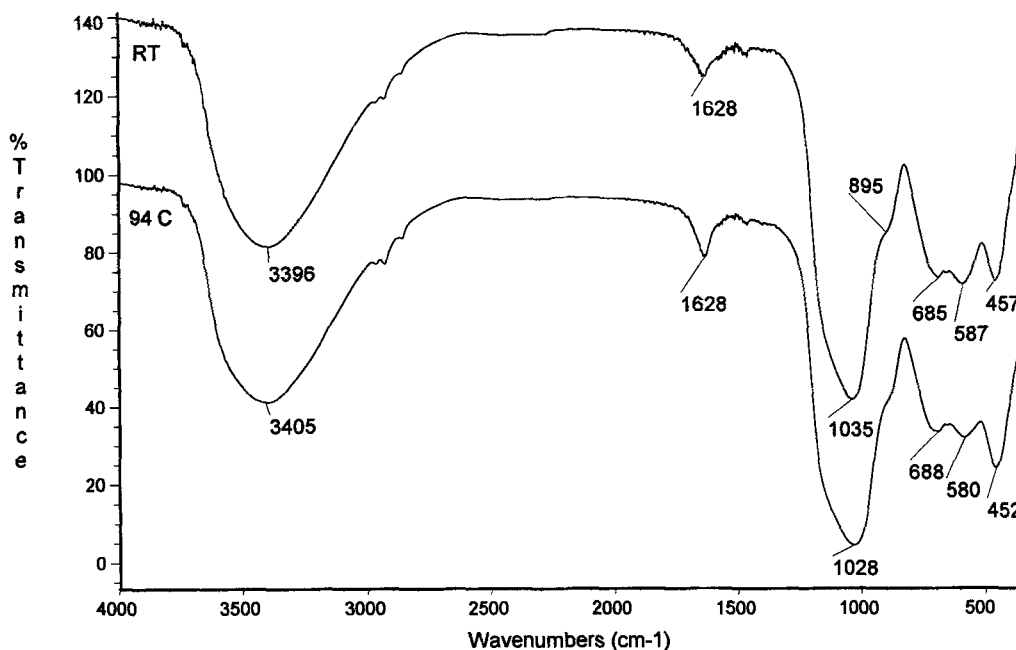


Figure 1. IR spectra of initial precipitates from solutions with Si:Al:Fe = 15:7:2 after 1 d at room temperature (RT) or at 94 °C. Spectra of KBr disks dried at 150 °C. Peak positions in cm^{-1} .

yellow-orange over 13–15 d as Fe(II) was oxidized to Fe(III) by oxygen diffusing through the polyethylene bottles used. Further additions of hydrazine to 2 mM were made every 14–15 d until the products were harvested after 10–13 weeks, when they were characterized by IR spectroscopy to assess degree of crystallinity. Selected apparently well-crystallized products were further examined by X-ray diffraction (XRD), transmission electron microscopy (TEM), electron diffraction (ED) and chemical analysis by inductively coupled plasma (ICP) of solutions prepared from Li metaborate fusions. The pH of the synthetic systems at harvest, measured at room temperature, lay near 9.5.

In the following, the concentrations in the starting solutions are presented in the form [Si]:[Al]:[Fe]/ 10^{-4} M; for example, a solution with 1500 μM Si, 700 μM Al and 200 μM Fe is identified as system 15:7:2.

RESULTS

The extent of crystallization was best followed by IR spectroscopy, which showed a transformation of the broad absorption bands of the initial ferruginous hydrous feldspathoid allophane (Figure 1) to the progressively sharper absorption bands of the intermediate nontronite–beidellite phase (Figure 2). The spectra of the initial precipitates (Figure 1) are typical of those of hydrous feldspathoid allophanes (Farmer et al. 1979). The presence of Fe in their structure is indicated by a weakening and displacement to lower frequency of an Si-O-Al absorption, which lies at 700–710 cm^{-1} in Fe-free allophanes, but shifts to around

685 cm^{-1} in ferruginous allophanes (Farmer, Krishnamurti and Huang 1991). It cannot be excluded that part of the Fe in the harvested initial precipitates is present as a separate amorphous or poorly ordered Fe oxide.

The positions of many of the beidellite bands were sensitive to the composition of the product, showing a progressive movement to higher frequencies with increasing beidellitic content. Figure 2 compares the IR spectra of a synthetic aluminous nontronite (Al:Fe = 1), a synthetic ferruginous beidellite (Al:Fe = 2.7) and an almost Fe-free natural beidellite (Unterrupsroth >3 μm fraction; Nadeau et al. 1985), where the following band progressions can be seen: OH stretching frequency, 3560, 3620, 3632 cm^{-1} ; Si-O stretching, 1015, 1020, 1036 cm^{-1} ; Si-O-Al vibration, 739, 755, 770 cm^{-1} ; octahedral sheet vibrations, 507, 530, 530 cm^{-1} , and 460, 475, 471 cm^{-1} . It should be noted, however, that the Unterrupsroth beidellite contains some octahedral Mg, which reduces some band frequencies compared with those in the very pure Black Jack Mine beidellite where the OH stretching frequency is centered on 3650 cm^{-1} , and the octahedral sheet vibrations lie at 537 and 479 cm^{-1} . These frequencies are taken from the spectrum of Farmer and Russell (1964), reproduced in Farmer (1974). The formulae of the natural beidellites are Black Jack Mine— $\text{Ca}_{0.46}(\text{Si}_{6.96}\text{Al}_{1.04})(\text{Al}_{3.86}\text{Fe}_{0.04}\text{Mg}_{0.02})\text{O}_{19.96}(\text{OH})_4$; Unterrupsroth— $\text{Ca}_{0.61}(\text{Si}_7\text{Al})(\text{Al}_{3.73}\text{Fe}_{0.04}^{\text{III}}\text{Mg}_{0.23})\text{O}_{20}(\text{OH})_4$, as determined, respectively, by Weir and Greene-Kelly (1962) and Nadeau et al. (1985).

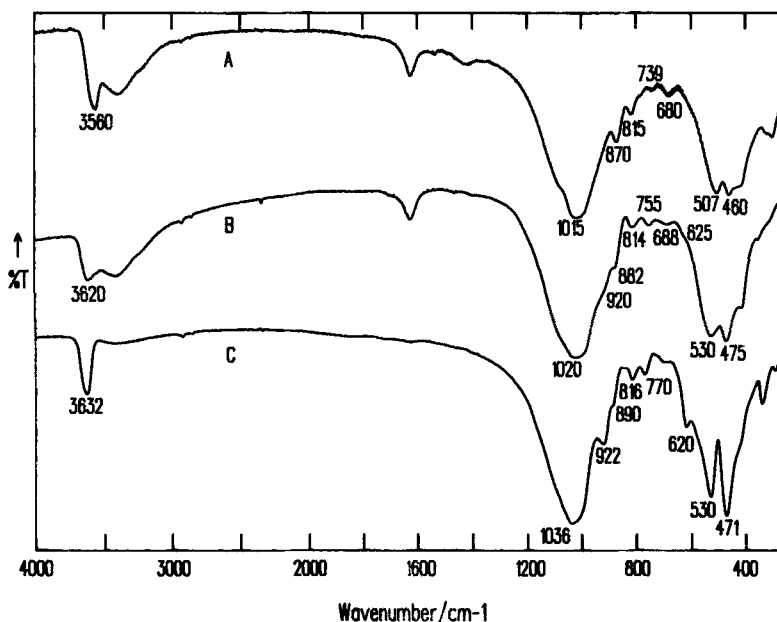


Figure 2. IR spectra of (A) a synthetic aluminous nontronite (initial solution ratios Si:Al:Fe = 14:5:5), (B) a synthetic ferruginous beidellite (initial ratios 14.5:4.9:1.8) and (C) a natural beidellite containing little Fe (Unterrupsroth >3 μm fraction). All in KBr disks dried at 150 °C. Peak positions in cm^{-1} .

OH bending frequencies are a poorer guide to composition than OH stretching frequencies. Thus, the Fe_2OH bending frequency at 815 cm^{-1} in nontronite is replaced by an Si-O-Al vibration at 816 cm^{-1} in beidellite with little change in intensity (Farmer 1974). The FeAlOH bending frequency at 870 cm^{-1} weakens and shifts to 882 cm^{-1} in the ferruginous beidellite, but a weak band persists at 875 cm^{-1} in the almost Fe-free Black Jack Mine beidellite, and at 890 cm^{-1} in the Unterrupsroth beidellite. The 922-cm^{-1} band of the Unterrupsroth beidellite may be largely an Al-MgOH band, as the Al_2OH absorption of the Black Jack Mine beidellite is a broad feature at 942 cm^{-1} . In the ferruginous beidellite (Figure 2), this band is only a broad shoulder near 920 cm^{-1} on the side of the Si-O stretching absorption at 1020 cm^{-1} .

The limiting Al:Fe ratio at which well-crystallized ferruginous beidellites have been obtained in the present investigation is 3.5, but the positions of the IR absorption bands in the products indicated that there was little or no change in their octahedral composition for Al:Fe ratios above 2.5. At ratios above 3.0, a weak broad band near 700 cm^{-1} became more obvious; this absorption can be assigned to residual hydrous feldspathoid (Figure 1), as it was greatly reduced by a 1-h extraction with 0.2 M oxalate at pH 3. However, the total decrease in adsorption with oxalate indicated that the allophane content was less than 10% of the products selected for analysis.

Chemical analyses of products with Al:Fe ratios of 2.5 and 3.5 indicated the presence of more Fe+Al than

could be accommodated in a dioctahedral structure. This excess cannot be ascribed to an allophanic component, as the composition of the allophane, harvested after 1 d at $94\text{ }^\circ\text{C}$, already approached that of the final crystallized beidellite. Thus, a solution with Si:Al:Fe = 15:7:2 gave an allophane with Si:Al:Fe:Ca ratios of 1:0.86:0.24:0.075, and a beidellite product with ratios 1:0.77:0.22:0.084. Assigning the excess Al+Fe to allophane of this composition would require over 50% allophane in the final product, whereas the IR spectrum shows allophane to be at most a minor component, no more than 10%. There was no evidence for crystalline Al or Fe hydroxides in the product. Amorphous Al hydroxides cannot form under the silicic acid concentrations present (Farmer, Palmieri et al. 1991), and the pale yellow color of the products argues against the presence of amorphous Fe hydroxides. Accordingly, it seems likely that the excess hydroxides are present as interlayer precipitates, whose presence is indicated by XRD (see below). Such interlayer precipitates are dominantly Al hydroxides (Barnhisel and Bertsch 1989) and the beidellite formulae have been calculated on this assumption. Thus, for the product from a solution containing 1.5 mM Si, 0.5 mM Al and 0.2 mM Fe, we calculate a formula $0.585\text{Ca}(\text{Si}_{6.83}\text{Al}_{1.17})(\text{Al}_{2.36}\text{Fe}_{1.64})\text{O}_{20}(\text{OH})_4 + 0.30\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$; for that from a solution containing 1.5 mM Si, 0.7 mM Al and 0.2 mM Fe, we calculate $0.575\text{Ca}(\text{Si}_{6.85}\text{Al}_{1.15})(\text{Al}_{2.47}\text{Fe}_{1.53})\text{O}_{20}(\text{OH})_4 + 0.80\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$; and for that from a solution containing 1.46 mM Si, 0.95 mM Al and 0.29 mM Fe, we

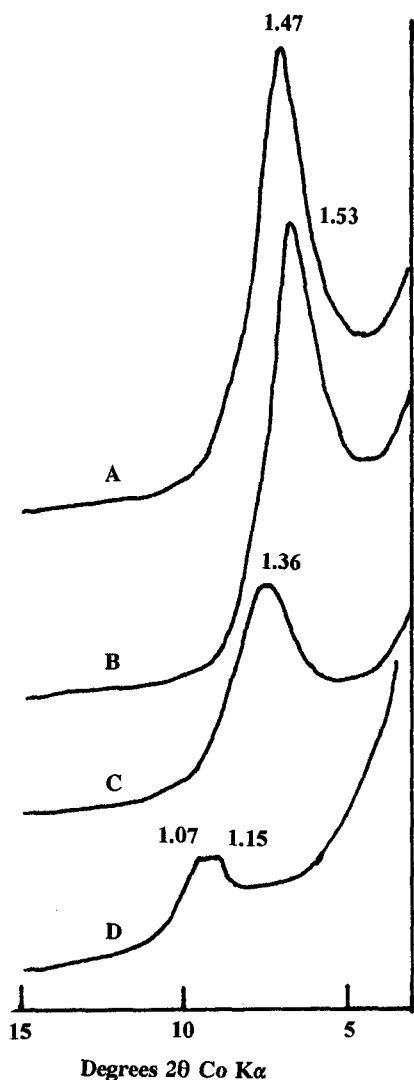


Figure 3. Basal XRD reflections given by an oriented deposit of a synthetic ferruginous beidellite (starting ratios Si:Al:Fe = 14.5:9.5:3.5). (A): Ca-saturated, air dry; (B): Ca-saturated, ethylene-glycol-treated; (C): K-saturated, room temperature; (D): K-saturated, 300 °C. Peak positions in nm.

calculate $0.565\text{Ca}(\text{Si}_{6.87}\text{Al}_{1.13})(\text{Al}_{2.36}\text{Fe}_{1.64})\text{O}_{20}(\text{OH})_4 + 0.80\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$.

It will be seen that the calculated compositions of the beidellites are close, in agreement with the IR spectra. The calculated octahedral Al:Fe ratios would be higher if some Fe were incorporated in interlayer or external precipitates. It is very possible, too, that these synthetic beidellites are inhomogeneous, and may include a range of Al:Fe ratios, some higher than the average. Thus, the calculated octahedral Al:Fe ratios represent a minimum value for what may be achieved by this synthetic process.

XRD supported the presence of interlayer precipitates in these synthetic beidellites. Potassium-saturated

material gave air-dry spacings of 1.36–1.37 nm, which contracted to broad bands at 1.07–1.15 nm at 300 °C (Figure 3). In contrast, a K-saturated synthetic aluminous nontronite (Al:Fe = 1), which was relatively free from interlayer precipitates, contracted from 1.24 nm, air dry, to give a sharp band at 1.05 nm at 300 °C (Farmer, Krishnamurti and Huang 1991).

The basal reflections of the synthetic Ca-saturated ferruginous beidellites were very much weaker relative to *hk* reflections (Figure 4) than those shown by the synthetic Ca-saturated aluminous nontronites (Farmer et al. 1994), indicating that the layers of the beidellites were more poorly aligned. Two beidellites gave basal air-dry (50% relative humidity) spacings of 1.47 nm, expanding to 1.53 nm with ethylene glycol (Figure 3), but contracting slightly to 1.43 nm with glycerol. A 3rd gave an air-dry spacing of 1.50 nm, expanding to 1.61 with ethylene glycol. These spacings are comparable to those given by a synthetic Al-nontronite: 1.51 nm air dry; 1.66 nm with ethylene glycol, but only 1.51 nm with glycerol (Farmer et al. 1994). The lack of expansion with glycerol in these synthetic clays contrasts markedly with the behavior of Black Jack Mine beidellite, which when Ca-saturated gives 1.52 nm air dry, 1.685 nm with ethylene glycol and 1.760 nm with glycerol (Weir and Greene-Kelly 1962). The limited expansion of the synthetic clays can be ascribed to their high tetrahedral charge, rather than to interlayer precipitates, which are absent from the nontronite (Farmer et al. 1994).

Examination by TEM indicated that the crystallites of the beidellites were much more poorly developed than those of the synthetic Al-nontronite, both in thickness and area. Whereas the Al-nontronite was seen to consist of distinguishable *hk*-ordered crystals (Farmer et al. 1994), the beidellite examined showed only crumpled sheets (Figure 5a) with ring diffraction patterns. Thin deposits did, however, show a distinct spottiness in the rings, suggesting that some incipient *hk*-ordering was present (Figure 5b).

The molar ratio of Si to (Al+Fe) used in the starting solutions for beidellite synthesis lay mostly in the range 1.7–2.2, and in these the residual concentration of Si in solution after incubation lay in the range 0.5–0.7 mM from a starting concentration of 1.5 mM. In experiments to determine the minimum Si:(Al+Fe) ratio for beidellite syntheses, with Al:Fe held at 2.7, a largely crystalline product was obtained with an Si:(Al+Fe) ratio of 1.12, leaving only 0.14 mM Si in solution. Lower ratios gave mixtures of amorphous and crystalline products, with residual Si concentrations falling to 0.06 mM.

Although well-crystallized products have been regularly obtained in syntheses with Al:Fe ratio between 2.5 and 3.0 after 10 weeks incubation at 95 °C, some preparations in this concentration range were still partly amorphous even after 12 weeks. Largely crystalline

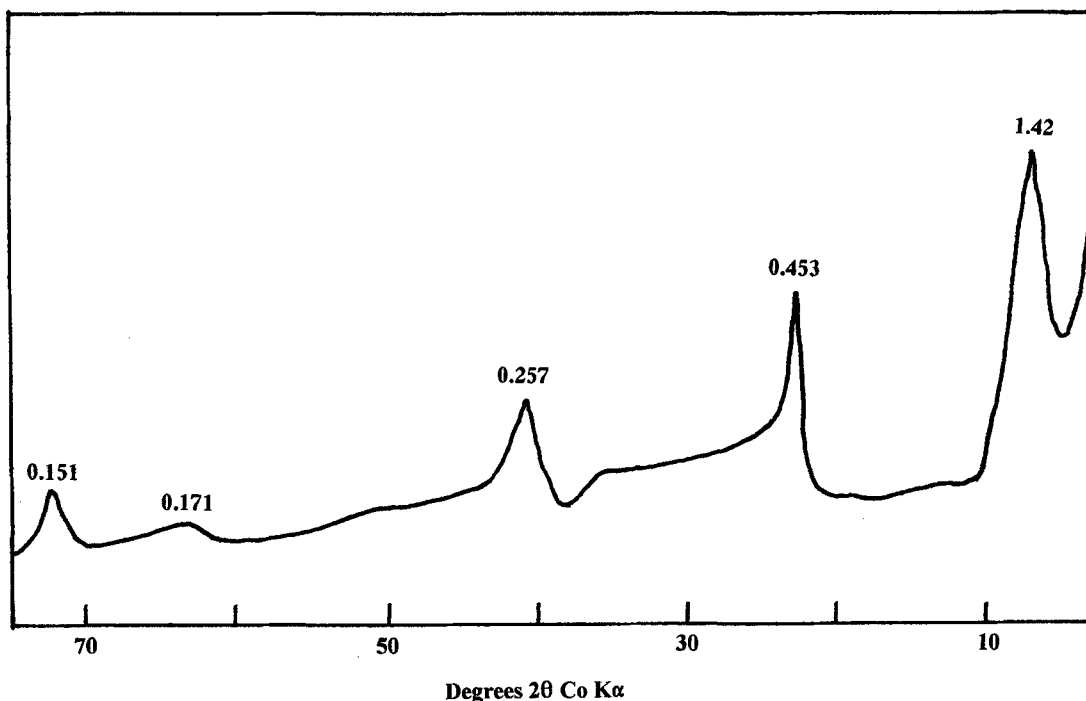


Figure 4. XRD of a randomly oriented preparation of the Ca-saturated ferruginous beidellite used for Figure 3. Peak positions in nm.

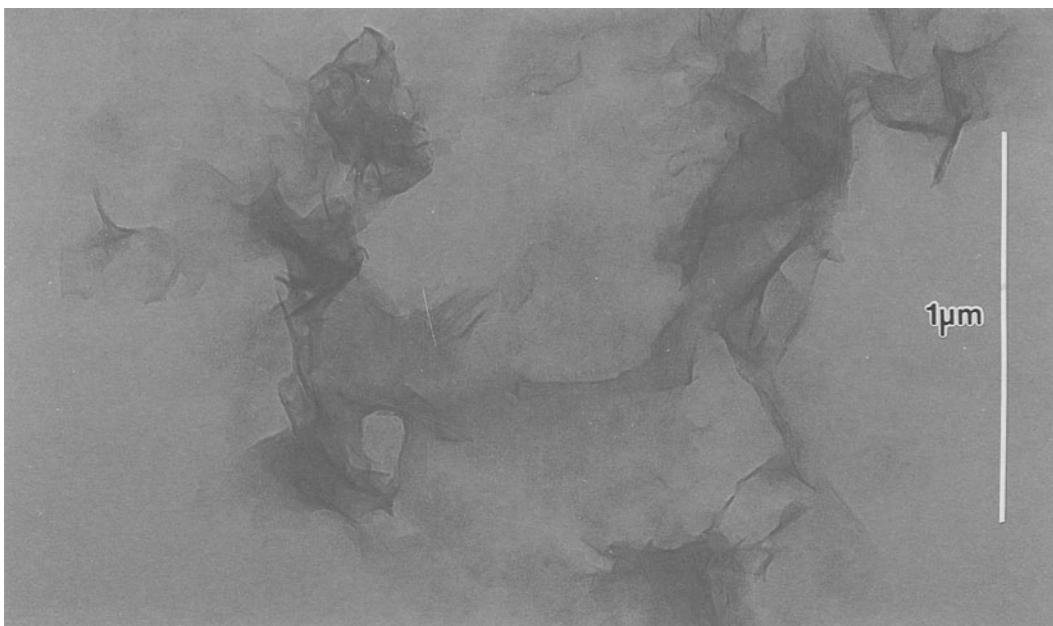
products were only obtained once for Al:Fe ratios of 3.25 and 3.5. It is not known whether this variability in the rate or extent of crystallization is due to unrecognized variations in the methods of synthesis, or to a natural randomness in the crystallization process.

DISCUSSION

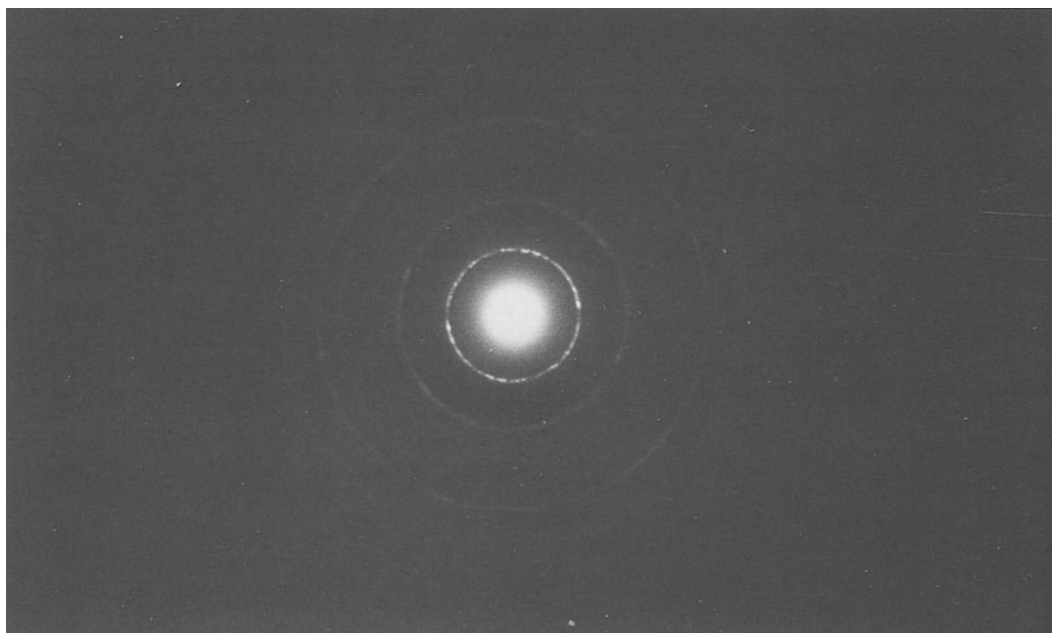
It has been established here that repeated oxidation-reduction cycles allow the crystallization of ferruginous beidellites at temperatures below 100 °C, although crystallization becomes erratic with Al:Fe starting ratios above about 2.7. Even in apparently well-crystallized products, chemical analysis showed the presence of more Al+Fe than can be incorporated into a dioctahedral formula. It is argued that the excess can be ascribed to interlayer Al hydroxides, and on this basis the calculated limiting composition of the synthetic ferruginous beidellite has an overall Al:Fe atomic ratio of 2.36, and an octahedral Al:Fe ratio of 1.61. These are conservative estimates, as any incorporation of Fe into interlayer or external precipitates would lead to higher Al:Fe ratios in the beidellite. Soil beidellites commonly have octahedral Al:Fe ratios in the range 1.5–4.0, but most of these also have substantial octahedral Mg contents (Wilson 1987). Soil beidellites with low Mg contents (0.01–0.12 Mg per 4 octahedral sites) have been reported by Ben-Dor and Singer (1987); these have octahedral Al:Fe ratios of 1.31–2.16, and overall Al:Fe ratios of 1.95–2.83, val-

ues that are comparable to those of the synthetic products. They also have high tetrahedral Al contents (0.77–1.62 per 8 sites), as have the synthetic beidellites (1.13–1.17 Al per 8 sites).

There remains, however, an apparent paradox in that aluminous nontronites crystallize much more readily than ferruginous beidellites at low temperature, whereas the neoformed clays in Vertisols almost all lie in the ferruginous beidellite field (Wilson 1987), and commonly have octahedral Al:Fe ratios in excess of those achieved in the present synthetic study. The incorporation of Mg into the octahedral sheet of soil beidellites may facilitate the crystallization of beidellites with lower Fe contents, but this has not been verified in our synthetic studies, where the presence of Mg in the systems led to trioctahedral clays (Farmer, Krishnamurti and Huang 1991). The scarcity of nontronitic compositions in Vertisol clays may be a result of their susceptibility to attack by the complexing acids produced by roots and microorganisms in the biologically active zone of soils (Farmer et al. 1994). As a result, the more resistant Al-rich beidellites will be favored in the long term. Because of the mixing process characteristic of Vertisols, the whole soil column is, in time, exposed to biologically produced acids. Nontronites are commonly formed in terrestrial and deep sea weathering of basic and ultra basic rocks, and are neoformed in alkaline lakes and deep sea trenches (Velde 1995).



a



b

Figure 5. TEM micrograph (a) and ED pattern (b) of a thin deposit of the synthetic ferruginous beidellite used for Figure 3.

Analyses of the synthetic clays reported here are average values for products that may well be inhomogeneous, and include a range of Al:Fe ratios, some higher than the average.

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