

## SYNTHETIC ALLOPHANE AND LAYER-SILICATE FORMATION IN $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ - $\text{FeO}$ - $\text{Fe}_2\text{O}_3$ - $\text{MgO}$ - $\text{H}_2\text{O}$ SYSTEMS AT 23°C AND 89°C IN A CALCAREOUS ENVIRONMENT

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**Abstract**—Solutions containing  $\text{AlCl}_3$  and  $\text{Si}(\text{OH})_4$  (concentrations  $\leq 1.5$  mM with molar Si:Al ratios of 1:2, 1:1 and 3:1) and  $\text{FeCl}_2$  (0, 0.5 and 1.0 mM) were adjusted to pH 8 with  $\text{Ca}(\text{OH})_2$ , and incubated at 23°C and 89°C without exclusion of air in the presence of  $\text{CaCO}_3$  for 8–12 weeks. The products were characterized by infrared spectroscopy and X-ray diffraction. Systems with 3:1 and 1:1 Si:Al ratios without Fe gave hydrous feldspathoids at 23° and 89°C. Systems with 3:1 Si:Al ratios containing Fe gave aluminous nontronites at 89°C, and noncrystalline, nontronite-like products at 23°C. Systems with 1:1 Si:Al ratios with added Fe gave Fe(III)-substituted hydrous feldspathoids at 23°C. At 89°C, the system with 1:1 Si:Al ratios and 0.5 mM Fe produced a “protohalloysite,” while that with 1.0 mM Fe gave a poorly ordered nontronite-like layer silicate. In systems with 1:2 Si:Al ratios, the formation of “protoimogolite” at 23°C was little affected by additions of Fe. At 89°C, the “protoimogolite” decomposed to boehmite and poorly ordered layer silicate phases. Inclusion of 1 mM  $\text{MgCl}_2$  in the above systems had no effect on the products at 23°C, but at 89°C produced saponites and a mixed layer saponite-chlorite in the 3:1 Si:Al systems, and saponite-like layer structures in the 1:1 and 1:2 Si:Al systems.

**Key Words**—Allophane, Hisingerite, Hydrous feldspathoid, Nontronite, Poorly-ordered layer silicates, “Protoimogolite,” Saponite, Synthesis.

### INTRODUCTION

A survey of the occurrence and Si:Al ratio of allophanes in soils (Parfitt and Kimble, 1989) has shown that allophanes seldom occur above pH 7, and tend to exhibit higher Si:Al ratios than the “protoimogolite” species (Si:Al about 0.5) that predominate in acidic soils. In part this can be ascribed to the less aggressive weathering environment in alkaline conditions, but biological and chemical weathering will still liberate Al and Si from primary minerals in such soils, and Al mobilized in overlying acidic horizons can enter and precipitate in alkaline subhorizons.

A possible explanation for the scarcity of allophanes in alkaline soils is that the initial aluminosilicate precipitates transform rapidly to more crystalline clay minerals in such environments. It is known that alkaline conditions do favor layer-silicate formation. Wada *et al.* (1988) and Farmer *et al.* (1991) reported the formation of halloysite-like structures in aluminosilicate precipitates digested at 80–100°C at pH near 8. Farmer *et al.* (1991) found evidence for saponite-like structures when hydrous feldspathoids were digested at 80°C and pH ~8 in solutions containing Mg. Decarreau (1981) has shown that trioctahedral smectites form readily by digesting  $\text{M}(\text{II})\text{O}-\text{SiO}_2-\text{H}_2\text{O}$  ( $\text{M} = \text{Mg}, \text{Ni}, \text{Zn}, \text{Co}$ ) precipitates below 100°C, but the experimental environments are more alkaline and more concentrated than would be expected in soils. Fe(II) is a more likely promoter of layer-silicate formation in soils. Coprecipitates containing Fe(II) and silicate initially form a poorly-ordered trioctahedral layer struc-

ture which transforms to nontronite when oxidized by air at temperatures of 25°–75°C (Harder, 1976; Decarreau and Bonnin, 1986). Fe(II) is largely hydrolyzed at pH 8.0 (the pK for  $\text{Fe}^{2+} + \text{H}_2\text{O} = \text{FeOH}^+ + \text{H}^+$  is ~9.5, Baes and Mesmer, 1976) and so might readily react with silicic acid in a calcareous environment, even when present in low concentration.

We have therefore examined the effect of added Fe(II) (0.5 and 1.0 mM) on the nature of the precipitates formed in solutions containing Al and Si after adjustment to pH ~8 and digestion at 23°C and 89°C in the presence of excess  $\text{CaCO}_3$ . Air was not excluded from the systems after the initial precipitation, as reducing conditions in calcareous soils are likely to be of limited duration. If Fe(II) promotes layer-silicate formation, such layer silicate might incorporate Mg, and possibly also K, since Al, Fe and Mg are common components of smectites and chlorites, and are associated with K in illites, celadonites and glauconites. Accordingly, the effect of added Mg and K (1 mM) was also examined. A previous investigation of allophanes formed in a calcareous environment (Farmer *et al.*, 1991) found that systems with Si:Al ratios of 0.5 yielded “protoimogolite” at 20°C, those with Si:Al ratios of unity yield protohalloysite at 80°C, and those with Si:Al ratios over 2 gave hydrous feldspathoids at 20°C. When Mg was added, saponite formation was indicated at 80°C for Si:Al ratios of 2 or more. Accordingly, we have selected Si:Al ratios near 0.5, 1 and 3 for the present investigation. For comparison, we have included systems with a Si:Fe ratio of 3:2, without Al.

Table 1. Initial concentrations of Si, Al and Fe, residual concentrations of Si and Al, and calculated molar ratios of Si, Al and Fe in precipitates in systems without Mg and K. The range of pH during the experiment and the final pH values are listed.

| System No. | Initial conc. ( $\mu\text{M}$ ) |      |      | Temp. | Final pH | pH range | Residual conc. ( $\mu\text{M}$ ) |     |      |                    | Precipitate molar ratios |       |
|------------|---------------------------------|------|------|-------|----------|----------|----------------------------------|-----|------|--------------------|--------------------------|-------|
|            | Si                              | Al   | Fe   |       |          |          | Si (in weeks)                    |     |      | Al (in weeks) 8/12 | Al/Si                    | Fe/Si |
|            |                                 |      |      |       |          |          | 2                                | 8   | 12   |                    |                          |       |
| 3600       | 695                             | 1340 | 0    | 23    | 7.8      | 7.8–8.2  | 38                               | 43  | 43   | 10                 | 2.01                     | 0     |
|            |                                 |      |      | 89    | 8.5      | 8.2–8.5  | 76                               | 54  | n.e. | 78                 | 1.96                     | 0     |
| 3620       | 695                             | 1340 | 500  | 23    | 7.8      | 7.7–8.0  | 31                               | 32  | 31   | <5                 | 2.02                     | 0.75  |
|            |                                 |      |      | 89    | 8.4      | 8.2–8.5  | 74                               | 60  | n.e. | 50                 | 2.01                     | 0.78  |
| 3640       | 695                             | 1340 | 1000 | 23    | 7.7      | 7.7–8.0  | 25                               | 29  | 30   | <5                 | 2.02                     | 1.50  |
|            |                                 |      |      | 89    | 8.4      | 8.2–8.5  | 70                               | 73  | n.e. | 30                 | 2.09                     | 1.60  |
| 6600       | 1400                            | 1340 | 0    | 23    | 7.9      | 7.9–8.2  | 234                              | 178 | 173  | 6                  | 1.09                     | 0     |
|            |                                 |      |      | 89    | 8.5      | 8.2–8.5  | 164                              | 113 | n.e. | 60                 | 0.99                     | 0     |
| 6620       | 1400                            | 1340 | 600  | 23    | 7.7      | 7.7–7.8  | 166                              | 133 | 131  | <3                 | 1.06                     | 0.39  |
|            |                                 |      |      | 89    | 8.5      | 8.2–8.5  | 111                              | 92  | n.e. | 48                 | 0.99                     | 0.38  |
| 6640       | 1400                            | 1340 | 1000 | 23    | 7.7      | 7.6–7.7  | 121                              | 98  | 99   | <5                 | 1.03                     | 0.77  |
|            |                                 |      |      | 89    | 8.3      | 8.3–8.5  | 105                              | 74  | n.e. | 21                 | 0.99                     | 0.75  |
| 6200       | 1400                            | 487  | 0    | 23    | 8.0      | 8.0–8.3  | 748                              | 679 | 675  | 17                 | 0.65                     | 0     |
|            |                                 |      |      | 89    | 8.5      | 8.2–8.5  | 694                              | 657 | n.e. | 11                 | 0.61                     | 0     |
| 6220       | 1400                            | 487  | 500  | 23    | 7.7      | 7.7–7.9  | 521                              | 447 | 445  | <5                 | 0.51                     | 0.52  |
|            |                                 |      |      | 89    | 8.4      | 8.1–8.4  | 442                              | 360 | n.e. | <5                 | 0.46                     | 0.47  |
| 6240       | 1400                            | 487  | 1000 | 23    | 7.6      | 7.5–7.8  | 330                              | 280 | 278  | <5                 | 0.43                     | 0.89  |
|            |                                 |      |      | 89    | 8.4      | 8.1–8.4  | 277                              | 246 | n.e. | <5                 | 0.42                     | 0.85  |
| 6040       | 1400                            | 0    | 1000 | 23    | 7.7      | 7.5–7.8  | 706                              | 665 | 673  | <5                 | 0                        | 1.38  |
|            |                                 |      |      | 89    | 8.4      | 8.1–8.4  | 638                              | 642 | n.e. | <5                 | 0                        | 1.25  |

n.e.—not examined

## EXPERIMENTAL

From stock solutions of approximately 2 mM  $\text{Si}(\text{OH})_4$  (prepared by the hydrolysis of  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ), 0.1 M  $\text{AlCl}_3$  and 0.1 M  $\text{FeCl}_2$ , a series of solutions (800 ml each) containing Si, Al and Fe(II) were prepared with the concentrations listed in Table 1. Each solution also contained 1 mM hydrazine to maintain Fe(II) in the reduced condition. The mixed stock solutions were deaerated by bubbling oxygen-free nitrogen through them, and were rapidly adjusted to pH 8.0 with a saturated ( $\sim 20$  mM)  $\text{Ca}(\text{OH})_2$  solution. Each solution with its dispersed precipitates was then subdivided into two 400-ml lots, contained in 500-ml screw-top, high-density polyethylene bottles, and 80 mg  $\text{CaCO}_3$  added to each bottle as a pH buffer. One set of 400-ml solutions was shaken gently at 23°C and the other kept in an oven at  $89^\circ \pm 1^\circ\text{C}$  (except when sampled) and usually shaken once or twice daily by hand, with release of any pressure arising from liberation of  $\text{CO}_2$ . No precautions were taken to exclude air after the initial pH adjustment. A further series of solutions containing 1 mM  $\text{MgCl}_2$  and 1 mM  $\text{KCl}$  in addition to Si, Al and Fe(II) (Table 2) were prepared in the same way.

The pH of the solutions (measured at room temperature) was monitored at biweekly intervals, when 5-ml samples were taken to measure  $\text{Si}(\text{OH})_4$  concentrations, after centrifugation at about 1500 g. The molybdenum blue procedure (Morrison and Wilson, 1963)

was modified to develop color in 5-ml analytical solution rather than 100 ml. Before harvesting the precipitates (after 8 weeks for the 89°C series, and after 12 weeks for the 23°C series), the residual Al in the supernatant solution was measured by the catechol violet method (Dougan and Wilson, 1974). Residual Mg was measured by flame atomic absorption, and residual K by flame emission.

At the end of the experiment, the solutions were saturated with  $\text{CO}_2$  and shaken overnight in the closed bottles to dissolve excess  $\text{CaCO}_3$ . The solids were then recovered by centrifuging, washed with water on the centrifuge, and freeze-dried. The precipitates were examined by IR spectroscopy (0.8–1.0 mg sample in 13 mm KBr disks, dried at 150°C) using Perkin-Elmer Model 983 grating spectrometer, and by X-ray diffraction as deposits from water dispersions on glass slides, using a Rigaku Rotaflex RU200 X-ray diffractometer with  $\text{CuK}\alpha$  radiation at 50 kV and 150 mA.

## RESULTS AND INTERPRETATION

### *Solution and precipitate compositions*

Tables 1 and 2 list the initial concentrations of Si, Al, Fe, Mg and K in the various systems studied, the pH ranges during the experiment, the residual concentrations of Si, Al, Mg and K (no Fe remained in solution), and the composition of the precipitates, calculated from the difference between the initial and

Table 2. Initial concentrations of Si, Al and Fe, residual concentrations of Si, Al, Mg and K, and calculated molar ratios of Si, Al, Fe, Mg and K in precipitates, in systems containing Mg and K (initial concentrations each 1000  $\mu\text{M}$ ).

| System No. | Initial concentration ( $\mu\text{M}$ ) |      |      | Temp. | Final pH | pH range | Residual concentration ( $\mu\text{M}$ ) |     |      |                    |                    |                   |       | Precipitate molar ratios |       |      |  |
|------------|---|------|------|-------|----------|----------|--|-----|------|--------------------|--------------------|-------------------|-------|--------------------------|-------|------|--|
|            | Si                                      | Al   | Fe   |       |          |          | Si (in weeks)                            |     |      | Al (in weeks) 8/12 | Mg (in weeks) 8/12 | K (in weeks) 8/12 | Al/Si | Fe/Si                    | Mg/Si | K/Si |  |
|            |   |      |      |       |          |          | 2  | 8   | 12   |                    |                    |                   |       |                          |       |      |  |
| 3604       | 765                                     | 1340 | 0    | 23    | 8.0      | 8.0–8.2  | 46                                       | 43  | 39   | 8                  | 990                | 1020              | 1.83  | 0                        | 0     | 0    |  |
|            |   |      |      | 89    | 8.3      | 7.9–8.5  | 33                                       | 66  | n.e. | 23                 | 590                | 1070              | 1.85  | 0                        | 0.70  | 0.14 |  |
| 3624       | 765                                     | 1340 | 500  | 23    | 7.8      | 7.8–8.2  | 25                                       | 31  | 32   | <5                 | 950                | 1010              | 1.83  | 0.68                     | 0     | 0    |  |
|            |   |      |      | 89    | 8.4      | 8.0–8.5  | 28                                       | 63  | n.e. | 16                 | 670                | 1130              | 1.86  | 0.70                     | 0.59  | 0.05 |  |
| 3644       | 765                                     | 1340 | 1000 | 23    | 7.8      | 7.8–8.2  | 22                                       | 28  | 29   | <5                 | 930                | 1020              | 1.83  | 1.36                     | 0     | 0    |  |
|            |   |      |      | 89    | 8.3      | 7.9–8.3  | 63                                       | 55  | n.e. | 15                 | 700                | 1070              | 1.86  | 1.40                     | 0.50  | 0.03 |  |
| 6604       | 1540                                    | 1340 | 0    | 23    | 7.9      | 7.8–8.2  | 236                                      | 177 | 176  | <5                 | 980                | 1000              | 0.98  | 0                        | 0     | 0    |  |
|            |   |      |      | 89    | 8.3      | 8.0–8.3  | 166                                      | 179 | n.e. | 21                 | 520                | 1060              | 0.96  | 0                        | 0.37  | 0    |  |
| 6624       | 1540                                    | 1340 | 500  | 23    | 7.7      | 7.7–7.9  | 183                                      | 139 | 140  | <5                 | 980                | 990               | 0.96  | 0.36                     | 0     | 0    |  |
|            |   |      |      | 89    | 8.2      | 8.0–8.2  | 150                                      | 133 | n.e. | 8                  | 330                | 1030              | 0.94  | 0.35                     | 0.49  | 0.07 |  |
| 6644       | 1540                                    | 1340 | 1000 | 23    | 7.7      | 7.7–7.9  | 120                                      | 101 | 104  | <5                 | 970                | 1000              | 1.00  | 0.75                     | 0     | 0    |  |
|            |   |      |      | 89    | 8.2      | 7.9–8.2  | 127                                      | 97  | n.e. | <5                 | 310                | 1010              | 0.92  | 0.69                     | 0.49  | 0.06 |  |
| 6204       | 1540                                    | 487  | 0    | 23    | 8.0      | 8.0–8.2  | 841                                      | 778 | 776  | 17                 | 1090               | 980               | 0.64  | 0                        | 0     | 0    |  |
|            |   |      |      | 89    | 8.2      | 8.0–8.2  | 700                                      | 388 | n.e. | <5                 | 310                | 1040              | 0.41  | 0                        | 0.60  | 0.06 |  |
| 6224       | 1540                                    | 487  | 500  | 23    | 7.8      | 7.8–8.0  | 574                                      | 496 | 493  | <5                 | 1030               | 990               | 0.47  | 0.48                     | 0     | 0    |  |
|            |   |      |      | 89    | 8.1      | 8.0–8.4  | 464                                      | 406 | n.e. | <5                 | 230                | 1050              | 0.41  | 0.42                     | 0.66  | 0.08 |  |
| 6244       | 1540                                    | 487  | 1000 | 23    | 7.7      | 7.7–7.8  | 346                                      | 289 | 289  | <5                 | 940                | 990               | 0.39  | 0.80                     | 0     | 0    |  |
|            |   |      |      | 89    | 8.3      | 8.0–8.3  | 289                                      | 151 | n.e. | <5                 | 560                | 1000              | 0.35  | 0.71                     | 0.35  | 0.07 |  |
| 6044       | 1540                                    | 0    | 1000 | 23    | 7.7      | 7.6–7.8  | 795                                      | 767 | 770  | <5                 | 1130               | 960               | 0     | 1.30                     | 0     | 0    |  |
|            |   |      |      | 89    | 8.1      | 8.0–8.4  | 564                                      | 278 | n.e. | <5                 | 740                | 1000              | 0     | 0.78                     | 0.24  | 0.06 |  |

n.e.—not examined.

residual concentrations. In addition, the concentrations of Si in solution after 2, 8 and 12 weeks provide information on the process of maturation of the precipitates. The various systems are identified by numbers that indicate the approximate relative concentrations of the components in the initial solution. Thus system 3624 had initial concentrations of Si, Al, Fe and Mg in the approximate ratio 3:6:2:4. To avoid fractional numbers, 4 corresponds to an initial concentration of 1 mM.

Systems with starting ratios of Si:Al = 3:6 showed small irregular changes in Si in solution over the period examined, whereas those with Si:Al of 6:6 and 6:2 mostly showed a decrease in Si in solution between two and eight weeks (Tables 1, 2). In systems at 23°C, little further change occurred between 8 and 12 weeks, indicating that a metastable condition had been attained. Systems at 89°C containing Mg and K and Si:Al ratios of 6:2 (Table 2) showed substantial declines of Si in solution between 2 and 8 weeks, when the precipitates were harvested. These precipitates would probably have continued to take up Si if the digestion had been prolonged.

Within experimental error, no Mg or K was taken up by precipitates incubated at 23°C, whereas substantial amounts of Mg were taken up by precipitates digested at 89°C (Table 2). The slight increases in concentration of K in solution after 8 weeks at 89°C are due to evaporation. When allowance was made for evaporative loss (monitored by weighing) a very small

uptake of K by most of these precipitates was indicated.

The color of the precipitates containing iron provided some indication of the progress of oxidation of Fe(II) to Fe(III). Initially the precipitates were pale green, but within a few hours they passed through darker green shades, which then faded and turned to yellow and yellow-orange shades as Fe(III) became predominant. Oxidation to yellow and yellow-orange shades occurred within two days for systems with Si:Al ratios of 3:6, but reduced colors persisted much longer in samples with higher Si:Al ratios. This is attributed to the greater influence of  $\text{Si}(\text{OH})_4$  on the oxidation of Fe(II) at higher Si:Al ratios (Krishnamurti and Huang, 1991). The 6222 product at 89°C was still pale green when harvested after 8 weeks, and the 6220 product was very pale yellow when harvested after 12 weeks. Color is a sensitive indicator of traces of ferrous iron in ferric silicates. Only the 6224 product at 89°C was green when harvested, and only this product is likely to contain significant amounts of Fe(II).

#### *Infrared spectroscopy and X-ray diffraction*

The infrared spectra of the precipitates indicated that the presence of Fe in these systems had a substantial effect on the products formed in systems with Si:Al ratios of 6:2 and 6:6, but little effect on products formed in systems with Si:Al ratios of 3:6. The presence of Mg in the systems changed the nature of all the products obtained at 89°C, but had little or no effect on the products obtained at 23°C. The very small uptake of

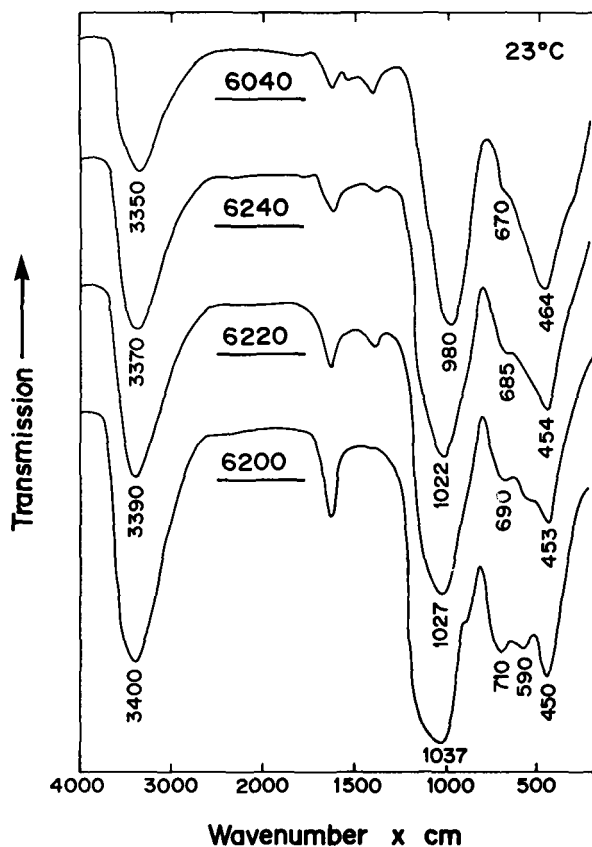


Figure 1. Infrared spectra of products from systems with starting ratios of Si:Al near 3, with or without added Fe as indicated in Table 1, and incubated at 23°C.

K by the precipitates digested at 89°C indicated that this cation had little effect on the products.

The spectra of products obtained from systems with Si:Al starting ratios of 6:2 and 6:0 are presented in Figures 1–3. Figure 1 shows the spectra of products obtained from systems 6200, 6220, 6240 and 6040 at 23°C. Almost identical products were obtained from systems containing Mg and K. The spectrum of the 6200 product is typical of hydrous feldspathoids (Farmer *et al.*, 1979), with: 1) characteristic maxima at 1037, 710, and 450  $\text{cm}^{-1}$  arising from a tetrahedral aluminosilicate network, 2) a band at 590  $\text{cm}^{-1}$  arising from octahedral aluminum, and 3) a shoulder at 900  $\text{cm}^{-1}$  arising from SiOH groups. In the 6240 product, with an initial concentration of 1 mM Fe(II), an obviously different product is obtained with absorption maxima at 1022 and 454  $\text{cm}^{-1}$ , and a shoulder at 685  $\text{cm}^{-1}$ . The spectrum of the 6220 product is intermediate between those of the 6200 and 6240 products. This indicates the influence of Fe(II) on the formation of hydrous feldspathoids. When Al is omitted from the system (product 6040), the infrared spectrum (Figure 1) shows marked similarities to that of the 6240 product, although the maxima are displaced and broadened.

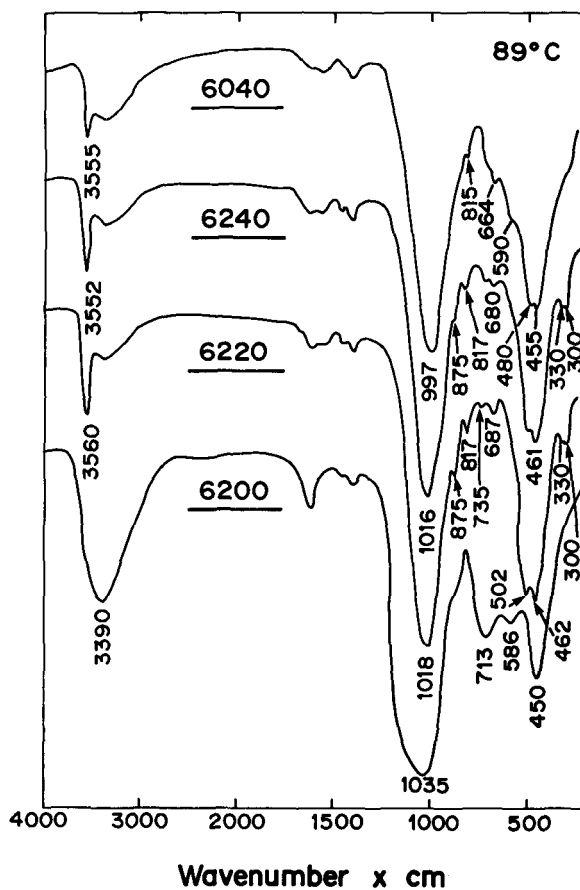


Figure 2. Infrared spectra of products from systems with starting ratios of Si:Al near 3, with or without added Fe as indicated in Table 1, and incubated at 89°C.

It appears possible, therefore, that in the 6240 product Al is incorporated into a structure that is determined by the presence of Fe, although the mixed Al-Fe silicate is better ordered than the pure Fe-silicate. None of the products 6220, 6240 and 6040 at 23°C gave distinctive X-ray diffraction patterns.

Figure 2 shows the spectra of the products obtained from the same systems as in Figure 1, but at 89°C. The 6200 product is still a hydrous feldspathoid, but with a reduced content of octahedral Al, absorbing at 586  $\text{cm}^{-1}$ . The 6220 product gives a sharp infrared pattern characteristic of a well-ordered aluminous nontronite (Goodman *et al.*, 1976), with bands at 817  $\text{cm}^{-1}$  ( $\text{Fe}_2^{3+}$  OH bending), 875  $\text{cm}^{-1}$  ( $\text{AlFe}^{3+}$  OH bending) and 3560  $\text{cm}^{-1}$  ( $\text{Fe}_2^{3+}$  OH and  $\text{AlFe}^{3+}$  OH stretching). The 6240 and 6040 products also give spectra characteristic of nontronites, with  $\text{Fe}_2^{3+}$  OH stretching and bending vibrations at 3555–3552 and 815–817  $\text{cm}^{-1}$ . The  $\text{Al-Fe}^{3+}$  OH bending vibration appears only as a shoulder at 875  $\text{cm}^{-1}$  in the spectrum of the 6240 product, and is absent from the Al-free 6040 product. The broad similarity between the spectra obtained from the 6240 and 6040 products at 89°C (Figure 2) and 23°C (Figure

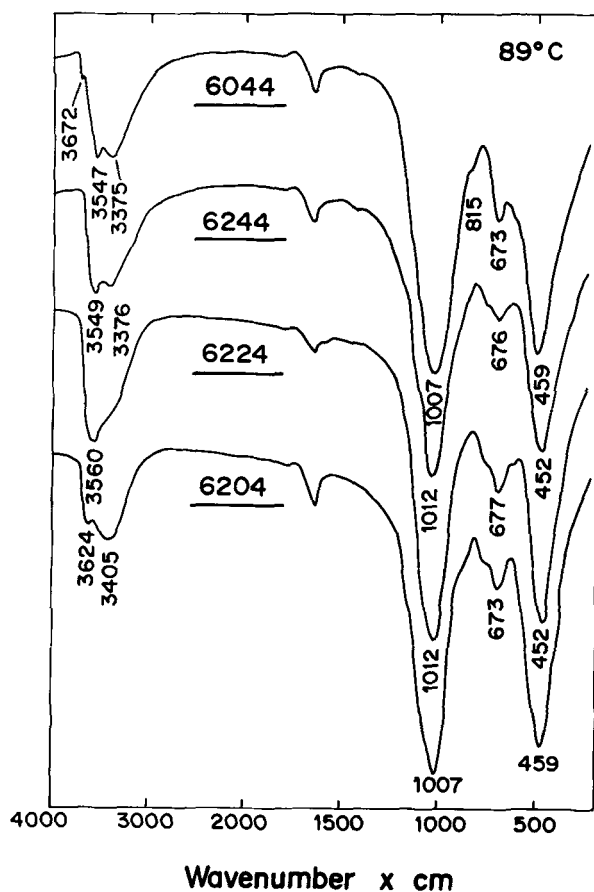


Figure 3. Infrared spectra of products from systems with starting ratios of Si:Al near 3, incorporating 1 mM of Mg and K, with or without added Fe as indicated in Table 2, and incubated at 89°C.

1) suggests that nontronite formation has been initiated at 23°C. The 23°C products have compositions (Table 1) and infrared spectra (Figure 1) similar to those reported for hisingerites (Whelan and Goldich, 1961; Shayan, 1984) and could be classified in this group.

X-ray diffraction traces of the 6220 and 6240 products at 89°C showed basal spacings of 13.5–13.6 Å (Ca-saturated), which expanded to 14.9–15.1 Å with glycerol. K-saturation gave spacings of 12.4–13.0 Å, which collapsed to 10.5 Å after heating to 300°C (illustrated for 6220 in Figure 4). These spacings are consistent with a smectite, whose limited expansion with glycerol might be due to a high charge located in the tetrahedral layer. The 6040 product gave no basal spacing, but had weak *hk* reflections near 4.6 Å (02), 2.55 Å (11) and 1.52 Å (06) similar to those exhibited by the 6220 product, indicating the formation of a layer silicate (not shown). The 6200 product gave no distinct XRD reflections.

Figure 3 shows the spectra of products from systems 6204, 6224, 6244 and 6044 at 89°C. Here the incorporation of Mg into the products as shown in Table 2,

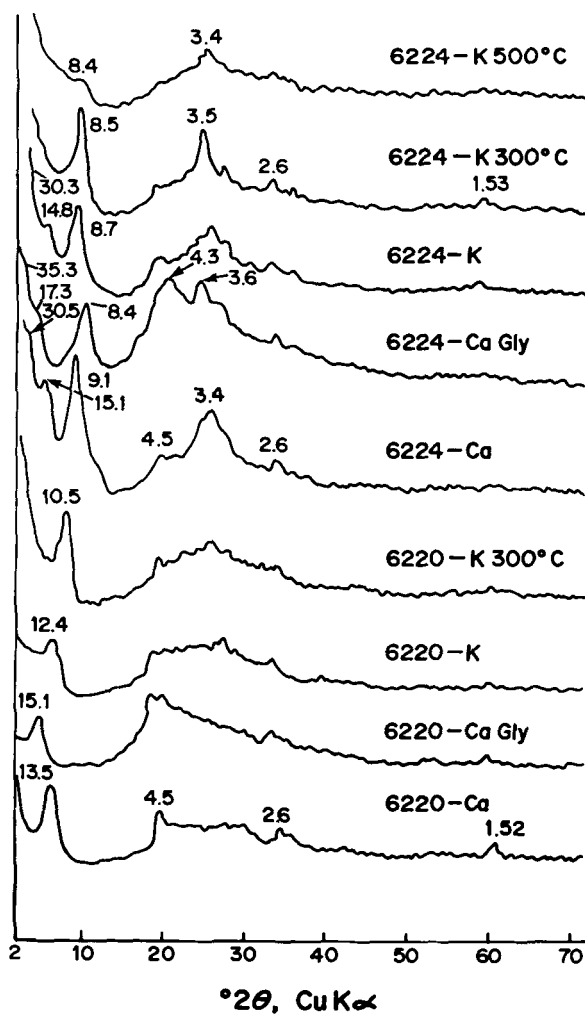


Figure 4. X-ray diffraction traces of products from systems 6220 and 6224 at 89°C, following the treatments indicated. d-spacings in Å.

has had a profound effect on their structure. All four products have spectra closely similar to that shown by Russell (1987) for a vermiculite, and clearly arise from trioctahedral 2:1 layer silicates with substantial substitution of Al and/or Fe in their octahedral and tetrahedral sheets. The vermiculite spectrum (Russell, 1987) had maxima at 3571 and 1005  $\text{cm}^{-1}$ , a shoulder at 740, 675, and 458  $\text{cm}^{-1}$ , which lie close to, or within the range of, those in Figure 3. The broad OH-stretching band of the vermiculite at 3571  $\text{cm}^{-1}$  arises from dioctahedral sites ( $\text{M}_2^{3+}\text{OH}$  or  $\text{M}^{3+}\text{MgOH}$ ) within the predominantly trioctahedral sheet. The corresponding band in Figure 3 shifts from 3624  $\text{cm}^{-1}$  in the 6204 product to 3547  $\text{cm}^{-1}$  in the 6044 product, as Fe(III) replaces Al in the structure. The weak, sharp band of MgOH stretching at 3672  $\text{cm}^{-1}$  was detected only in the spectrum of the 6044 product. A weak shoulder was present near 815  $\text{cm}^{-1}$  in the spectra of the 6044

and 6244 products, indicating the presence of  $\text{Fe}_2^{3+}\text{OH}$  groups. These could be present as dioctahedral sites in the trioctahedral layer silicate, or in a small nontronite component.

X-ray diffraction traces (not shown) of the 6204 product at 89°C (presumably largely Ca-saturated) gave a basal spacing at 14.4 Å, expanding to 18.4 Å with glycerol. When K-saturated it gave a spacing of 13.0 Å, collapsing to 10.9 Å at 300°C. This product is therefore a saponite, rather than a vermiculite. The 6224 product gave an unusual reflection at 8.5–9.1 Å, depending on the conditions, together with wider spacings (Figure 4). These suggest the presence of an almost regularly interstratified chlorite-saponite. The hydrated Ca-saturated sample gave reflections at 30.5 Å, 15.1 Å and 9.1 Å, which approximate to the first, second and third orders of a 30.5 Å repeat of saponite (16 Å) plus chlorite (14.5 Å). On glycerol treatment the reflections move to 35.3 Å (first order), 17.3 Å (second order) and 8.4 Å (fourth order), with expansion of the saponite component to 18.5 Å. On K-saturation and heating to 300°C, only the 8.5 Å basal reflection persisted, which can be considered to be the third order of a 25 Å repeat (K-saponite, 10.5 Å plus chlorite, 14.5 Å). The 8.5 Å reflection was almost lost on heating the K-saturated sample to 500°C. The unusual intensity of the 8.5–9.1 Å reflection is probably due to the presence of an iron-rich chlorite component. Such chlorites give a very weak 001 reflection at 14 Å, and strong 002 reflection near 7 Å (Wilson, 1987), so that the 8.5–9.1 Å reflection could derive its intensity from the iron-rich chlorite component of the regularly interstratified saponite-chlorite. The low temperature (<500°C) at which this reflection loses intensity is also consistent with an Fe-rich chlorite component. The 6244 product gave only weak basal reflections, best developed at 10.3 Å when K-saturated and heated to 300°C, indicating a saponite component (Brindley, 1980). The 6044 product gave no distinct XRD reflections.

The infrared spectra of products obtained from systems with Si:Al starting ratios of 6:6 are shown in Figures 5–7. Figure 5 shows the spectra of products from systems 6600, 6620 and 6640 at 23°C. Essentially the same spectra (not shown) were obtained at 23°C from systems 6604, 6624 and 6644 that contained 1 mM Mg and K. The infrared spectrum of the 6600 product is that of a hydrous feldspathoid, with maxima at 1025, 700, 600, and 448  $\text{cm}^{-1}$ . With increasing Fe in the system, the Si–O stretching vibration shifts from 1025 to 1014  $\text{cm}^{-1}$  (6620), then to 1002  $\text{cm}^{-1}$  (6640), indicating increasing Fe incorporation in the silicate structure. At the same time absorption increases in the 600–575  $\text{cm}^{-1}$  region, indicating an increase in octahedral Al. Fe could also be present as a hydrous ferric oxide, but would absorb principally at 487  $\text{cm}^{-1}$ . The spectra suggest, therefore, that Fe displaces Al from the hydrous feldspathoid structure. However, there is

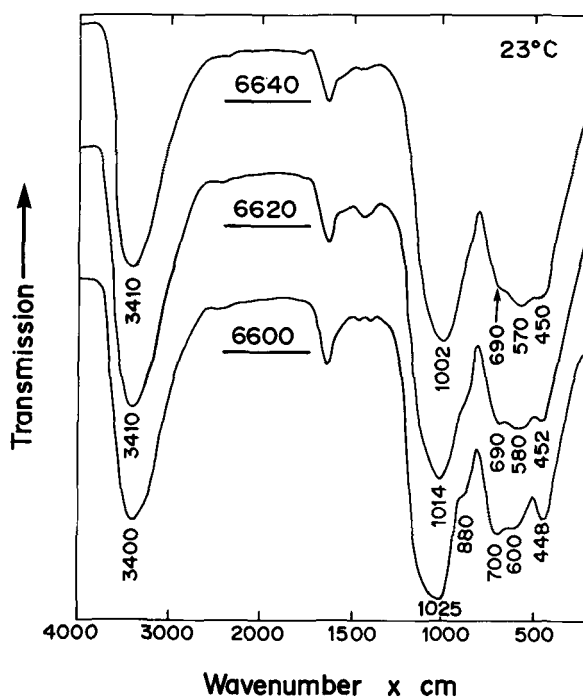


Figure 5. Infrared spectra of products from systems with starting ratios of Si:Al near 1, with or without added Fe as indicated in Table 1, and incubated at 23°C.

little evidence for layer silicate formation, such as was indicated by the development of a sharp feature 454  $\text{cm}^{-1}$  in the spectrum of the 6240 product at 23°C (Figure 1).

Figure 6 shows the infrared spectra of the products from the same systems as in Figure 5, but at 89°C. The 6600 product shows only small changes in band positions and band intensity compared with the 23°C product. The 6620 product shows a major change in spectrum at 89°C, giving a pattern related to that of halloysite. Similar products have been obtained by Wada *et al.* (1988) and Farmer *et al.* (1991) from systems with Si:Al ratios near unity at 80–100°C and pH 8–9. The 6640 product at 89°C has developed a pattern like that of a poorly-crystallized nontronite, with a lattice OH-stretching band at 3535  $\text{cm}^{-1}$ , indicating layer-silicate formation. Weak hk reflections near 4.6 Å (02), 2.5 Å (20) and 1.52 Å (06) were given by the 6640 product, but not by the 6600 and 6620 products. No basal reflections were observed.

Figure 7 shows the spectra of the products at 89°C from systems 6604, 6624 and 6644, containing Mg and K. The spectra of all three products have bands near 1010, 685, and 465  $\text{cm}^{-1}$ , suggesting the formation of a trioctahedral layer-silicate structure, similar to that present in the 6204, 6224 and 6244 products (Figure 3). The spectra in Figure 7 all show additional broad hydroxyl absorption peaking at 3420–3450  $\text{cm}^{-1}$ , which can be ascribed to hydroxyl associated with the excess Al, Mg and Fe over that necessary to form the layer-

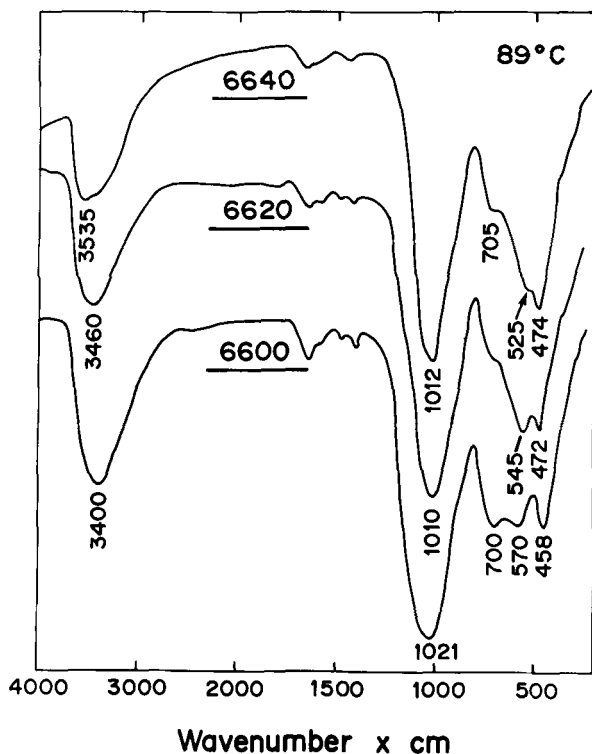


Figure 6. Infrared spectra of products from systems with starting ratios of Si:Al near 1, with or without added Fe as indicated in Table 1, and incubated at 89°C.

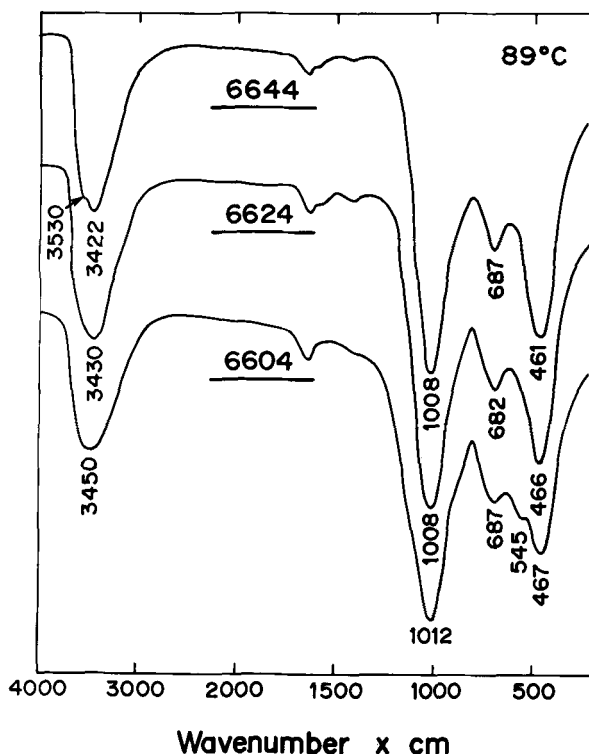


Figure 7. Infrared spectra of products from systems with starting ratios of Si:Al near 1, incorporating 1 mM of Mg and K, with or without added Fe as indicated in Table 2, and incubated at 89°C.

silicate structure. A well-defined shoulder at  $3530\text{ cm}^{-1}$  in the spectrum for the 6644 product could arise from dioctahedral sites in a layer silicate or from the hydroxide sheet of a chorite. The spectrum of the 6604 product shows an additional band at  $545\text{ cm}^{-1}$ , which may arise from a dioctahedral layer-silicate component. X-ray diffraction traces showed no basal reflections from these products, but  $hk$  reflections of a layer silicate were clearly present at  $4.45\text{ \AA}$  (02),  $2.55\text{ \AA}$  (20) and  $1.53\text{ \AA}$  (06) in the XRD pattern (not shown) of the 6624 product.

The infrared spectra of products with starting Si:Al ratios 3:6 are shown in Figures 8–10. At  $23^\circ\text{C}$ , the presence of Mg and K had little effect on the products obtained, so only the products from systems 3600, 3620 and 3640 are shown in Figure 8. These spectra all show the general features of “protoimogolite” allophane (Farmer *et al.*, 1979), with maxima at  $969\text{--}979\text{ cm}^{-1}$ , a shoulder near  $700$ ,  $565\text{--}600\text{ cm}^{-1}$ , and a shoulder near  $440$  and  $350\text{ cm}^{-1}$ . It is uncertain whether the small displacements in band position can be ascribed to some substitution of iron into the “protoimogolite” structure. The apparent increase in intensity and displacement to lower frequencies of the  $600\text{ cm}^{-1}$  band with increasing iron in the system could arise from the presence of a separate hydrous ferric oxide phase.

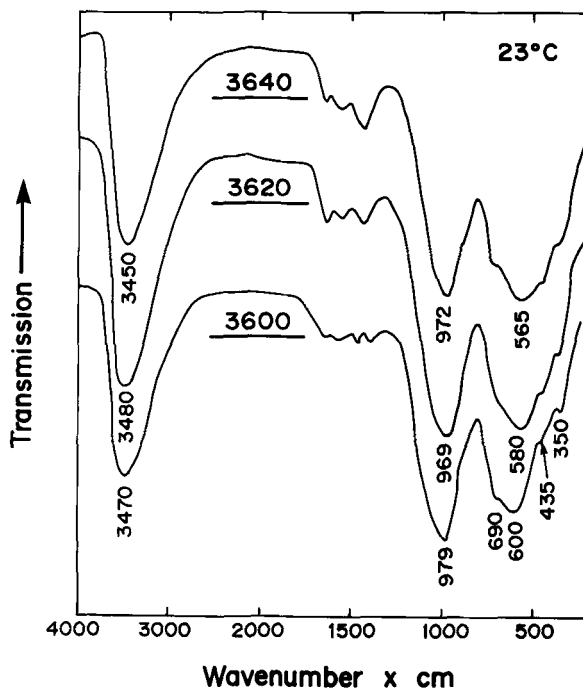


Figure 8. Infrared spectra of products from systems with starting ratios of Si:Al near 0.5, with or without added Fe as indicated in Table 1, and incubated at  $23^\circ\text{C}$ .

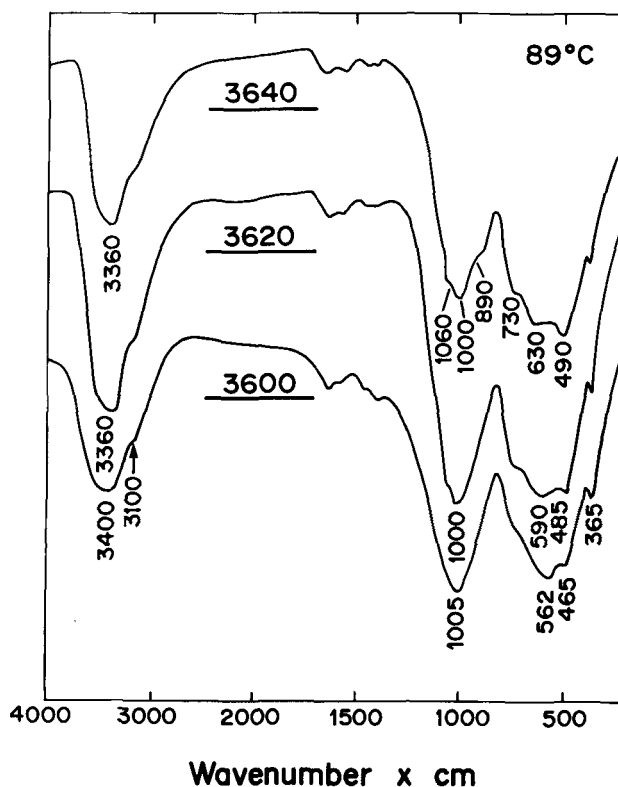


Figure 9. Infrared spectra of products from systems with starting ratios of Si:Al near 0.5, with or without added Fe as indicated in Table 1, and incubated at 89°C.

Figure 9 shows the spectra of the same systems, but at 89°C. Features assignable to boehmite are clearly present in the 3640 spectrum (a shoulder at 3100, 1060, 730, 630, and 365  $\text{cm}^{-1}$ ); some of these features are also detectable in the others. The separation of boehmite from the “protoimogolite” structure leaves a more silica-rich phase, possibly layer silicate as indicated by the shift in Si–O stretching frequency from about 975  $\text{cm}^{-1}$  at 23°C to 1000–1005  $\text{cm}^{-1}$  at 89°C in these samples. Because of the presence of boehmite absorption bands, it is difficult to distinguish the contribution of the silicate component to absorption in the 300–700  $\text{cm}^{-1}$  region, but changes in the absorption pattern with increasing Fe in the systems indicate some changes in the silicate structure and/or composition. It is possible to interpret the spectra as indicating that the 3600 product contains boehmite and “protohalloysite,” while the 3640 product contains boehmite and a nontronite-like layer silicate, but the results are not conclusive.

Figure 10 shows the spectra of products 3604, 3624 and 3644 at 89°C. Considerable amounts of magnesium were taken up by these materials, and all three show features assignable to a trioctahedral layer silicate at 1007, 687, and 478  $\text{cm}^{-1}$ . Traces of boehmite are indicated, principally by a weak, sharp peak or shoulder at 365  $\text{cm}^{-1}$ , and broad shoulder at 3100  $\text{cm}^{-1}$ .

None of the products with Si:Al ratios of 3:6 gave basal or hk reflections in the XRD patterns. A broad diffraction peak at 6.3 Å due to poorly crystalline boehmite was most obvious in the 3600 and 3604 traces (not shown).

## DISCUSSION

The present investigation shows that Fe is readily incorporated into the structure of aluminosilicate precipitates formed at 23°C and a pH near 8 in the presence of Fe(II), and in systems with Si:Al ratios of unity or more. The limiting factor may be the free silicic acid concentration, which exceeded 100  $\mu\text{M}$  in the supernatant of precipitates incorporating Fe in their structure (Table 1). Below this concentration “protoimogolite” is formed (Farmer *et al.*, 1991), which does not readily incorporate Fe (McBride *et al.*, 1984). In the absence of Fe(II), the hydrous feldspathoid structure is formed when Si in solution exceeds about 120  $\mu\text{M}$  (Farmer *et al.*, 1991). In the presence of Fe(II) either Fe-substituted hydrous feldspathoids or a nontronite-like layer-silicate structure was indicated by infrared spectra. The layer-silicate structure was formed when Fe:Al exceeded unity, and when free Si concentrations exceeded 280  $\mu\text{M}$  (Table 1). It is as yet uncertain whether either or both of these factors are determinative.



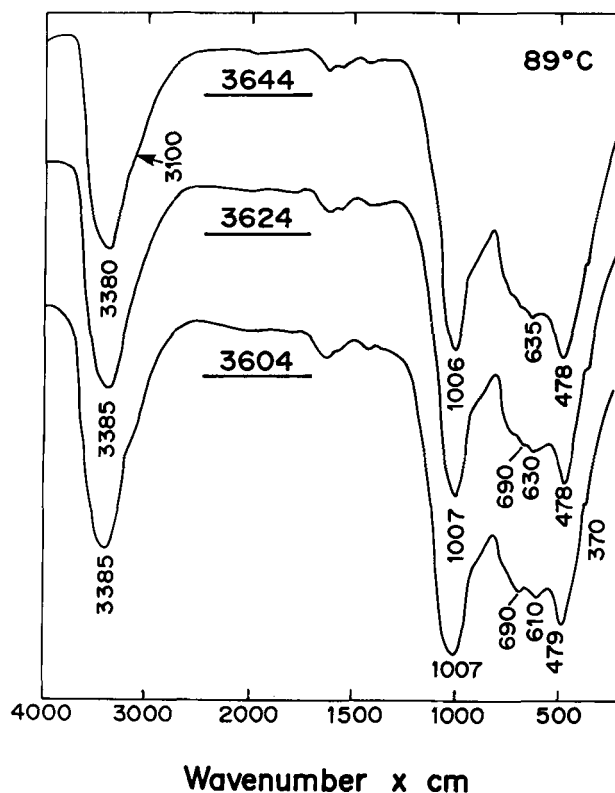


Figure 10. Infrared spectra of products from systems with starting ratios of Si:Al near 0.5, incorporating 1 mM of Mg and K, with or without added Fe as indicated in Table 2, and incubated at 89°C.

When these precipitates were digested at 89°C, nontronite, or products with nontronite-like IR spectra were obtained in all systems with Fe:Al exceeding 0.75. The best-crystallized product was obtained with an Fe:Al ratio near unity (1.02), and with a free Si concentration of 360  $\mu\text{M}$ . A "protohalloysite" was obtained from a system with an Si:Al ratio of 1.05 and an Fe:Al ratio of 0.37 at 89°C. Previously, Farmer *et al.* (1991) obtained "protohalloysite" under similar conditions in the absence of Fe, but in the present investigation little conversion of the hydrous feldspathoid product to "protohalloysite" occurred at 89°C in the absence of Fe. A possible explanation of the difference is that Farmer *et al.* (1991) precipitated their product by adding  $\text{CaCO}_3$ , so that the pH rose slowly to the final pH. This favored the precipitation of octahedral Al species and their 20°C product was a mixed "protoimogolite"-hydrous feldspathoid. In the present study the pH was adjusted rapidly with  $\text{Ca}(\text{OH})_2$  that favored the formation of tetrahedral Al species, and the precipitate contained little octahedral Al. Adding Fe to this system gave a product with a substantial octahedral Al content, as indicated by IR spectroscopy. Octahedral Al is the dominant form in "protohalloysite" (Wada *et al.*, 1988), and its presence in the initial precipitate may favor "protohalloysite" formation.

As a control, a system with an Si:Fe ratio of 3:2, but without Al was included in the present study. The nontronite obtained was less well-ordered than those obtained by Harder (1976) at 25°C and Decarreau and Bonnin (1986) at 75°C under somewhat different conditions. In contrast, the aluminous nontronite obtained here from a system with an Si:Al:Fe ratio of 3:1:1 at 89°C appeared better ordered than any previously synthesized below 100°C.

When 1 mM Mg and K were added to the above systems, neither was taken up by the precipitates formed at 23°C. Either a higher pH or a much higher Mg concentration would be necessary for incorporation of Mg in the 23°C precipitate (Decarreau, 1981). In these systems substantial amounts of Mg were incorporated into all precipitates digested at 89°C, and their infrared spectra showed the development of trioctahedral silicate layers with substantial incorporation of Al and/or Fe into their structure. Particularly well-crystallized species were formed at the highest Si:Al and Si:Fe ratios. These included saponites, and a regular mixed-layer saponite-chlorite with unusual basal reflections. In systems with lower Si:Al ratios, the excess sesquioxides probably prevented the regular alignment of the layers necessary for basal reflections. A previous study of similar Fe-free systems showed only the initiation

of trioctahedral silicate layers in systems heated to 80°C. The marked improvement in crystallinity of the products at 89°C indicates a high energy of activation for the incorporation of Mg into the products. It seems likely, therefore, that the formation of trioctahedral Mg-rich layer silicates at 20°C will be extremely slow.

### CONCLUSIONS

The data indicate that Fe(II) in a calcareous environment will inhibit the formation of feldspathoids and promote layer silicate formation in aluminosilicate precipitates under soil conditions. This is consistent with the widespread occurrence of a ferruginous beidellite in vertisols (Duchaufour, 1982). The presence of Fe(II) may also allow the crystallization of mixed Mg-Fe trioctahedral layer silicates under less concentrated or less alkaline conditions than would be required for a pure Mg form, although this has not been proven in the present investigation.

### ACKNOWLEDGMENTS

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