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SYNTHESIS OF 1:1 AND 2:1 IRON PHYLLOSILICATES AND CHARACTERIZATION OF THEIR IRON STATE BY MÖSSBAUER SPECTROSCOPY

TADASHI MIZUTANI,[1] YOSHIAKI FUKUSHIMA, AKANE OKADA, OSAMI KAMIGAITO,
AND TAKAYUKI KOBAYASHI[2]

Toyota Central Research and Development Labs, Inc., Nagakute, Aichi-gun 480-11, Japan

[2] Department of Physics, Shiga University of Medical Science
Ohtsu-shi, Shiga 520-21, Japan

Abstract—Iron phyllosilicates with 1:1 and 2:1 layer structures were prepared from silicic acid, ferrous sulfate and sodium hydroxide. Hydrothermal treatment at 100–200°C of a reaction mixture with an initial Fe/Si ratio of 1.5 gave the 2:1 iron phyllosilicate, whereas a Fe/Si ratio of 2.25 gave the 1:1 phyllosilicate. The ^{57}Fe Mössbauer spectroscopy showed that 60% of the iron in the 1:1 phyllosilicate is ferrous, versus only 3% in the 2:1 phyllosilicate. The values of quadrupole coupling showed that the iron-oxygen tetrahedra and octahedra in the 2:1 phyllosilicate were more deformed than those in the 1:1 phyllosilicate.

Key Words—Iron, Mössbauer spectroscopy, Phyllosilicate, Synthesis.

INTRODUCTION

Iron phyllosilicates or iron-containing clay minerals have been studied for their oxidation-reduction reactions (Rozenson and Heller-Kallai, 1976a, 1976b; Russell *et al.,* 1979; Stucki *et al.,* 1984a, 1984b; Wu *et al.,* 1989), their catalytic and adsorption properties (Fanale and Cannon, 1979; Heller-Kallai *et al.,* 1984; Wang and Huang, 1989), and their magnetic properties (Coey *et al.,* 1982; Gangas *et al.,* 1985). Because iron has two common oxidation states (ferrous and ferric), and a ferric ion shows two common coordination numbers (fourfold and sixfold), the crystallization of iron silicates and iron-containing phyllosilicates is complex and difficult to control (Roy and Roy, 1954; Harder, 1973, 1977, 1989; Petit and Decarreau, 1990). A detailed phase equilibrium diagram of iron silicates studied by Flaschen and Osborn (1957), shows that a 1:1 layer silicate (greenalite) was formed at 220–250°C and a 2:1 layer silicate (minnesotaite) was formed at 470–480°C. Harder (1977) reported that iron phyllosilicate formed at 20°C from dilute aqueous solutions of silicic acid (20 ppm) and iron (7.5 ppm).

We have studied the copolymerization reaction of transition metal ions (Mn, Fe, Co, and Ni) and silicic acid under alkaline conditions. We found that iron and nickel ions gave distinctly crystallized phyllosilicates (Mizutani *et al.,* 1990), whereas manganese and cobalt ions gave poorly crystallized products. The selective synthesis of iron phyllosilicates was accomplished by controlling the metal ion-to-silicon ratio and hydroxide ion-to-metal ion ratio in the starting mixtures. The oxidation state and coordination number of the iron in the reaction products are based on Mössbauer spectroscopic studies.

EXPERIMENTAL

Preparation of 1:1 iron phyllosilicate

Sodium orthosilicate hydrate (4.35 g, Nacalai Tesque) was dissolved in 420 ml of distilled water and the solution acidified by the addition of 0.5 M sulfuric acid to pH 3. Atomic absorption spectroscopy showed that the concentration of silicic acid in the solution was 45 mM. Ferrous sulfate heptahydrate (11.83 g; Fe/Si ratio of 2.25) and sodium dithionite (4.2 g) were dissolved in this solution. To the clear solution we added 59.4 ml of 5 M sodium hydroxide (with an OH^-/Fe ratio of 7). The suspension was aged for one day at room temperature and heated at 150°C in a Teflon-lined autoclave for 50 hr. The product was then collected by suction filtration, washed with water, and dried in vacuo. The yield was 4.82 g.

Preparation of 2:1 iron phyllosilicate

In 420 ml of aqueous silicic acid (45 mM, prepared as above), we dissolved 3.94 g of ferrous sulfate heptahydrate (Fe/Si ratio of 0.75) and 4.2 g of sodium dithionite. To the clear solution we added 19.8 ml of 5 M sodium hydroxide solution (OH^-/Fe ratio of 7). The suspension was aged for one day, then subjected to hydrothermal treatment at 150°C for 50 hr. The product was suction filtered, washed with water, and vacuum dried. The yield was 2.25 g.

Measurements

Powder X-ray diffraction (XRD) was carried out on a Rigaku RAD-B diffractometer with Co-Kα radiation.

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[1] Present address: Department of Materials Science, Tottori University, Koyama-cho, Tottori 680, Japan.

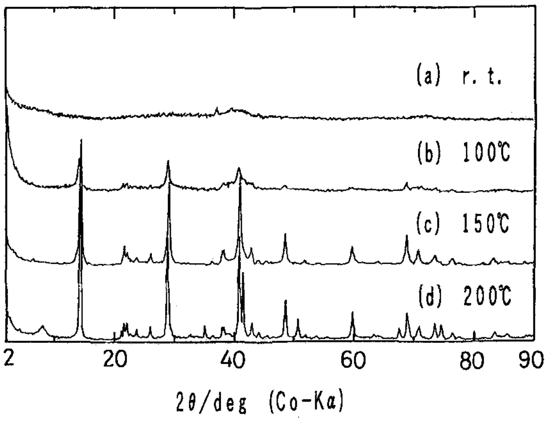

Figure 1. XRD patterns of the hydrothermal products at various reaction temperatures. The starting gels were prepared from 45 mM of $Si(OH)_4$, Fe/Si = 2.25 and OH^-/Fe = 7, and were heated for 50 hr.

Transmission electron microscopy was performed on a JEOL JEM-200 CX electron microscope at an accelerating voltage of 200 kV.

^{57}Fe Mössbauer spectra were recorded at 300 K and 95 K. A ^{57}Co/Rh source was used and velocity calibration was carried out with native iron.

RESULTS

The XRD patterns of the iron phyllosilicate products prepared at temperatures ranging from room temperature to 200°C are shown in Figure 1. The XRD peaks became sharper with increasing temperature up to 150°C, indicating that crystal growth is facilitated by heat treatment. At 200°C, the crystal size was almost the same as that at 150°C and the formation of iron oxide was observed. Therefore, 150°C appears to be the optimum reaction temperature for the synthesis of the iron phyllosilicate.

Table 1. Hydrothermal synthesis of iron phyllosilicates.

Run	Fe/Si	OH^-/Si	Reaction temp (°C)	Main product	By-product
1	0.75	3	150	—	
2	0.75	5	150	2:1	
3	0.75	7	150	2:1	
4	1.5	3	150	2:1	
5	1.5	5	150	2:1	1:1
6	1.5	7	150	2:1	1:1
7	2.25	3	150	1:1	
8	2.25	5	150	1:1	
9	2.25	7	150	1:1	
10	0.75	3	200	—	
11	0.75	5	200	2:1	
12	0.75	7	200	2:1	
13	1.5	3	200	2:1	iron oxide
14	1.5	5	200	2:1	1:1
15	1.5	7	200	2:1	1:1, iron oxide
16	2.25	3	200	1:1	iron oxide
17	2.25	5	200	1:1	2:1, iron oxide
18	2.25	7	200	2:1	1:1, iron oxide

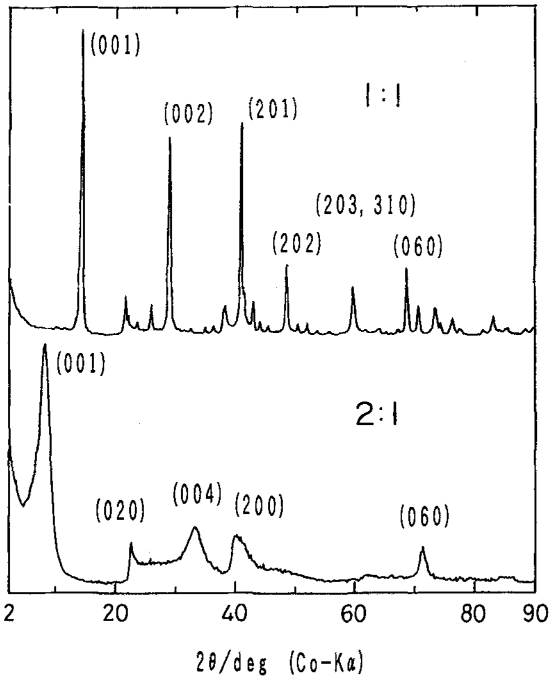

Figure 2. XRD patterns of products 1 and 2.

The reaction products prepared from starting mixtures with varying initial Fe/Si ratios and OH^-/Fe ratios are summarized in Table 1. The selectivity of the formation of 1:1 iron phyllosilicate (product 1) and 2:1 iron phyllosilicate (product 2) was determined by the initial Fe/Si ratios. At an Fe/Si ratio of 2.25, product 1 is the predominant form, whereas at an Fe/Si ratio of 1.5 or 0.75, product 2 is the main form. The XRD patterns of the two products are shown in Figure 2. The sharp XRD peaks for product 1 indicate a high degree of crystallinity for this material.

Figures 3 and 4 are transmission electron micrographs of products 1 and 2, respectively. All of the crystals of the 1:1 phyllosilicate are hexagonal platelets, whereas the 2:1 phyllosilicate particles do not exhibit any distinct shape (Figure 4). The selected area diffraction pattern of product 1 (Figure 5) indicates that the platelets are single crystals. Product 2 exhibited ring patterns by selected area electron diffraction, and this suggests the presence of many small crystallites in the particles. No amorphous phases were detected for either product by means of either XRD or electron microscopy.

The X-ray diffraction data indicate that the crystal structure of product 1 is orthorhombic, with a = 5.50 Å, b = 9.52 Å, and c = 7.14 Å. Table 2 lists the observed and calculated d values based on these lattice constants (Bailey, 1980). The lattice constants are 1.0–1.8% smaller than those of orthorhombic greenalite, a = 5.598 Å, b = 9.696 Å, c = 7.213 Å. This difference may be attributed to the fact that some of the iron of product

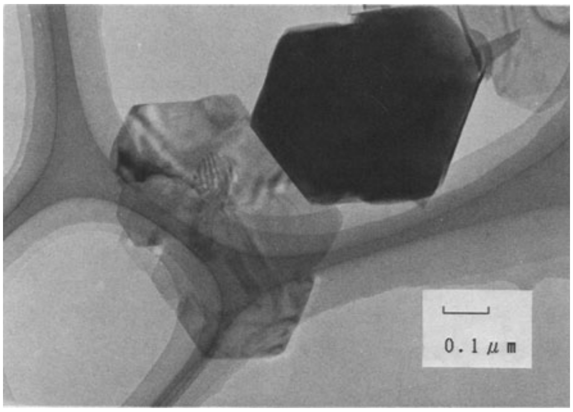

Figure 3. TEM photograph of product 1.

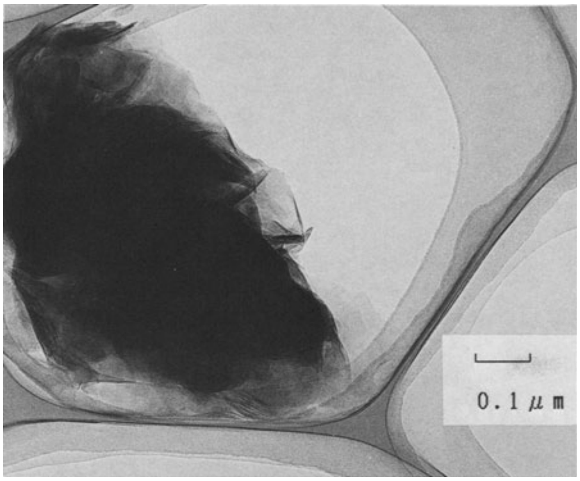

Figure 4. TEM photograph of product 2.

1 is ferric while most of the iron in greenalite is ferrous. The d(060) of product 2 is 1.542 ± 0.004 Å. This value is larger than that of nontronite [2:1 dioctahedral, d(060) = 1.51–1.52 Å].

Mössbauer spectra of products 1 and 2 recorded at 300 K and 95 K are shown in Figures 6 and 7, respectively. Values of isomer shift (IS), quadrupole splitting (QS), and line width (W) shown in Tables 3 and 4 were calculated by non-linear, least square curve fitting, assuming that each iron component exhibits two Lorentzian peaks. The isomer shift of the Mössbauer spectra of product 2 showed that the silicate is composed mostly of ferric ions. However, the values of the quadrupole coupling (Fe^{3+}, octahedral, 0.91–0.93 mm/s; tetrahedral, 0.83–0.84 mm/s) are larger than those for nontronite (Fe^{3+}, octahedral, 0.23–0.70 mm/s; tetrahedral, 0.43–0.74 mm/s) as reported by Goodman *et al.* (1976); Cardile and Johnston (1985); Johnston and Cardile (1985); Cardile *et al.* (1986); Luca and Cardile (1989). The Mössbauer spectra of product 1 indicates that 60% of the iron exists in the ferrous state. At 300 K the ferrous ion consisted of two components, one with a larger QS and the other with a smaller QS. These two components coalesced at 95 K and the isomer shift became larger.

Table 2. Observed and calculated d values of 1:1 phyllosilicate.

d(obs) Å	Intensity	(hkl)	d(calc) Å
7.161	100	001	7.14
4.762	14	020	4.76
		110	4.762
3.961	10	111	3.962
		021	3.961
3.572	65	002	3.570
2.744	9	200	2.75
2.563	70	201	2.566
2.443	12	211	2.478
2.38	5	003	2.38
		040	2.38
2.177	25	202	2.179
2.096	5		
1.797	16	203	1.800
		310	1.800
1.585	23	060	1.587
1.547	10	061	1.549
1.496	10	204	1.497
1.482	5		
1.448	6	062	1.450
1.347	7	401	1.350

DISCUSSION

The selectivity of 1:1 and 2:1 phyllosilicate formation was accomplished by controlling the Fe/Si ratio. The 2:1 phyllosilicate was formed preferentially even when the Fe/Si ratio was 1.5. For the synthesis of nickel phyllosilicate the same Ni/Si ratio gave 1:1 nickel phyllosilicate as a sole product (Mizutani *et al.*, 1990). Excess ferrous ion was needed to prepare the 1:1 iron silicate, a fact we attribute to the isomorphous substi-

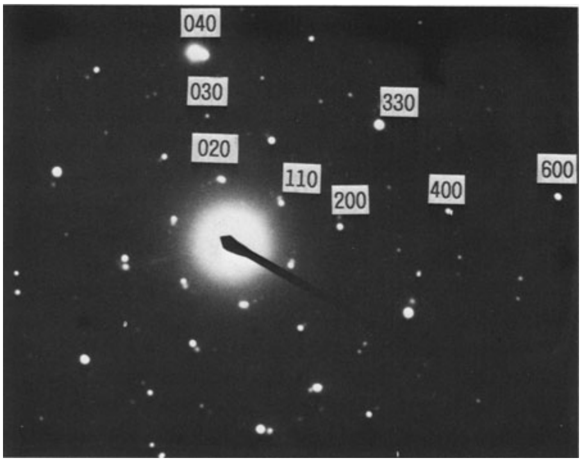

Figure 5. Electron diffraction pattern of product 1.

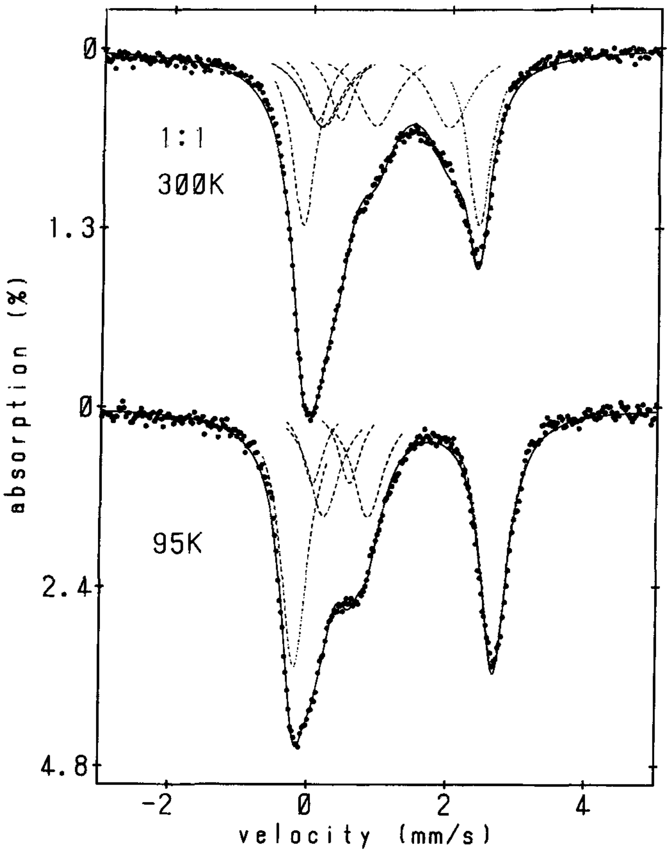

Figure 6. Mössbauer spectrum of product 1.

tution of ferric iron for silicon at tetrahedral sites. Nickel ion does not replace tetrahedral silicon due to its larger ionic radius, while ferric ion does. This isomorphous substitution is also supported by the results of Mössbauer spectroscopy.

As shown in Tables 3 and 4, the Mössbauer spectra are composed of components A, B, C and D. Components A and B can be ascribed from their isomer shifts to Fe^{3+}, whereas components C and D are ascribed to Fe^{2+}. The IS and QS values of component C are typical for Fe^{2+} in octahedral sites and are in agreement with those of greenalite (IS = 1.15 mm s^{-1} and QS = 2.75 mm s^{-1}) (Ballet and Coey, 1978).

There is a striking difference between products 1 and 2 with respect to the oxidation state of iron. The 1:1 phyllosilicate was found to be composed of 60% ferrous and 40% ferric ions, whereas the 2:1 phyllosilicate was composed of 3% ferrous and 97% ferric ions. Addition of 1% by weight of sodium dithionite did not prevent oxidation of the ferrous ion. Further studies will be necessary to clarify the possibility of controlling the oxidation state of iron in phyllosilicate synthesis.

There appear to be two ferric ion components for both products 1 and 2. Component A exhibits an IS value of 0.47–0.54 and component B a value of 0.23–0.31. Comparison with the IS values of nontronites

Table 3. Mössbauer parameters at 300 K.

Sample		IS mm·s^{-1}	QS mm·s^{-1}	Width mm·s^{-1}	Intensity %
1:1	A	0.52 ± 0.04	0.79 ± 0.07	0.70 ± 0.03	25.4
	B	0.23 ± 0.01	0.34 ± 0.02	0.44 ± 0.03	14.4
	C	1.14 ± 0.02	2.53 ± 0.01	0.42 ± 0.01	33.8
	D	1.06 ± 0.03	1.82 ± 0.07	0.73 ± 0.04	26.4
2:1	A	0.47 ± 0.01	0.93 ± 0.01	0.49 ± 0.01	42.4
	B	0.25 ± 0.01	0.83 ± 0.01	0.52 ± 0.01	54.0
	C	1.13 ± 0.02	2.06 ± 0.04	0.35 ± 0.05	3.6

Table 4. Mössbauer parameters at 95 K.

Sample		IS mm·s⁻¹	QS mm·s⁻¹	Width mm·s⁻¹	Intensity %
1:1	A	0.53 ± 0.02	0.63 ± 0.01	0.54 ± 0.03	28.3
	B	0.31 ± 0.01	0.53 ± 0.02	0.38 ± 0.03	13.7
	C	1.24 ± 0.01	2.87 ± 0.01	0.47 ± 0.01	58.0
2:1	A	0.54 ± 0.01	0.91 ± 0.01	0.55 ± 0.01	51.7
	B	0.27 ± 0.01	0.84 ± 0.01	0.51 ± 0.01	44.8
	C	1.22 ± 0.07	2.39 ± 0.13	0.50 ± 0.08	3.5

(Goodman *et al.*, 1976; Luca and Cardile, 1989) suggests that component A is an octahedral ferric ion, whereas component B is a tetrahedral ferric ion. The QS values of product 2 for both components A and B are larger than those of product 1. Thus, the electric gradient at the iron nucleus of product 2 proved to be larger than that of product 1. This suggests that the iron-oxygen tetrahedra and octahedra of product 2 are deformed more than those of product 1. The QS values of ferric ions for product 2 (0.8–0.9) are larger than those of nontronite (0.2–0.7). This suggests that the iron-oxygen tetrahedra and octahedra of product 2 are more highly deformed than those of nontronite. This deformation may be attributed to the rapid crystallization of the synthetic samples.

It should be noted that product 1 exhibited different spectra at 95 K and 300 K. Two ferrous ion states (components C and D) occur at 300 K, while one ferrous ion state (component C) occurs at 95 K. The occurrence of component D, observed at 300 K, is ascribed to the presence of the iron in a symmetrical environment. This observation suggests that by heating product 1 from 95 K to 300 K, the coordination sphere (of about 45% of ferrous ion, component D) became more symmetrical due to thermal fluctuation.

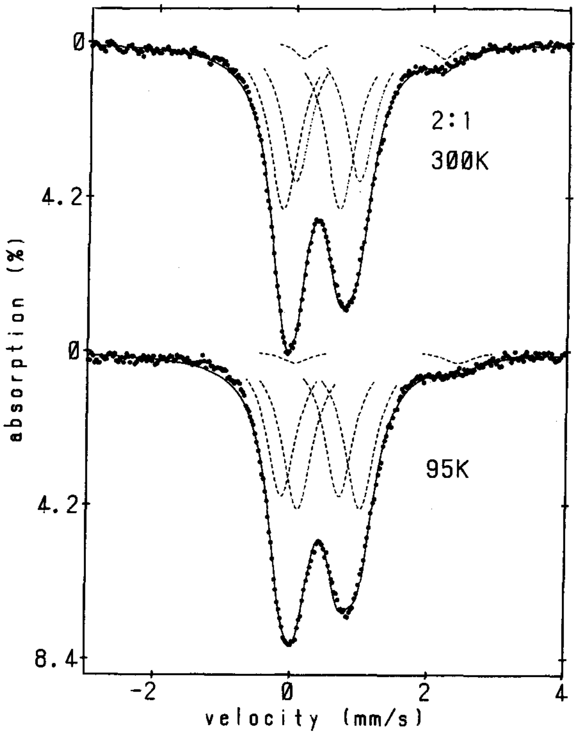

Figure 7. Mössbauer spectrum of product 2.

CONCLUSIONS

This study has demonstrated that the 1:1 and 2:1 iron phyllosilicates can be prepared selectively by controlling the Fe/Si ratio of the initial reaction mixtures. Mössbauer spectroscopic studies have suggested that a considerable amount of the iron was oxidized and some of the ferric ion occurs in tetrahedral sites. Control of the oxidation state of iron will be the subject of future studies.

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