Synthesis of Nickel and Magnesium Phyllosilicates with 1:1 and 2:1 Layer Structures

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Nickel and magnesium phyllosilicates with 1:1 and 2:1 layer structures were prepared from silicic acid and metal chlorides ($NiCl_2$ or $MgCl_2$) in water. The phyllosilicates were allowed to crystallize at room temperature or 200 °C. The 1:1 and 2:1 phyllosilicates were selectively prepared by adjusting the metal ion to silicon ratio (M/Si) in the starting mixtures. The 1:1 phyllosilicate was crystallized from the starting mixture with an M/Si ratio of 1.5 and the 2:1 phyllosilicate was crystallized from the mixture with an M/Si ratio of 0.5. The increase in the OH^-/M ratio in the starting mixture accelerated the crystallization to phyllosilicates. Crystallization to the phyllosilicates occurred even at room temperature, and a hydrothermal treatment at 200 °C accelerated this process. The crystal size of the 1:1 phyllosilicates was larger than that of the 2:1 phyllosilicates. The nickel phyllosilicates crystallized faster than the magnesium phyllosilicates. These results can be explained by assuming successive copolymerization reactions of silicic acid and aqua metal ions, in which an intermediate with a 1:1 structure is involved. The acidity of the aqua metal ions plays an important role in the mechanism of the copolymerization process.

Clay minerals have attracted much attention because of their interesting intercalation chemistry and characteristic surface properties. Applications to new materials[1] and novel reaction media[2–4] have recently been investigated with intense efforts. There should be crucial advantages to using synthetic clay mineral analogs over natural ones for such studies, since clay minerals with the desired chemical compositions and crystal or defect structures can be synthesized. It is known that under carefully controlled reaction conditions clay minerals can be allowed to crystallize even at room temperature.[5–7] We described the mechanism of copolymerization of silicic acid and metal ions in a previous paper.[8] Based on studies of the crystallization process of the metal silicate gels, it was recognized that controlling the nucleation (or the initial process of crystallization) is important for the selective synthesis of clay minerals. In this work we investigated the crystallization behavior of nickel and magnesium silicates at both room temperature and 200 °C.[9] We wish to report that the 1 : 1 and 2 : 1 nickel and magnesium phyllosilicates can be selectively prepared by controlling the copolymerization reaction of silicic acid and metal ions.

Experimental

Materials. Silicic acid was prepared by neutralizing an aqueous solution of sodium orthosilicate (Nacalai Tesque) with 2 M hydrochloric acid just before use. Nickel chloride and magnesium chloride were purchased from Wako Pure Chemical Industries, Ltd.

Preparation of Nickel Phyllosilicate with 1:1 Structure. Sodium orthosilicate (2.07 g) was dissolved in 200 ml of deionized water and 2 M[10] of hydrochloric acid (ca. 18 ml) was added to make the pH of the solution 3.0. Nickel chloride hexahydrate (3.21 g, Ni/Si=1.5) was dissolved in this clear solution.[11] This solution was mixed slowly with 40.5 ml of 1 M sodium hydroxide by a dropwise addition at a rate of 2—4 ml min^{-1} ($OH^-/Ni=3.0$). The obtained suspension was aged for 3 d at room temperature. A green precipitate was collected by suction filtration, and washed with distilled water. The product was dried in vacuo at 40 °C for 10 h (yield 1.53 g), and then studied by powder X-ray diffraction (XRD) with Co*K*α radiation and 1°—0.3—1° slits.

Preparation of Nickel Phyllosilicate with 2:1 Structure. An aqueous solution of silicic acid (45 mM, 200 ml) was prepared, as shown above, and 1.07 g of nickel chloride hexahydrate was dissolved (Ni/Si=0.5). This solution was mixed slowly with 22.5 ml of 1 M sodium hydroxide ($OH^-/Ni=5$). The obtained suspension was aged for 3 d at room temperature. A green precipitate was collected by suction filtration and washed with distilled water. The product was dried in vacuo at 40 °C for 10 h (yield 0.63 g).

Preparation of Nickel Phyllosilicate with 1:1 Structure under Hydrothermal Conditions. Nickel chloride hexahydrate (3.21 g, Ni/Si=1.5) was dissolved in 200 ml of an aqueous solution of silicic acid (45 mM), prepared as shown above. This solution was slowly mixed with 40.5 ml of 1 M sodium hydroxide ($OH^-/Ni=3$). The obtained suspension was aged for 3 d at room temperature, followed by a hydrothermal treatment in a teflon-lined autoclave at 200 °C for 50 h under autogeneous pressure. A green precipitate was collected by suction filtration and washed with distilled water. The product was dried in vacuo at 40 °C for 10 h (yield 1.50 g).

Preparation of Magnesium Phyllosilicate. Magnesium phyllosilicates were prepared in the same manner as shown above, except that magnesium chloride was used instead of nickel chloride.

Chemical Analysis. The amounts of Si, Ni, and Na of the nickel phyllosilicates were determined by gravimetric analysis, volumetric analysis, and atomic absorption spectroscopy, respectively, after the samples were dried at 110 °C for 3 h in air.

Results

Formation of Nickel Phyllosilicates at Room Tem-

perature. The XRD spectra of the products obtained from Ni/Si molar ratios of 1.5 and 0.5 and an OH^-/Ni molar ratio of 5.0 are shown in Fig. 1. These spectra exhibited the (020) peak at 4.5—4.6 Å, the (200) peak at 2.6 Å, and the (060) peak at 1.54 Å, indicating a phyllosilicate crystal structure, such as pecoraite.[12] There was also a peak in the low-angle region (7—16 Å) due to the (001) reflection. The values of *d*(001) varied with reaction conditions. Figure 2 shows the *d*-spacings of the (001) interlayer distances as a function of the Ni/Si and OH^-/Ni molar ratios of the starting mixtures. This figure indicates that the *d*(001) values are determined mainly from the Ni/Si molar ratio in the reaction mixtures. Thus, 1:1 phyllosilicate is formed from a Ni/Si ratio larger than 1.5 and 2:1 phyllosilicate from a Ni/Si ratio of about 0.5. The effects of the OH^-/Ni ratio are to improve the crystallinity of the products. Thus, a small value of the OH^-/Ni ratio, especially at a low Ni/Si ratio, gave amorphous nickel silicates. No formation of nickel hydroxide was detected by XRD, even when the Ni/Si ratio was 3.

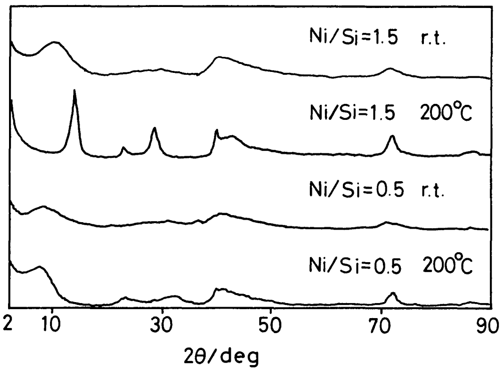

Fig. 1. X-Ray powder diffraction patterns (Co *Kα* radiation) of the nickel phyllosilicates prepared from a Ni/Si ratio 1.5 or 0.5 and an OH^-/Ni ratio 5.

Formation of Nickel Phyllosilicates at 200 °C. The values of the *d*(001) spacings of the products crystallized under hydrothermal conditions at 200 °C for 50 h are shown in Fig. 3. Under hydrothermal reaction conditions, the Ni/Si molar ratio was again the main factor governing the crystal structure of the products. Thus, 1:1 and 2:1 nickel phyllosilicates can be selectively prepared by choosing the Ni/Si molar ratios of the starting mixtures. Hydrothermal treatment accelerated the crystallization, and phyllosilicate crystals were obtained from the starting mixture with

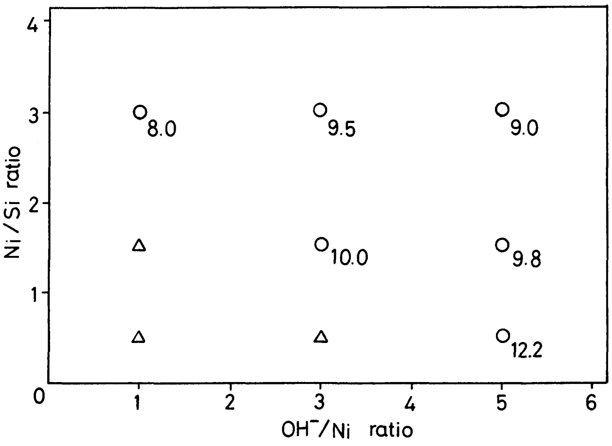

Fig. 2. Variation of *d*-spacings of (001) peaks (Å) as a function of OH^-/Ni ratios and Ni/Si ratios. The reaction was carried out at room temperature for 3 d. Triangles show that no (001) peak was observed.

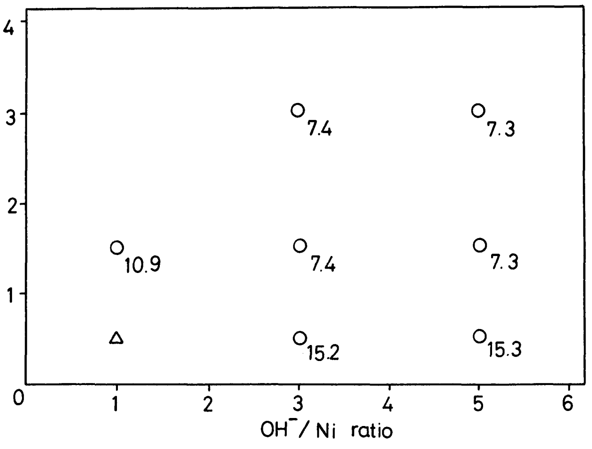

Fig. 3. Variation of *d*-spacings of (001) peaks (Å) as a function of OH^-/Ni ratios and Ni/Si ratios. The reaction was carried out at 200 °C for 50 h. Triangles show that no (001) peak was observed.

Table 1. Elemental Analysis (wt%) of Nickel Phyllosilicates[a]

Sample[b]	Temp.	Found/%			Calcd/%[a]			x[a]	n[a]
		Si	Ni	Na	Si	Ni	Na		
A	R.t.	12.9	42.5	1.0	13.7	41.7	1.0	0.09	1.73
B	R.t.	21.5	34.0	1.8	22.5	33.1	1.7	0.19	1.07
C	200 °C	14.3	46.6	0.2	14.7	45.7	0.2	0.02	0.18
D	200 °C	18.8	32.5	3.1	21.5	30.1	2.8	0.31	2.48

a) Theoretical atomic weight percentages were calculated from the formulas $Na_{2x}Ni_{(3-x)}Si_2O_5(OH)_4 \cdot nH_2O$ (for samples A and C; 1:1 type) and $Na_{2x}Ni_{(3-x)}Si_4O_{10}(OH)_2 \cdot nH_2O$ (for samples B and D; 2:1 type). b) Samples A, C: Ni/Si=1.5, OH^-/Ni=5.0 (molar ratios in the starting mixture), Samples B, D: Ni/Si=0.5, OH^-/Ni=5.0 (molar ratios in the starting mixture).

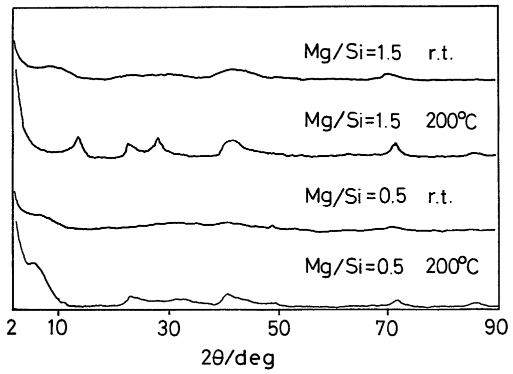

Fig. 4. X-Ray powder diffraction patterns (Co $K\alpha$ radiation) of the magnesium phyllosilicates prepared from a Mg/Si ratio 1.5 or 0.5 and an OH^-/Mg ratio 5.

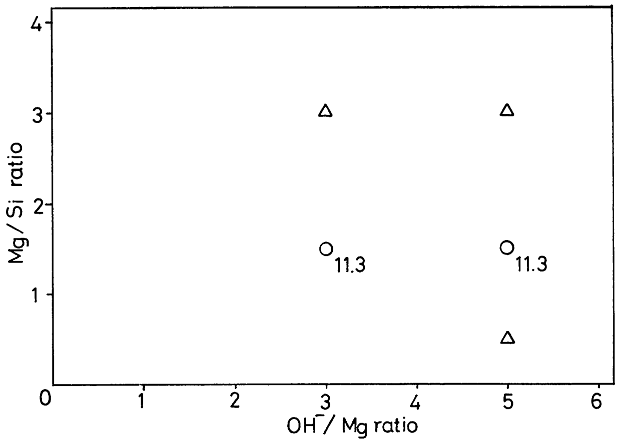

Fig. 5. Variation of d-spacings of (001) peaks (Å) as a function of OH^-/Mg ratios and Mg/Si ratios. The reaction was carried out at room temperature for 3 d. Triangles show that no (001) peak was observed.

an OH^-/Ni ratio of 3 and a Ni/Si ratio of 0.5, where only amorphous materials were obtained at room temperature (see Fig. 2). The XRD spectra show that nickel hydroxide was formed in addition to the phyllosilicates from the starting mixtures with a Ni/Si ratio of 3.0. No nickel hydroxide was detected when the Ni/Si ratio was 1.5. A narrower half width of the (001) peak in the XRD spectra of the 1:1 phyllosilicate than that of the 2:1 phyllosilicate indicates the larger crystal size of the former sample.[13]

Elemental Analysis of Nickel Phyllosilicates. The elemental analysis of the nickel phyllosilicates is listed in Table 1 along with the theoretical values calculated from the nickel phyllosilicate formulas, $Na_{2x}Ni_{3-x}Si_2O_5(OH)_4\cdot nH_2O$ (1:1 type) and $Na_{2x}Ni_{3-x}Si_4O_{10}(OH)_2\cdot nH_2O$ (2:1 type). The observed Ni/Si molar ratio was larger than the theoretical ratio for sample D (the 2:1 phyllosilicate prepared at 200 °C), indicating that the sample contained about 10 wt% of nickel hydroxide. Other samples also exhibited Ni/Si molar ratios larger than the theoretical values, indicating a small amount (3—6 wt%) of nickel hydroxide in the samples.

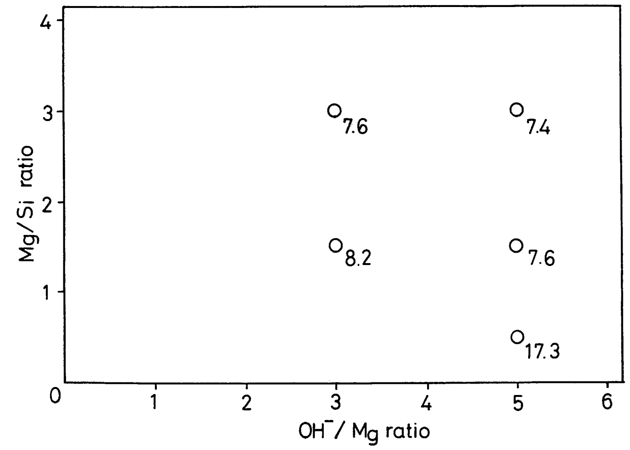

Fig. 6. Variation of d-spacings of (001) peaks (Å) as a function of OH^-/Mg ratios and Mg/Si ratios. The reaction was carried out at 200 °C for 50 h. Triangles show that no (001) peak was observed.

Formation of Magnesium Phyllosilicates at Room Temperature. Figure 4 shows the XRD spectra of the magnesium phyllosilicates prepared from the starting mixtures with a Mg/Si ratio of 1.5 or 0.5 and an OH^-/Mg ratio of 5. The d(001) spacings of the silicates that crystallized at room temperature are summarized in Fig. 5. Only the reaction conditions with a Mg/Si molar ratio of 1.5 gave a product with a distinct (001) peak. The products obtained from a Mg/Si ratio of 3 or 0.5 exhibited no (001) peaks, indicating that the formation of a layer structure was very slow.

Formation of Magnesium Phyllosilicates at 200 °C. The d(001) spacings of the magnesium phyllosilicates that crystallized under hydrothermal conditions are shown in Fig. 6. Phyllosilicates with the 1:1 structure formed from reaction mixtures with a Mg/Si molar ratio of 1.5 or larger, and phyllosilicates with the 2:1 structure formed from mixtures with a Mg/Si ratio of 0.5. The peak area of (001) of the magnesium phyllosilicates was smaller than that of the nickel phyllosilicates. This indicates that crystallization of the magnesium silicate is slower than that of the nickel silicate under hydrothermal conditions.

Discussion

Comparison between Nickel and Magnesium Phyllosilicate Formation. Although the ionic radii of nickel and magnesium ions are similar (Mg 0.65 Å, Ni 0.69 Å, 6-coordination[14]), their acidity strength is quite different ($\mathrm{p}K_1^*=12.2$—12.8 for the aquamagnesium ion and 6.5—10.6 for the aquanickel ion[15]). As shown in Figs. 2 and 5, the two ions exhibited a different crystallization profile at room temperature. The nickel phyllosilicates formed from the reaction mixtures with a wide range of Ni/Si ratios (0.5 to 3). However, magnesium phyllosilicate with a distinct (001) peak formed only from mixtures with a Mg/Si molar ratio of 1.5, and other Mg/Si ratios gave phyllosilicates with no (001) peaks in the XRD spectra. Under hydrothermal conditions at 200 °C, both nickel and magnesium ions gave 1:1 and 2:1 phyllosilicates, depending on the composition of the starting mixtures. Crystallization of the nickel phyllosilicates was faster than that of the magnesium phyllosilicates, both at room temperature and 200 °C. This difference can be attributed to a difference in the acidity of the aqua metal ions. A more acidic aquanickel ion has a stronger tendency to make bonds to oxygen, and an octahedral nickel oxide layer can form easily. We tentatively propose that this would help in the nucleation of phyllosilicate crystals. An aquamagnesium ion is less acidic and should be slow in making an octahedral magnesium oxide sheet.

Crystallization at Room Temperature. The selective formation of 1:1 and 2:1 phyllosilicates can be explained by considering copolymerization reactions in water. Because the aquanickel cation is a stronger acid than silicic acid,[8] the copolymerization reaction between silicic acid and the nickel ion can be initiated by a deprotonation of the aquanickel cation (Eq. 1). The deprotonated aquanickel cation is then condensed with silicic acid (Eq. 2), giving intermediate **1**:

$$\mathrm{Ni^{2+}\text{-}OH_2 + OH^- \longrightarrow Ni^{+}\text{-}OH + H_2O}, \qquad (1)$$

$$\mathrm{Ni^{+}\text{-}OH + Si\text{-}OH \longrightarrow \underset{\mathbf{1}}{Si\text{-}O\text{-}Ni^{+}\text{-}OH_2}}. \qquad (2)$$

If excess silicic acid is present, further condensation of intermediate **1** with silicic acid occurs upon the addition of a hydroxide ion (Eq. 3—4):

$$\mathrm{Si\text{-}O\text{-}Ni^{+}\text{-}OH + OH^- \longrightarrow Si\text{-}O\text{-}Ni\text{-}OH}, \qquad (3)$$

$$\mathrm{Si\text{-}O\text{-}Ni\text{-}OH + HO\text{-}Si \longrightarrow \underset{\mathbf{2}}{Si\text{-}O\text{-}Ni\text{-}O\text{-}Si} + H_2O}. \qquad (4)$$

This mechanism suggests that the Ni/Si ratio is the main factor determining which intermediate (**1** or **2**) is dominant after the initial copolymerization reactions have come to completion, provided that a sufficient amount of the hydroxide ion is present.

We assume that the structure of the first intermediate **1** is close to a 1:1 phyllosilicate for the following reasons: (1) The XRD spectra of the initial precipitates exhibited broad peaks ascribable to (200) and (060) of phyllosilicate structures.[16] (2) No other crystalline phase appeared in the reactions. Based on this assumption we can estimate the critical Ni/Si ratios from the stoichiometric ratios in the crystals. The stoichiometric ratio of the formation of a 1:1 nickel phyllosilicate is

$$\mathrm{Si(OH)_4 : Ni^{2+} : OH^- = 2:3:6 \ (Ni/Si = 1.5)},$$

and that of a 2:1 phyllosilicate is

$$\mathrm{Si(OH)_4 : Ni^{2+} : OH^- = 4:3:6 \ (Ni/Si = 0.75)}.$$

If the Ni/Si ratio is higher than 1.5, all silicic acid will be consumed in the reaction (Eq. 2), and intermediate **1** forms predominantly. Therefore, 1:1 phyllosilicate will be selectively crystallized. On the other hands, if the Ni/Si ratio is lower than 1.5, silicic acid is still available after the reaction (Eq. 2) has come to completion, making the reaction (Eq. 4) proceed. When the Ni/Si ratio is about 0.75, intermediate **2** forms predominantly, and the final product is a 2:1 nickel phyllosilicate.

These conclusions are consistent with the observed results that the 1:1 phyllosilicate is formed from a Ni/Si ratio of 1.5 and the 2:1 phyllosilicate is formed from a Ni/Si ratio of 0.5.

In contrast to the nickel ion, the magnesium ion gave poor crystals of silicates at room temperature from most starting mixtures, except for a Mg/Si molar ratio of 1.5. This can be attributed to the difference in the reaction mechanism of the copolymerization processes. Thus, the copolymerization between magnesium and silicic acid is initiated by the formation of a silicate anion[8] which can be condensed with silicic acid as well as aquamagnesium ion. We suggest that this competitive reaction tends to proceed to give a non-crystalline silicate.

Crystallization at 200 °C. Under hydrothermal conditions at 200 °C, both the 1:1 and 2:1 phyllosilicates can be selectively prepared by adjusting the M/Si ratio of the starting mixtures to the stoichiometric ratios. It should be noted that the crystal size of the 1:1 phyllosilicate is larger than that of the 2:1 phyllosilicate. This also supports the idea that the 1:1 type intermediate forms first during the initial copolymerization process. At 200 °C the crystallization of nickel phyllosilicates is faster than that of the magnesium analogs. These results indicate that control of the structure of intermediates formed during the initial step of copolymerization is important for the following hydrothermal crystallization.

Conclusion

Nickel phyllosilicates were prepared by the reaction of silicic acid, nickel chloride, and sodium hydroxide. The Ni/Si molar ratios in starting mixtures of 1.5 or larger lead to 1 : 1 phyllosilicate, while a Ni/Si ratio of 0.5 lead to 2 : 1 phyllosilicates. The 1 : 1 phyllosilicate was larger than the 2 : 1 phyllosilicate in crystal size. An increase in the OH^-/Ni ratio accelerated the crystallization, but showed no effects on the selectivity of the crystal structure. The effects of the M/Si ratio on the selectivity of the crystal structure can be explained by a mechanism in which a 1 : 1 nickel silicate is the intermediate of copolymerization. Though magnesium phyllosilicate was similarly obtained at room temperature, the reaction conditions giving phyllosilicates were more limited and the crystallization was slow. Hydrothermal treatment accelerated the crystallization of both nickel and magnesium phyllosilicates. M/Si ratios larger than 1.5 lead to 1 : 1 phyllosilicate, while an M/Si ratio of 0.5 lead to 2 : 1 phyllosilicates. At room temperature and 200 °C, the magnesium phyllosilicates crystallized slower than did the nickel phyllosilicates.

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10) M=mol dm^{-3}.

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12) G. T. Faust, J. J. Fahey, B. Mason, and E. J. Dwornik, *Science*, **165**, 59 (1960).

13) Transmission electron microscopy studies showed that the 1 : 1 phyllosilicates crystallized at 200 °C were cylindrical rolls with the inner diameters ranging 90—180 Å, the outer diameters 200—400 Å, and the lengths 700—2500 Å. Details will be reported elsewhere.

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16) The initial precipitates prepared from a mixture ($Si(OH)_4$ 45 mM, Ni/Si=1.5 and OH^-/Ni=5) exhibited broad peaks centered at 8.4 Å, 2.6 Å, and 1.53 Å in the XRD spectrum.