

## Mn-smectites: Hydrothermal synthesis and characterization

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Received 20 November 2006; accepted 31 January 2007

### **Abstract**

Three varieties of Mn-smectites (hectorite, stevensite and saponite) were hydrothermally synthesized for the first time using silicic acid,  $\text{MnCO}_3$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  mixed with aqueous solutions of NaOH or LiOH. The starting materials were treated in the temperature range of 125-200°C for 72-168 h and the best synthesis temperature was found to be 175°C. A lower Mn/Si molar composition than stoichiometric ideal composition was found to be most effective for the formation of almost pure and crystalline phases, apparently high Si is needed for their stability.

Powder X-ray diffraction (XRD) and thermal properties of the Mn-hectorite product have been investigated and compared to those of Zn-hectorite, which was previously synthesized by us. Manganese hectorite showed slightly larger expandability upon glycerol treatment and lower dehydroxylation temperature in the range of 300 - 450°C by DTA and TG as compared to Zn- hectorite.

*Keywords:* Manganese-smectites; Manganese-hectorite; Manganese-stevensite;  
Manganese-saponite; Hydrothermal synthesis

## 1. Introduction

Manganese is a minor component of naturally occurring trioctahedral clay minerals with the exception of a few rare minerals such as Mn-chlorite of pennantite or grovesite (Peacor et al., 1974), Mn-rich serpentine of kellyite (Peacor et al., 1974) and Mn-mica of shirozulite (Ishida et al., 2004). Manganese-rich smectite is also of extremely rare occurrence in nature although Nahon et al., (1982) described a sample with  $\text{Ca}_{0.05}(\text{Mn}^{2+}_{2.38} \text{Mg}_{0.30} \text{Fe}^{3+}_{0.004} \text{Cr}^{3+}_{0.007} \text{Al}_{0.20})(\text{Si}_{3.92} \text{Al}_{0.08}) \text{O}_{10}(\text{OH})_2$  in an initial weathering stage of tephroite (Mn-olivine) under tropical conditions. Even though smectites with transition metals such as Zn, Co, Ni, etc. as the predominant octahedral cations are rare in nature, they have been synthesized in the laboratory (Decarreau, 1985; Usui et al., 1985; Bruce et al., 1986; Urabe et al., 1989; Luca et al., 1992; Yamada et al., 1994; Xiang and Villemure, 1996; Klopogge et al., 1999). Low temperature hydrothermal synthesis of micas with Zn in octahedral sheets was reported by Perrotta and Garland (1975) and Komarneni and Newalkar (2003). Higashi et al. (2002) hydrothermally synthesized Zn-smectites in the temperature range of 100-125°C indicating preferred incorporation of Zn in octahedral sites as compared to Cu, Co or Ni. To the best of the authors' knowledge, syntheses of Mn containing smectites have not been reported probably because of the difficulty in controlling the oxidation state of Mn. Here we report for the first time the syntheses of several Mn-smectites under mild hydrothermal conditions.

## 2. Materials and methods

Manganese-smectites of the following ideal formulas were tentatively synthesized in this study: Mn-hectorite:  $\text{Na}_{0.4}\text{Mn}_{2.6}\text{Li}_{0.4}\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ ;

Mn-stevensite:  $\text{Na}_{0.4}\text{Mn}_{2.8}\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ ;

Mn-saponite:  $\text{Na}_{0.4}\text{Mn}_3(\text{Si}_{3.6}\text{Al}_{0.4})\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ .

The starting materials were solid mixtures (0.3-0.5g) + alkaline aqueous solutions (18 mL) given below. The silica source is silicic acid (containing 81.4%SiO<sub>2</sub>, Aldrich Chemicals Co.). Manganese sources are MnO<sub>2</sub>, MnCl<sub>2</sub> · 4H<sub>2</sub>O, MnCO<sub>3</sub>, and Mn(CH<sub>3</sub>COO)<sub>2</sub> · 4H<sub>2</sub>O. Aluminum source is Al(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O, sodium source is 0.2% NaOH solution and lithium source is 0.1% LiOH solution. The different molar ratios of solid chemicals and aqueous solutions of NaOH or LiOH (see Tables 1-3) were mixed in a Teflon cup of 30 mL capacity (60% filling) and were hydrothermally treated in stainless steel hydrothermal vessels in the temperature range of 100-250 °C for 72-168 h under autogeneous pressure. After the various hydrothermal treatments, the solid and solution phases were separated by centrifugation and the solid was repeatedly washed with deionized water to remove any remaining soluble salts. The synthetic solid samples were dried in an oven and subsequently investigated to determine crystallinity and phase purity using a Rigaku X-ray diffractometer with Cu K $\alpha$  radiation. The X-ray diffraction (XRD) data were obtained using oriented samples prepared on glass slides in the 2  $\theta$  range of 2-40° at a scanning speed of 2° min<sup>-1</sup>. The Mn-hectorite was also characterized by XRD after heat treatment at 300°C and after glycerol solvation at room temperature to determine the collapse and swelling properties of this synthetic clay. No attempts were made to control the humidity of the atmosphere during XRD. This product was also

characterized by differential thermal analysis (DTA) and thermogravimetric (TG) analysis using a Rigaku DTA-TG simultaneous apparatus. For DTA-TG experiments, twenty mg of sample was heated from room temperature to 1000°C at a heating rate of 10 °C min<sup>-1</sup>.

Morphological aspects and phase purity of the crystallized Mn-hectorite product were investigated by scanning electron microscope (SEM) observation using a JSM-6500F equipped with a EDS analyzing system.

### **3. Results and discussion**

#### *3.1. Synthesis of Mn-hectorite*

The various synthetic preparations of Mn-hectorite are given in Table 1 along with different synthetic parameters such as starting compositions, sources of Mn and temperature and duration of treatment. These results reveal that the best Mn source to prepare Mn-hectorite is Mn carbonate in the temperature range of 125 - 200°C. Soluble Mn sources such as Mn chloride and acetate did not yield Mn-hectorite probably because of the oxidation of Mn before the hectorite had started to form. This result is consistent with the result of MnO<sub>2</sub> as a precursor, which had Mn in tetravalent state to begin with and hence did not yield any Mn-hectorite (Table 1). The use of relatively insoluble Mn carbonate, on the other hand, yielded Mn-hectorite as this source of Mn supplied mainly Mn<sup>2+</sup> and probably some Mn<sup>3+</sup> slowly to the reactants during crystallization reaction. Thus the key to the synthesis of Mn-hectorite appears to be the availability of Mn<sup>2+</sup> during the hydrothermal reaction. Mn remained in divalent state with the use of Mn carbonate but not with Mn chloride or acetate. This result is supported by the natural

occurrence of regularly interstratified chlorite-smectite minerals with varying MnO contents (0.1-11.9 wt.%), which are associated with carbonates such as calcite ( $\text{CaCO}_3$ ) and rhodochrosite ( $\text{MnCO}_3$ ) in some gold-silver vein-type deposits in Japan (Yoneda and Watanabe, 1989). Peacor et al. (1974) also demonstrated that Mn-serpentine (kellyite) occurs within Mn carbonates in close association with Mn-chlorite (grovesite) at the Bald Knob manganese mine, North Carolina.

Relatively crystalline Mn-hectorite could be synthesized at 175°C but not at 100, 125, 150, 200 and 250°C after treatment for 72 h (Figure 1). However, there is still some unreacted Mn carbonate coexisting with Mn-hectorite after 72 h of hydrothermal treatment at 175°C. Increasing the duration of hydrothermal treatment to 168 h yielded somewhat better crystallized Mn-hectorite although trace amounts of Mn carbonate still persisted when stoichiometric Mn:Si ratio was used (Fig.2; see patterns for H-225 and H-227). The use of lower Mn:Si ratio as in the case of H-226 and H-228 samples yielded the most crystalline Mn-hectorite with no detectable amounts of Mn carbonate (Fig. 2; Table 1) at 150 and 175°C, respectively. Thus apparently pure phases of Mn-hectorite were obtained by using a lower Mn:Si ratio than a stoichiometric ratio (Fig. 2).

### *3.2. Synthesis of Mn-stevensite*

Various syntheses of Mn-stevensite are given in Table 2. Mn-stevensite could only be synthesized from Mn carbonate as a Mn precursor but not from  $\text{MnO}_2$ ,  $\text{MnCl}_2$  or Mn acetate. These results are consistent with the syntheses of Mn-hectorite and can be explained in the same fashion i.e., Mn carbonate was able to supply  $\text{Mn}^{2+}$  ions during the synthesis while other sources apparently oxidized immediately and hence  $\text{Mn}^{2+}$  was

unavailable for the formation of Mn-stevensite. At 175°C, Mn-stevensite could be synthesized with stoichiometric or lower Mn:Si ratio after 72 h treatment (Table 2; Fig. 3). However, with stoichiometric Mn:Si ratio, a small amount of MnCO<sub>3</sub> persisted at 175°C but not with a sample prepared from lower than stoichiometric Mn:Si ratio (Fig. 3). Treatment for a longer duration of 168 h yielded somewhat better crystallized Mn-stevensite with both stoichiometric as well as lower Mn:Si ratio at 175°C (Figs. 3 and 4). Apparently pure Mn-stevensite without any detectable Mn carbonate was obtained with a smaller than stoichiometric Mn:Si ratio (Figs. 3 and 4). These results of Mn-stevensite syntheses are similar to those of Mn-hectorite (*vide supra*). At a temperature of 150°C or 200°C, only a small amount of poorly crystallized Mn-stevensite formed after 72 h treatment with either stoichiometric or lower Mn:Si ratio (Fig. 3). Thus a temperature of 175°C appears to be better suited for the synthesis of Mn-stevensite under these hydrothermal conditions.

### *3.3. Synthesis of Mn-saponite*

We also attempted to synthesize two Mn-saponite samples, one with stoichiometric Mn:Si ratio and the other with lower than stoichiometric Mn:Si ratio at 175°C for 72 h (Table 3 ; Fig. 5). The latter sample was slightly better crystallized than the former sample (Fig. 5). Again, these results are consistent with those of Mn-hectorite and Mn-stevensite syntheses as better crystallized phases were obtained with lower than stoichiometric Mn:Si ratios in the case of Mn-saponite also (Fig. 5). Small amounts of Mn carbonate, however, persisted in both synthesis products of Mn-saponite (Fig. 5).

### *3.4. Characterization of Mn-hectorite product*

Among the many synthetic samples of Mn-smectites, the Mn-hectorite product of H-228 prepared with a initial ratio of Na:Mn:Li:Si= 0.4:1.3:0.4:4.0 at 175 °C for 168 hours is the best crystallized and apparently pure by XRD investigation. This product was used for further mineralogical characterization.

### *3.5. Expansion-collapse and thermal properties*

Fig. 6 shows the XRD patterns of air dried, heated and glycerol solvated Mn-hectorite. The air dried sample showed a broad 13.8 Å peak which collapsed to a slightly sharper 9.9 Å peak upon heat treatment at 300°C for 1 h. When the air dried sample was solvated with glycerol, it expanded to 22.6 Å which is a greater expansion than that of Zn-hectorite previously synthesized by us (Higashi et al., 2002). The larger expansion of the Mn-hectorite upon glycerol solvation may reflect a lower charge density (Komarneni and Breval, 1985).

The differential thermal analysis and thermogravimetric analysis for the Mn-hectorite product are given in Fig. 7. When compared to Zn-hectorite (Higashi et al., 2002), the dehydroxylation of Mn-hectorite occurred in a lower temperature range of 300-450 °C as evident in TG although the corresponding endothermic reaction is not well developed in DTA. The Mn-hectorite showed a recrystallization temperature of 761°C, which is comparable to 770°C of Zn-hectorite. The Mn-hectorite showed a sharp endotherm at 755°C immediately before recrystallization unlike the Zn-hectorite (Fig. 7).

### 3.6. SEM observation

SEM observation of the Mn-hectorite product (sample H-228) indicates that starting materials of both silicic acid and Mn carbonate still remained in small amounts, which could not be detected by XRD. Silicic acid is of irregular form with smooth surface like that of fragmented glass and Mn carbonates consists of peculiar aggregates formed from very small platy grains (Fig. 8a). Manganese-hectorite is predominant and has been crystallized as thin lamellar flakes, which aggregated to give particles of up to 100  $\mu$  m in lateral dimension (Fig. 8a). A detailed structure of these lamellar aggregates of Mn-hectorite could be seen in Fig. 8b. These starting materials and synthetic phases were also effectively distinguished by optical microscopy: silicic acid is colorless while both Mn carbonate and Mn-hectorite are brown. Manganese-hectorite product is brightly colored with lower refractive index compared to Mn carbonate.

Unfortunately, completely pure Mn-smectites were not obtained in this study. More prolonged reaction time greater than 168 h (7 days) may be required for obtaining pure phases.

## 4. Conclusions

Mn-smectites (hectorite, stevensite and saponite) were hydrothermally synthesized for the first time. The main key for Mn-smectite synthesis was the use of Mn carbonate as a Mn source during the hydrothermal synthesis.

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# Mn-hectorite [Mn:Si=2.6:4.0]

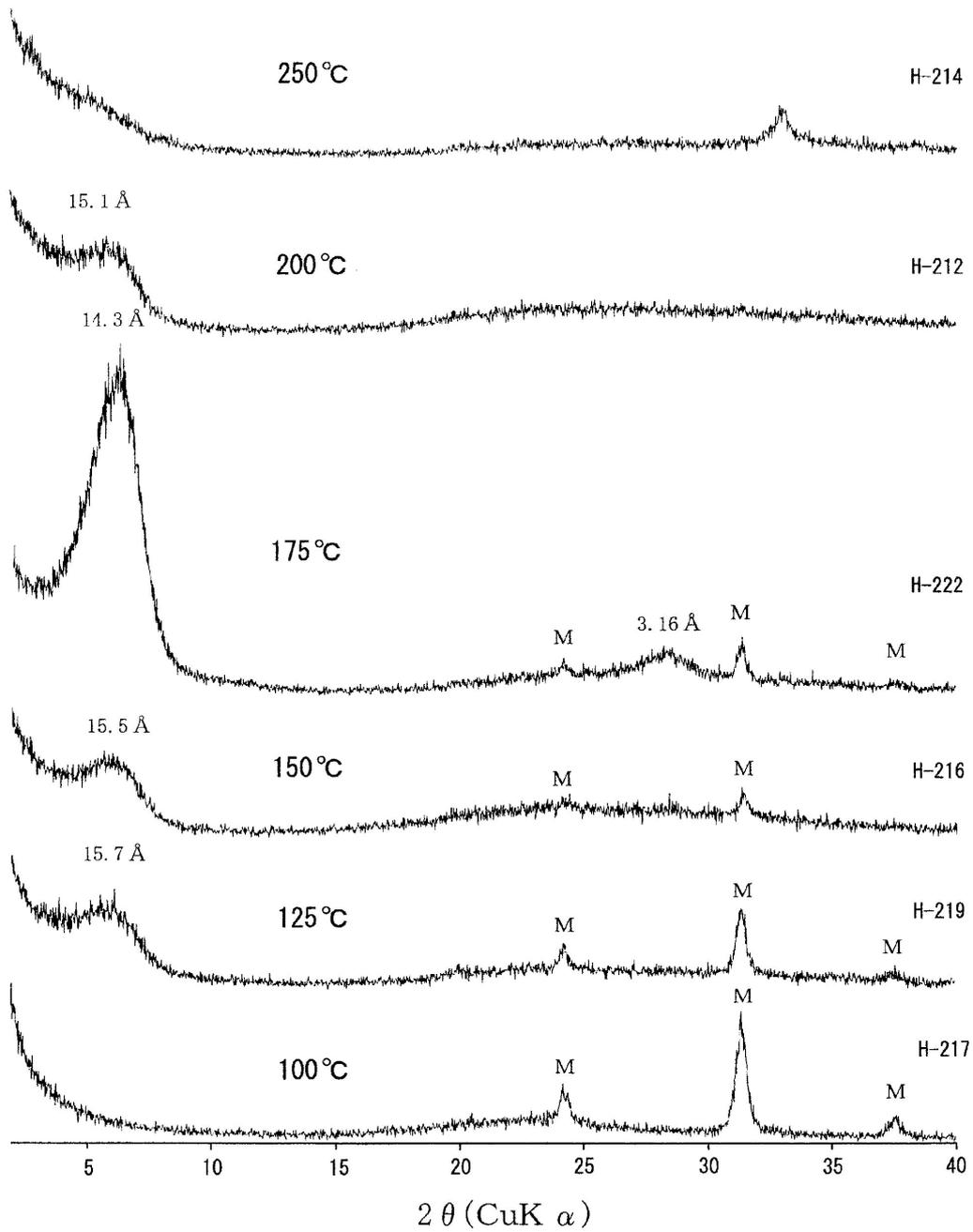


Fig. 1. XRD of synthetic Mn-hectorite specimens prepared at different temperatures for 72 h. M=MnCO<sub>3</sub>.

# Mn-hectorite

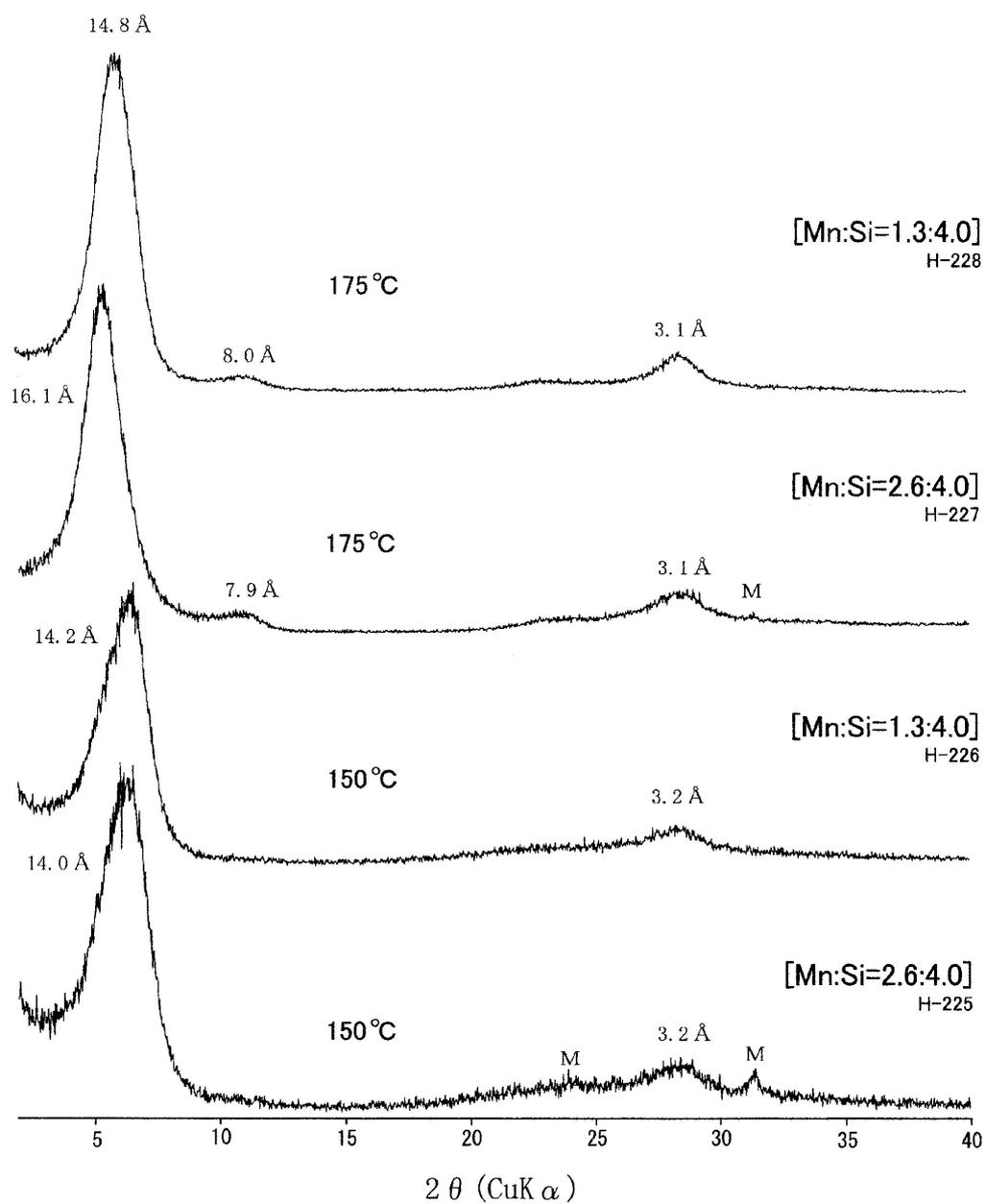


Fig. 2. XRD of synthetic Mn-hectorite specimens prepared at 150 $^{\circ}\text{C}$  and 175 $^{\circ}\text{C}$  for 168 h. M=MnCO<sub>3</sub>.

# Mn-stevensite

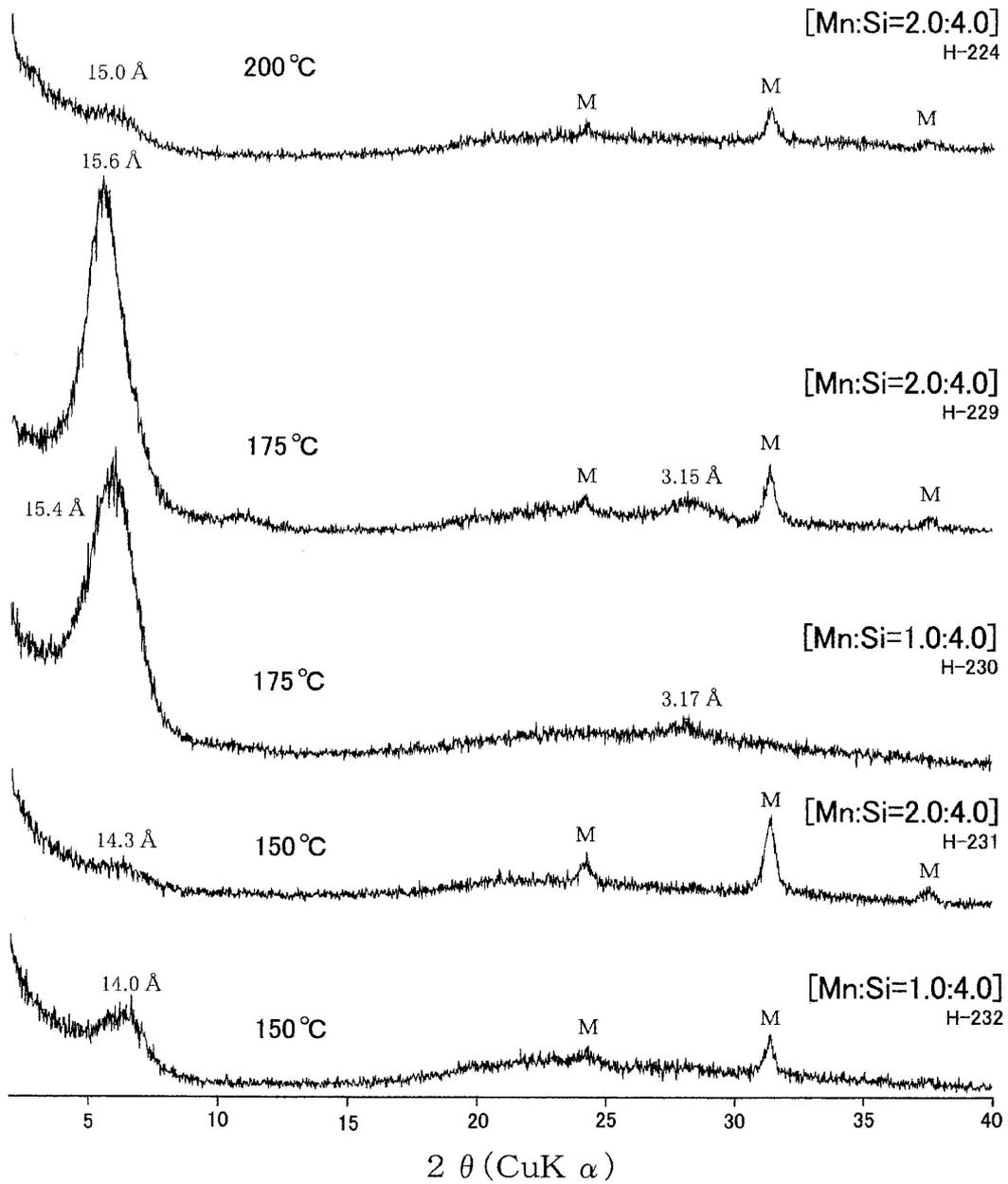


Fig. 3. XRD of Mn-stevensite specimens prepared at different temperatures for 72 h. M=MnCO<sub>3</sub>.

## Mn-stevensite

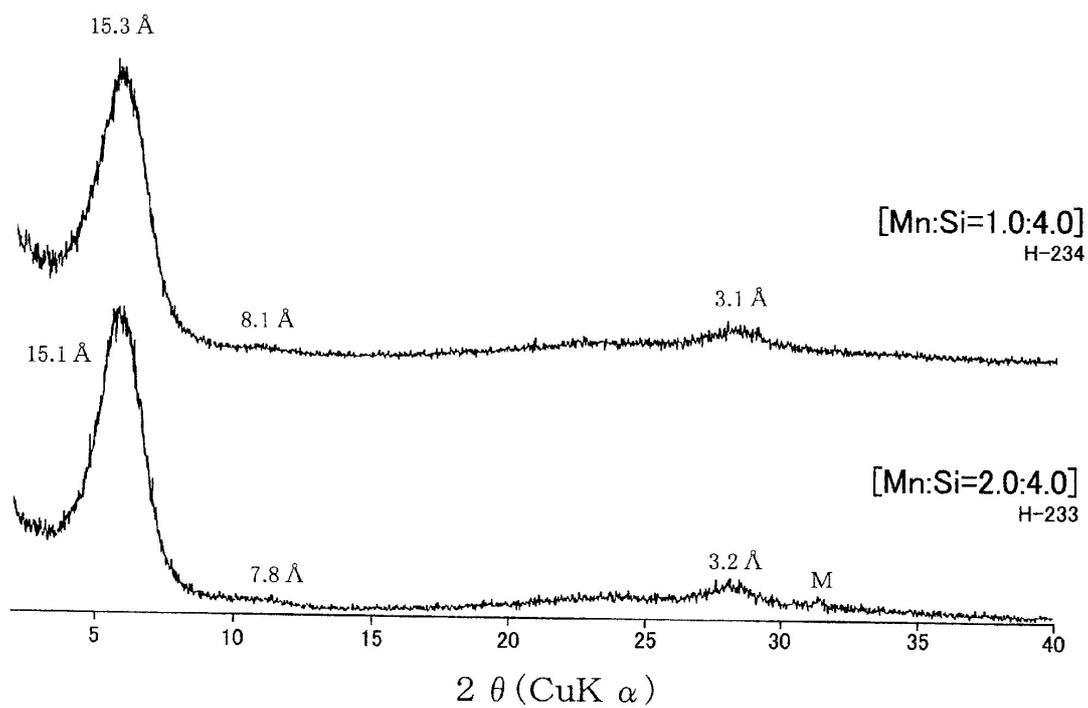


Fig. 4. XRD of synthetic Mn-stevensite specimens prepared at  $175^\circ\text{C}$  for 168 h.  
M= $\text{MnCO}_3$ .

# Mn-saponite

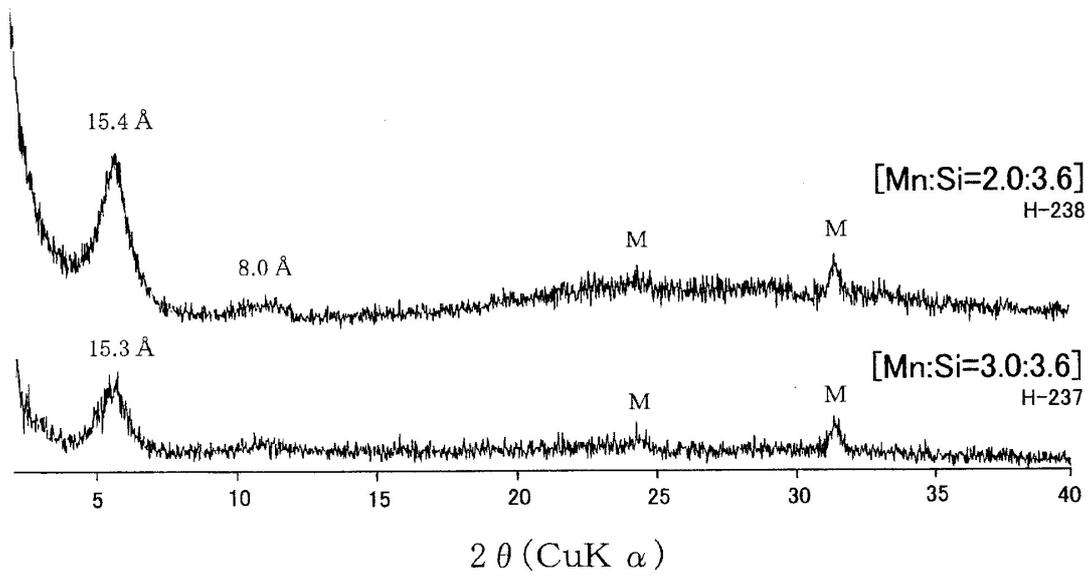


Fig. 5. XRD of synthetic Mn-saponite specimens prepared at  $175^\circ\text{C}$  for 72 h. M= $\text{MnCO}_3$ .

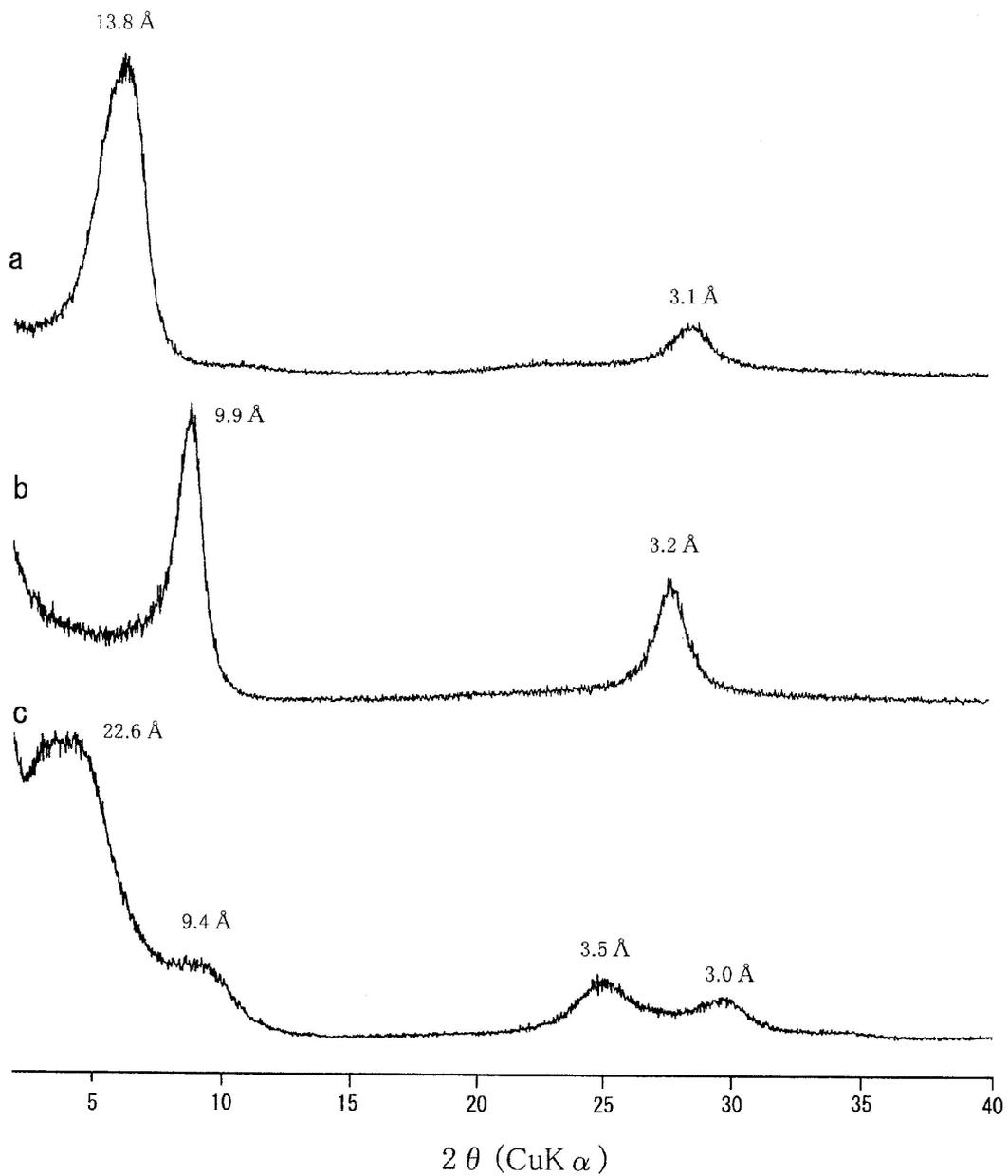


Fig. 6. XRD changes of Mn-hectorite (H-228) by heating and glycerol solvation.  
a.. Air dried, b. Heated at  $300^\circ\text{C}$  for 1h, c. Glycerol solvation.

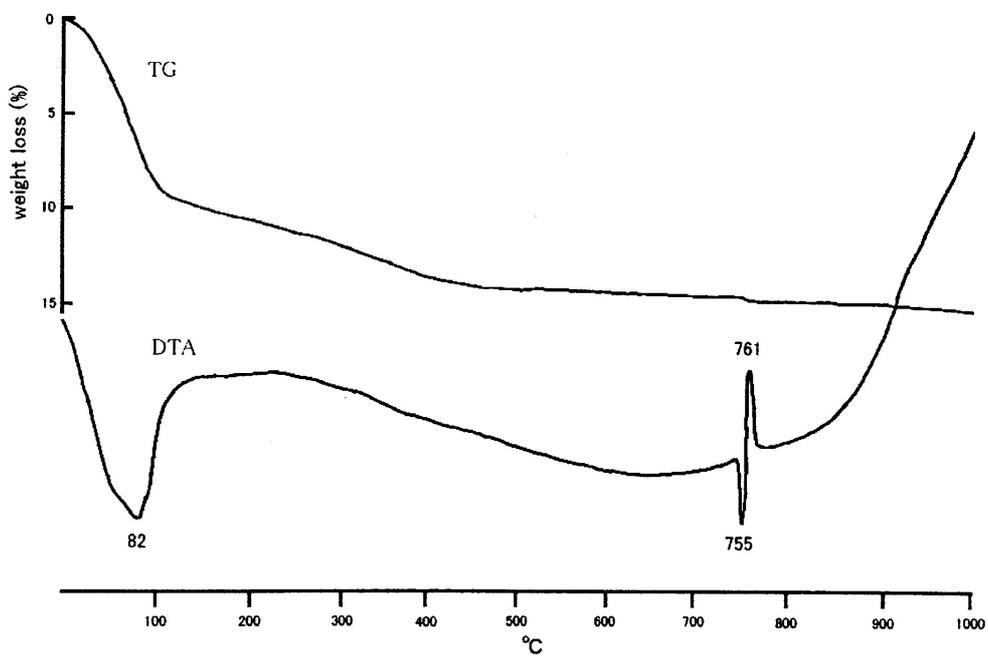


Fig. 7. TG and DTA curves of synthetic Mn-hectorite product.

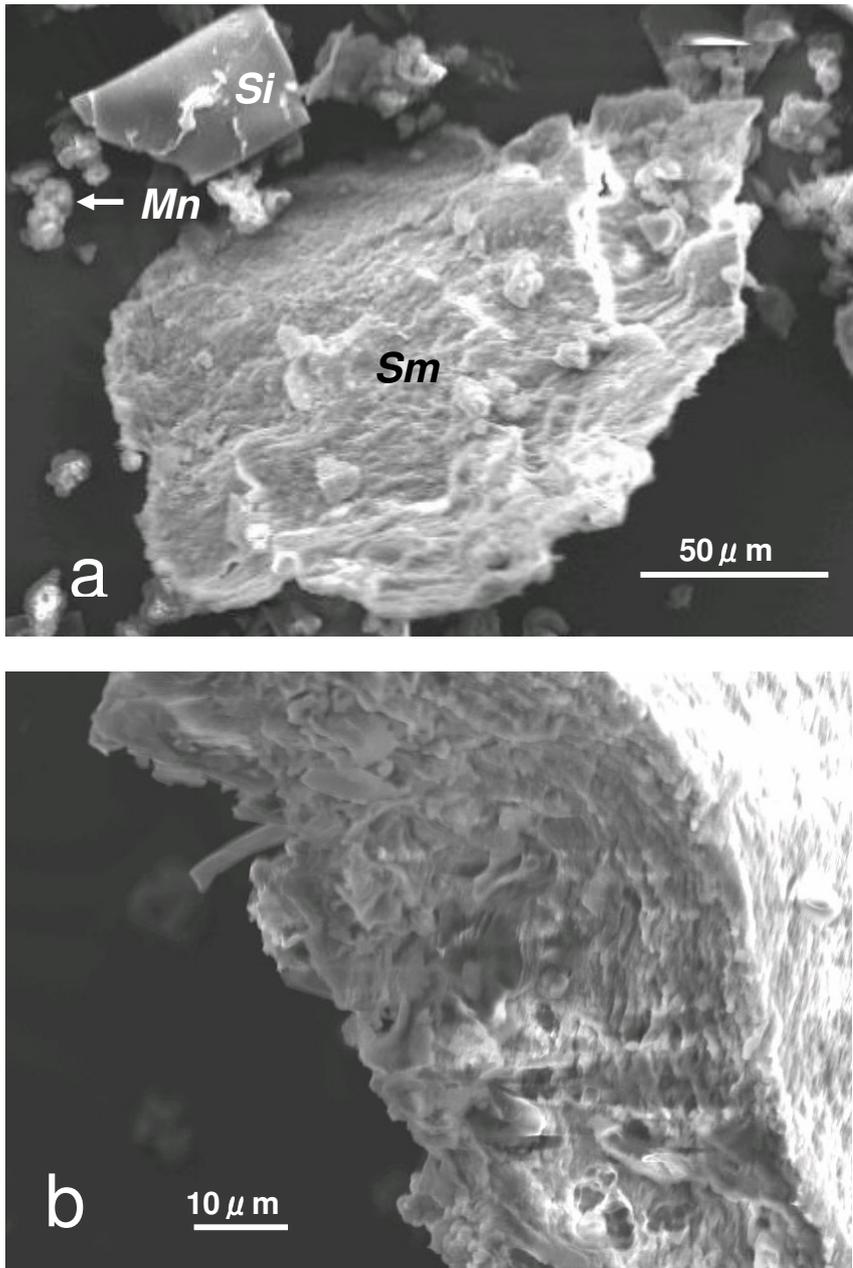


Fig. 8. Scanning electron micrographs of synthetic Mn-hectorite product (H-228).

- a. Low magnification micrograph (original  $220\times$ ), showing larger lamellar aggregates of Mn-hectorite (Sm) and unreacted starting materials of silicic acid (Si) and very small grained Mn carbonate (Mn).
- b. Enlarged micrograph of Mn-hectorite (original  $660\times$ ), showing lamellar aggregate.

Table 1 Hydrothermal synthesis of Mn-hectorite

Run No.	Mn Sources <sup>a</sup>	Initial Composition Na:Mn:Li:Si	Temperature °C	Duration Hours	Products
H-201	1	0.4:2.6:0.4:4.0	200	72	No reaction
H-208	2	0.4:2.6:0.4:4.0	200	72	No reaction
H-217	3	0.4:2.6:0.4:4.0	100	72	No reaction
H-219	3	0.4:2.6:0.4:4.0	125	72	Hectorite <sup>b</sup>
H-216	3	0.4:2.6:0.4:4.0	150	72	Hectorite <sup>b</sup>
H-225	3	0.4:2.6:0.4:4.0	150	168	Hectorite
H-226	3	0.4:1.3:0.4:4.0	150	168	Hectorite
H-222	3	0.4:2.6:0.4:4.0	175	72	Hectorite
H-227	3	0.4:2.6:0.4:4.0	175	168	Hectorite
H-228	3	0.4:1.3:0.4:4.0	175	168	Hectorite
H-212	3	0.4:2.6:0.4:4.0	200	72	Hectorite <sup>b</sup>
H-214	3	0.4:2.6:0.4:4.0	250	72	Unidentified
H-235	4	0.4:2.6:0.4:4.0	175	72	No reaction

<sup>a</sup> 1=MnO<sub>2</sub>; 2=MnCl<sub>2</sub> · 4H<sub>2</sub>O; 3=MnCO<sub>3</sub>; 4=Mn(CH<sub>3</sub>COO)<sub>2</sub> · 4H<sub>2</sub>O.

<sup>b</sup> Poorly crystallized.

Table 2 Hydrothermal synthesis of Mn-stevensite

Run No.	Mn Sources <sup>a</sup>	Initial Composition Na:Mn:Si	Temperature °C	Duration Hours	Products
H-204	1	0.4:2.0:4.0	200	72	No reaction
H-210	2	0.4:2.0:4.0	200	72	No reaction
H-231	3	0.4:2.0:4.0	150	72	Stevensite <sup>b</sup>
H-232	3	0.4:1.0:4.0	150	72	Stevensite <sup>b</sup>
H-229	3	0.4:2.0:4.0	175	72	Stevensite
H-233	3	0.4:2.0:4.0	175	168	Stevensite
H-230	3	0.4:1.0:4.0	175	72	Stevensite
H-234	3	0.4:1.0:4.0	175	168	Stevensite
H-221	3	0.4:3.0:4.0	175	72	Stevensite
H-224	3	0.4:2.0:4.0	200	72	Stevensite <sup>b</sup>
H-213	3	0.4:3.0:4.0	250	72	Unidentified
H-236	4	0.4:2.0:4.0	175	72	No reaction

<sup>a</sup> 1=MnO<sub>2</sub>; 2=MnCl<sub>2</sub> · 4H<sub>2</sub>O; 3=MnCO<sub>3</sub>; 4=Mn(CH<sub>3</sub>COO)<sub>2</sub> · 4H<sub>2</sub>O

<sup>b</sup> Poorly crystallized

Table 3 Hydrothermal synthesis of Mn-saponite

Run No.	Mn Sources <sup>a</sup>	Initial Composition Na:Mn:Al:Si	Temperature °C	Duration Hours	Products
H-237	3	0.4:3.0:0.4:3.6	175	72	Saponite
H-238	3	0.4:2.0:0.4:3.6	175	72	Saponite

<sup>a</sup> 3=MnCO<sub>3</sub>