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HYDROTHERMAL SYNTHESIS OF Zn-SMECTITES

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Abstract—Two varieties of Zn-smectite were synthesized hydrothermally: sauconite, with an ideal composition of $Na_{0.4}Zn_3(Si_{3.6}Al_{0.4})O_{10}(OH)_2{\cdot}nH_2O$; and a Zn equivalent of hectorite, with an ideal composition of $Na_{0.4}(Li_{0.4}Zn_{2.6})Si_4O_{10}(OH)_2{\cdot}nH_2O$ (referred to here as Zn-hectorite). For comparison, hydrothermal synthesis of the related trioctahedral smectites of hectorite, $Na_{0.4}(Li_{0.4}Mg_{2.6})Si_4O_{10}(OH)_2{\cdot}nH_2O$ and hectorites containing Cu, Co or Ni in the octahedral sheets instead of Mg were also attempted. The results showed that sauconite, Zn-hectorite and hectorite could be synthesized in the temperature range 100–125°C but hectorites containing Cu, Co or Ni in the octahedral sheet, under the same conditions or even at a temperature of 150°C, could not.

Key Words— Hectorite, Hydrothermal Synthesis, Sauconite, Smectite, Synthetic Clays.

INTRODUCTION

Sauconite is a zinciferous smectite (Ross, 1946) with a generalized formula of $Na_{0.4}(Al,Fe,Mg,Zn)_3(Si,Al)_4O_{10}(OH)_2{\cdot}nH_2O$ and usually occurs in the oxidation zone of Zn deposits, occasionally accompanied by hemimorphite ($Zn_4Si_2O_7(OH)_2{\cdot}H_2O$) and smithsonite ($ZnCO_3$). Its geological occurrence is suggestive of formation under near-surface weathering conditions and therefore may have implications for the chemistry of Zn in soils and sediments. Tiller and Pickering (1974) demonstrated that poorly-crystallized zinciferous smectite was formed when the precipitates from the mixed solution of silicic acid and Zn chloride with or without aluminate were aged at 20°C for a year or more. Zinc silicate minerals such as willemite (Zn_2SiO_4), hemimorphite and sauconite are also found in nature in the oxidation of some sulfide ore bodies (Tiller and Pickering, 1974). Synthesis experiments conducted by Roy and Mumpton (1956), Esquevin (1960) and Decarreau (1985) elucidated the formation and stability of these minerals at different temperatures and pressures. A recent review of the synthesis of smectite clay minerals (Kloprogge *et al.*, 1999) shows that there have been only a small number of studies on the synthesis of sauconite, examination of which suggests that among the transition metals such as Zn, Cu, Co and Ni, Zn seems to be preferred in the octahedral sheets of 2:1 clays at lower temperatures. A study of low-temperature (85°C) synthesis of Zn-phlogopite by Perrotta and Garland (1975) supports the above thesis. To substantiate this thesis, we embarked on a systematic synthesis of smectites containing different transition metals. These transition metal-substituted smectites and their pillared counterparts may have use in catalytic applications.

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MATERIALS AND METHODS

The hydrothermal synthesis of sauconite with an ideal composition of $Na_{0.4}Zn_3(Si_{3.6}Al_{0.4})O_{10}(OH)_2{\cdot}nH_2O$, the Zn equivalent of hectorite (referred to below as Zn-hectorite) with an ideal composition of $Na_{0.4}(Li_{0.4}Zn_{2.6})Si_4O_{10}(OH)_2{\cdot}nH_2O$, hectorite [$Na_{0.4}Li_{0.4}Mg_{2.6}Si_4O_{10}(OH)_2{\cdot}nH_2O$] and the Cu, Co or Ni equivalents of hectorite were attempted using stoichiometric starting chemical mixtures. The starting materials were solid mixtures (0.3–0.5 g) of silicic acid (containing 81.4% SiO_2; Aldrich chemical Co.) and MgO or ZnO, to which an aqueous solution mixture (18 ml) of NaOH (0.2% concentration) and LiOH(0.1% concentration) was added according to the structural formula of hectorite or Zn-hectorite. For the synthesis of sauconite, $Al(NO_3)_3{\cdot}9H_2O$ or $NaAlO_2$ was used as a source of Al or both Al and Na. For syntheses of Ni, Co or Cu hectorites, Ni, Co and Cu oxides, respectively, were used. All the reagents used were of analytical grade except for $NaAlO_2$ (industrial grade having a molecular ratio of Al/NaOH = 0.78). The above chemicals were mixed in the Teflon cup of a Parr reactor (35 mL), sealed, and then treated hydrothermally under autogenous pressure (~50% filling rate) in a temperature range of 100–250°C for a period varying from 12 to 168 h (most reactions were for 72 h). After the hydrothermal experiments, the solid and solution phases were separated by centrifugation and the solids were washed repeatedly with distilled water before drying in an oven at 50°C.

No chemical analysis of the starting slurries or the reaction products (both the solid and the solution) was performed. The solid reaction products were characterized by X-ray diffraction (XRD) with a Rigaku diffractometer using CuKα radiation, a graphite monochromator and fixed slits. The XRD patterns were recorded using oriented specimens on glass slides in the range 2–40°2θ at a scanning speed of 2° min^{-1}. No

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Table 1. Hydrothermal synthesis of sauconite.

Initial composition Na:Zn:Al:Si	Temp. (°C)	Duration (h)	Products	
			Main	Associated
0.4:2.25:0.4:3.6	100	168	No reaction	
0.4:2.25:0.4:3.6	125	168	Sauconite	
0.4:3.00:0.4:3.6	125	168	Sauconite	Trace hemimorphite
0.4:2.25:0.4:3.6	150	72	Sauconite	
0.4:2.25:0.4:3.6	200	72	Sauconite	
0.4:2.25:0.4*:3.6	200	72	Sauconite**	Trace hemimorphite
0.4:2.50:0.4:3.6	200	72	Sauconite	Trace hemimorphite
0.4:3.00:0.4:3.6	200	72	Sauconite	Hemimorphite
0.4:2.25:0.4:3.6	250	72	Sauconite	Trace hemimorphite

* $Al(NO_3)_3 \cdot 9H_2O$ was used in place of $NaAlO_2$
** Poorly crystallized

special precautions were taken to control the relative humidity of the ambient atmosphere.

Some representative specimens of hectorite, Zn-hectorite and sauconite were investigated after treatment with glycerol and heat treatment at 500°C for 1 h to confirm the expansion and contraction behavior of these smectites. The measurement of d_{060} was also made with randomly-oriented specimens using Si as an internal standard.

Some of the samples were further investigated by differential thermal analysis (DTA) and infrared (IR) methods. The DTA was performed using a Rigaku DTA-TG simultaneous apparatus: 20 mg of specimen were heated from room temperature to 1000°C at a heating rate of 10°C min^{-1}. The IR spectra were recorded with a Perkin Elmer FTIR spectrometer using KBr pressed discs (1 mg sample/200 mg KBr) in the spectral region 4000–400 cm^{-1}.

RESULTS AND DISCUSSION

Synthesis of sauconite

Table 1 summarizes the synthesis results of sauconite from various compositions at different temperatures and treatment times. Sauconite with some hemimorphite impurity resulted when a stoichiometric composition was used at 125°C. The results show, however, that well-crystallized sauconite formed at a temperature as low as 125°C with a composition deficient in Zn. There is little or no crystallization of sauconite at 100°C after treatment for 168 h (Figure 1). Sauconites with no detectable impurities were obtained in the temperature range 125–200°C with some Zn-deficient compositions (Table 1). However, at 250°C a small amount of hemimorphite crystallized along with sauconite (Figure 1). Figure 2 shows XRD patterns of various products obtained after hydrothermal treatment at 200°C over 72 h using different Zn:Si ratios and two different sources of Al. Higher Zn/Si ratios appear to have promoted the crystallization of hemimorphite along with sauconite (Table 1). The use of Al nitrate as an Al source led to a poorly-crystallized sauconite compared to that of Na aluminate as an Al source (Figure 2), probably because of effective solubilization of components at higher pH with the latter source. The above results show that sauconite forms preferentially at lower temperatures and under Zn-deficient conditions. Hemimorphite, however, appears to be more stable than sauconite at higher temperatures and in the presence of larger amounts of Zn in the starting materials. These results help to elucidate the natural occurrence of sauconite and hemimorphite.

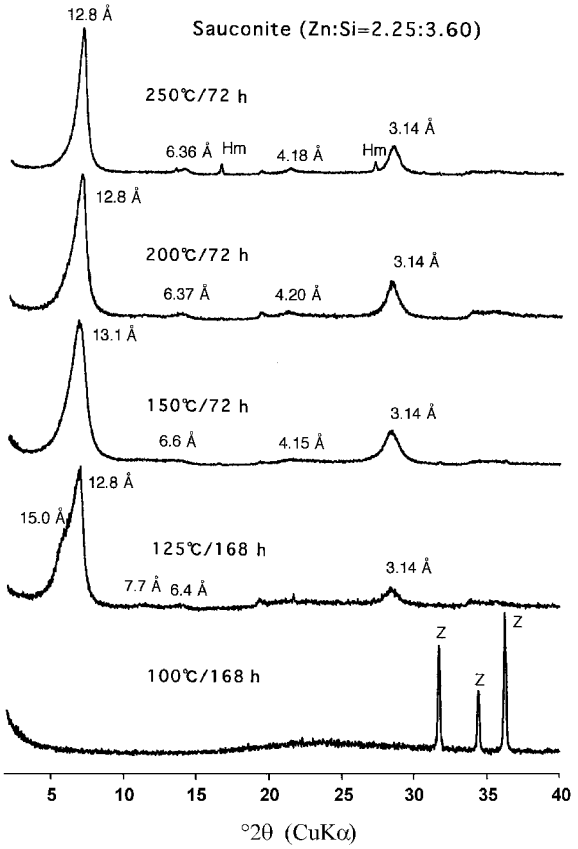


Figure 1. XRD patterns of synthetic sauconites prepared at different temperatures. HM = hemimorphite; Z = ZnO.

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Table 2. Hydrothermal synthesis of Zn-hectorite.

Initial composition Na :Zn :Li:Si	Temp. (°C)	Duration (h)	Products	
			Main	Associated
0.4:2.6:0.4:4.0	100	168	No reaction	
0.4:2.6:0.4:4.0	125	72	Zn-hectorite*	
0.4:2.6:0.4:4.0	125	168	Zn-hectorite	
0.4:2.6:0.4:4.0	150	72	Zn-hectorite	
0.4:2.6:0.4:4.0	200	72	Zn-hectorite	
0.4:2.6:0.4:4.0	250	72	Zn-hectorite	Unknown+ Cri

* Very poorly crystallized
Cri = Cristobalite

Synthesis of Zn-hectorite and hectorite

The results of hydrothermal synthesis of Zn-hectorite at different temperatures and durations are presented in Table 2 and, of hectorites, in Table 3. These show that well-crystallized Zn-hectorites were formed at a lower temperature than the hectorites containing Mg and Li. The formation temperature of highly-crystallized Zn-hectorite was lowered considerably compared to that of hectorite (Tables 2 and 3; Figures 3 and 4). Zn-hectorite was poorly crystallized at 125°C after treatment for 3 days but was well-crystallized when treated for 7 days (Figure 3). No crystallization of Zn-hectorite was observed at 100°C even after treatment for 168 h. In contrast, well-crystallized hectorite having Mg as the principal octahedral divalent cation was formed only at 250°C (Figure 4). A poorly crystallized hectorite resulted below 200°C but well-crystallized hectorite was obtained at 250°C when treated for 3 days (Figure 4). At higher Mg/Si ratio, only hectorite was obtained but with lower Mg/Si ratio (*i.e.* higher silica), quartz crystallized as an impurity along with hectorite (Figure 4). The above results suggest that Zn, which has a higher electronegativity than Mg (Evans, 1964) is preferentially incorporated in the octahedral sheets during clay formation.

Additional XRD measurements were made on representative specimens of hectorite, Zn-hectorite and sauconite to characterize them more thoroughly. All these smectites expanded to 18–19 Å when treated with

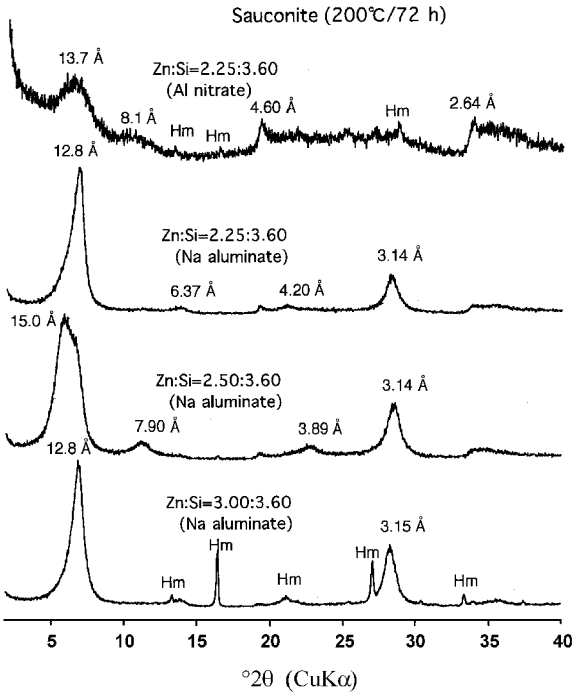


Figure 2. XRD patterns of synthetic sauconites prepared with different Zn/Si ratios and different precursors. HM = hemimorphite.

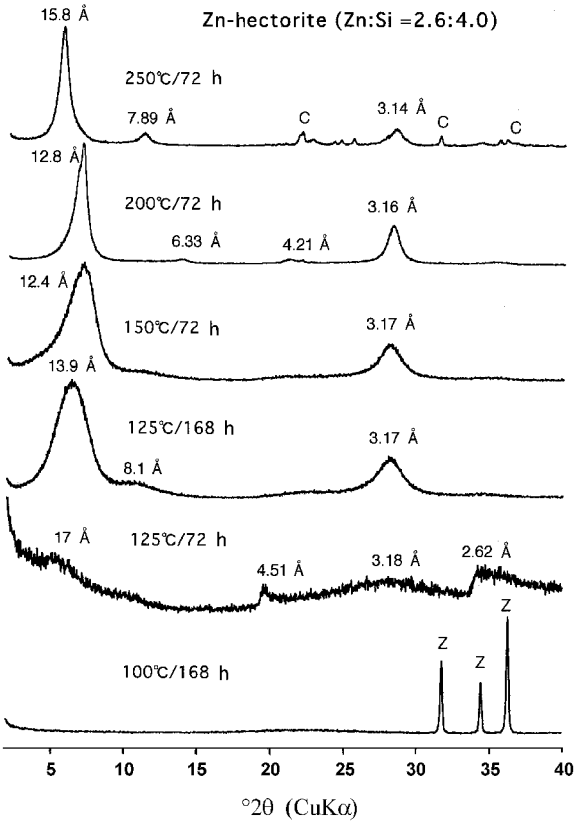


Figure 3. XRD patterns of synthetic Zn-hectorites prepared at different temperatures. C = cristobalite; Z = ZnO.

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Table 3. Hydrothermal synthesis of hectorite.

Initial composition Na:Mg:Li:Si	Temp. (°C)	Duration (h)	Products Main	Associated
0.4:2.6:0.4:4.0	100	168	Hectorite*	
0.4:2.6:0.4:4.0	125	168	Hectorite*	
0.4:2.6:0.4:4.0	150	72	Hectorite*	
0.4:2.6:0.4:4.0	200	72	Hectorite*	
0.4:2.6:0.4:4.0	250	72	Hectorite	Quartz
0.4:2.6:0.4:4.0	250	72	Hectorite	

*Very poorly crystallized

glycerol and contracted to 9.7–9.8 Å when heated at 500°C for 1 h as shown in Table 5. These results are consistent with the behavior of typical smectites (Jackson, 1979). The d_{060} values of hectorite, Zn-hectorite and sauconite were determined to be 1.520, 1.525 and 1.532 Å, respectively, indicating the trioctahedral nature of these smectites (Brindley and Brown, 1980).

Synthesis of Cu-, Ni- and Co-hectorites

Hectorites containing Cu, Ni or Co in place of Mg could not be synthesized at 150°C for 3 days (Table 4). The starting materials remained unchanged under these conditions (Figure 5), which shows that the incorporation of Cu, Co and Ni in the 2:1 layer of smectite could not be achieved at that temperature over that period of time. It is, however, possible to synthesize Ni, Co and Mg-Cu smectites even at 75°C depending on the nature of the starting materials and treatment time (Decarreau *et al.*, 1992; Kloprogge *et al.*, 1999). It is also possible to incorporate Ni and Co in the octahedral sheets at higher temperatures (Yamada *et al.*, 1994; Bruce *et al.*, 1986). Incorporation of the Zn transition metal was extremely effective in Zn-smectites as indicated by the results presented in Figure 5. Zinc has an electronegativity value of 1.6 while the electronegativities of Mg, Cu, Ni and Co are 1.2, 1.9, 1.8 and 1.8, respectively (Evans, 1964). We suggest that the intermediate electronegativity of Zn with Mg at the low end and Cu at the high end, among these divalent metals, may be ideal for the formation of the octahedral sheet during clay formation.

Table 4. Hydrothermal synthesis of Cu-, Ni,-, Co- and Zn-hectorites.

Initial composition Na:M^{2+}:Li:Si	Temp. (°C)	Duration (h)	Products Main	Associated
0.4:Cu2.6:0.4:4.0	150	72	No reaction	
0.4:Ni2.6:0.4:4.0	150	72	No reaction	
0.4:Co2.6:0.4:4.0	150	72	No reaction	
0.4:Zn2.6:0.4:4.0	150	72	Zn-hectorite	
0.4:Mg2.6:0.4:4.0	150	72	Hectorite*	

M^{2+} = Octahedral metal cation
*Very poorly crystallized

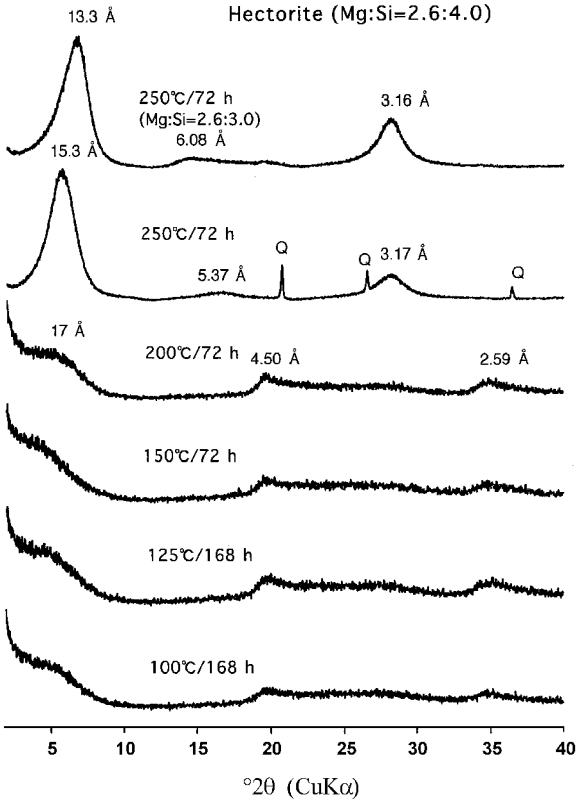


Figure 4. XRD patterns of synthetic hectorites prepared at different temperatures. Q = Quartz.

IR characterization of hectorite and Zn-smectites

The IR spectra of the synthetic specimens above are shown in Figure 6. Hectorite gave two well-resolved bands at 3680 and 3638 cm^{-1} in the OH-stretching region. The higher frequency band is comparable to that of natural hectorite (3676 cm^{-1}; Farmer, 1974) and is unambiguously ascribed to the 3Mg–OH stretching vibration (Wilkins and Ito, 1967; Farmer, 1974). The band at 3638 cm^{-1} can be ascribed to the 2Mg1Li–OH stretching vibration. A somewhat similar feature of double bands in the OH-stretching region (3620 and

Table 5. Change in d_{001} and d_{060} for representative specimens of hectorite, Zn-hectorite and sauconite (Å).

	Air dried	Glycerol	500°C/h	d_{060}
[1] Hectorite	15.3	19.3	9.80	1.520
[2] Zn-hectorite	13.9	18.5	9.69	1.525
[3] Sauconite	12.8	18.2	9.84	1.532

[1] Product of initial composition Na/Mg/Li/Si = 0.4/2.6/0.4/4.0 treated at 250°C for 72 h; associated with small amount of quartz
[2] Product of initial composition Na/Zn/Li/Si = 0.4/2.6/0.4/4.0 treated at 125°C for 168 h
[3] Product of initial composition Na/Zn/Al/Si = 0.4/2.25/0.4/3.6 treated at 200°C for 72 h

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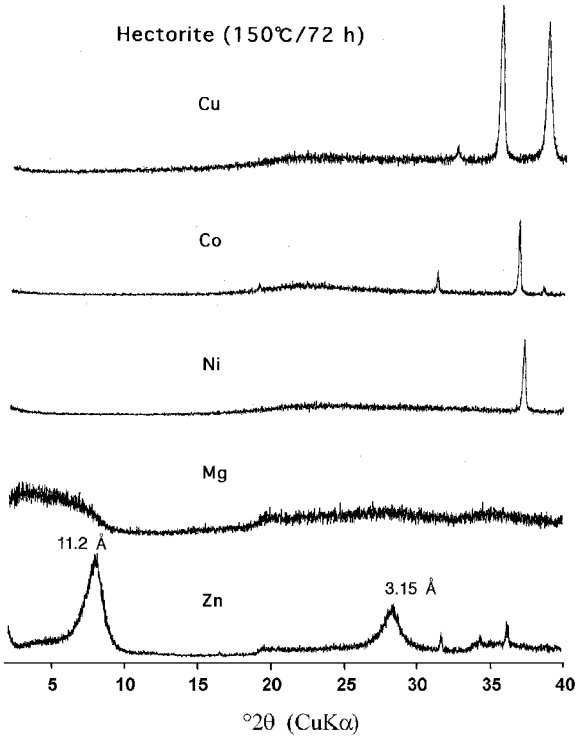


Figure 5. XRD patterns of synthetic products prepared by reacting SiO_2 with ZnO, MgO, NiO, CoO and CuO.

3565 cm^{-1}) was reported for synthetic Co-smectite by Bruce *et al.* (1986). The presence of such double OH bands rather than the single band of 3634 cm^{-1} for synthetic Co-talc was ascribed by the authors above to the existence of two sites of different symmetry involving OH groups close to an octahedral vacancy. The lower frequency band (3638 cm^{-1}) of the present hectorite may be affected by the presence of octahedral Li or a vacancy. In contrast to the double OH bands of hectorite, Zn-hectorite and sauconite yielded a distinctive single band at 3641 cm^{-1} which is slightly higher than that of 3Zn—OH stretching (3634 cm^{-1}) for synthetic MgZn-talc (Wilkins and Ito, 1967). In the lattice vibration region 1200—400 cm^{-1}, Zn-hectorite and sauconite yielded distinctive bands around 1000, 660 and 450 cm^{-1}; the band frequencies are nearly the same for both Zn-smectites. Hectorite also yielded comparable bands in the lattice vibration region with discernible double splitting of bands in the 660 and 450 cm^{-1} regions.

DTA characterization of hectorite and Zn-smectites

The DTA curves of the synthetic specimens above are given in Figure 7. The interlayer water of all these smectites was released in the 80—90°C range as indicated by the pronounced endothermic reaction. However, they behave differently at elevated temperatures, reflecting their chemical composition. Hectorite gave an asymmetric endothermic peak at 682°C (dehydroxylation), and this is followed immediately by weak exothermic peaks at 700 and 800°C. These exothermic reactions can be ascribed to recrystallization of enstatite and cristobalite, respectively (Granquist and Pollack, 1960). The final heating products of the present hectorite after DTA were investigated here by XRD which showed enstatite, quartz and cristobalite. Zn-hectorite and

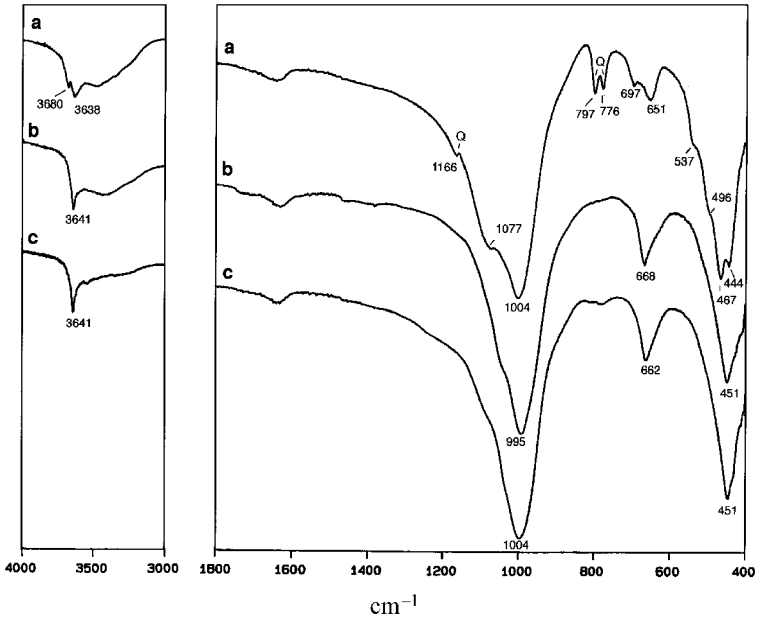


Figure 6. IR spectra of different synthetic smectites: (a) hectorite, (b) sauconite, and (c) Zn-hectorite (samples are the same as in Table 5).

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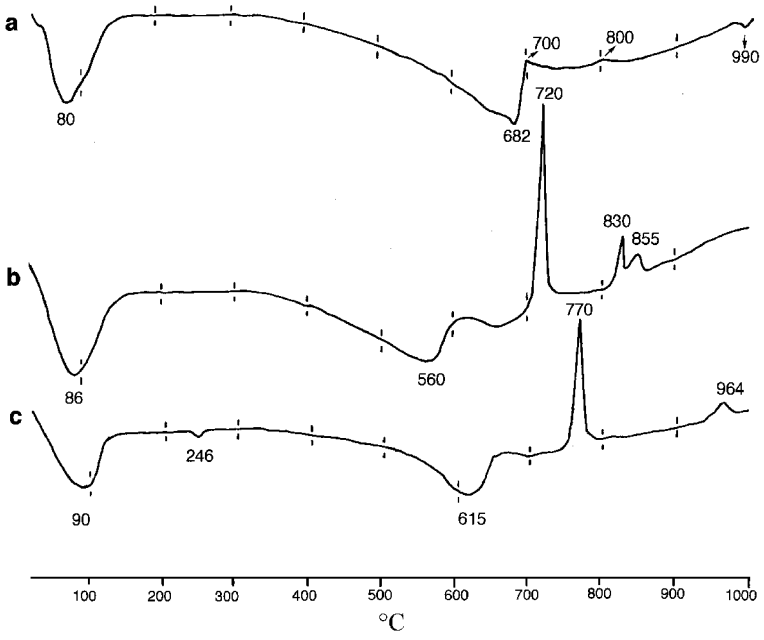


Figure 7. DTA curves of different synthetic smectites: (a) hectorite, (b) sauconite, and (c) Zn-hectorite (samples are the same as in Table 5).

sauconite showed intense exothermic reactions at 720°C (Zn-hectorite) and 770°C (sauconite) following dehydroxylation at 560°C (Zn-hectorite) and 615°C (sauconite). The final heating products after DTA of both Zn-smectites were determined, by XRD, to be willemite. The DTA curve of the present synthetic sauconite showed pronounced reactions (90, 615, 770°C) accompanied by weak reactions (246, 964°C) and these results are in good agreement with that of natural sauconite described by Faust (1951). Zn-hectorite, on the other hand, showed peculiar extra exothermic reactions at 830 and 855°C with a lowering of reaction temperature for dehydroxylation (Figure 7). The difference in chemical composition between sauconite and Zn-hectorite may be responsible for such thermal reaction behavior because dehydroxylation of 2:1 clays is dependent mainly on their octahedral composition (Zelazny and White, 1989). Precise chemical analysis of these synthetic smectites is required for any further discussion of their differences.

CONCLUSIONS

The present study shows that well-crystallized smectites containing Zn in the octahedral sheet can be synthesized hydrothermally at considerably lower temperatures than smectites such as hectorites which contain Mg in the octahedral sheet. Hectorites containing transition metals such as Cu, Ni and Co in the octahedral sheet could not be prepared at the same temperature as hectorite or Zn-hectorite.

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