THE DEHYDROXYLATION OF CHLORITE AND THE FORMATION OF TOPOTACTIC PRODUCT PHASES

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Abstract—Single-crystal, X-ray examination of Mg,Fe-rich chlorites that were heated at 650°C for 24 hours in air and have undergone dehydroxylation of the interlayer shows that two product phases result with a topotactic relationship, with the c axis of both phases parallel. One phase ("modified chlorite" or "14-A phase") has relatively sharp reflections with a 14-A c-axis repeat, indicating that it is well crystallized and maintains the 2:1 layer from the parent. Cell parameters are $a = 5.368(1)$A, $b = 9.297(2)$A, $c = 14.215(6)$A, $\alpha = 89.86(3)°$, $\beta = 97.15(3)°$, $\gamma = 89.98(2)°$, and it crystallizes in $C\bar{1}$ symmetry. A structure refinement, details of which will be reported later, indicates that the interlayer consists of two planes, each containing (M + O), where M is the interlayer cation species. These planes show about ±0.5A positional disorder along the [001] direction. There is no evidence for scattering material at $z = 0.5$ between the 2:1 layers. The second phase in the topotactic relationship is based on a 27-A unit c axis ("27-A phase"). The diffraction data are limited with about 15 diffuse reflections observed, indicating that it is poorly crystallized. The 27-A spacing suggests that both octahedral sheets in the parent chlorite contribute to the formation of this phase.

Heating Mg,Fe-rich chlorite powder in a closed system to 550°C, under either reducing or oxidizing conditions, prevents the formation of the 27-A phase. Because the 27-A phase forms in an open system, we infer that water fugacity is an important factor in its formation. Heating experiments involving samples with different polytypes and octahedral "type" (dioctahedral vs trioctahedral) of the 2:1 layer suggests that these two variables are important. However, the results are equivocal, and an ill-defined B-rich chlorite from Madagascar breaks the observed trends for both variations in stacking sequence and octahedral type. However, B-content may be a factor in the transformation also for those chlorites that contain B.

Key Words—Chlorite, Dehydroxylation, Topotactic phases, X-ray diffraction.

INTRODUCTION

When chlorite is heated in air near 550°C, dehydroxylation of the interlayer occurs by the loss of half or more of the OH groups as H_2O (Brindley and Ali 1950). The resulting "modified chlorite structure" (Brindley and Ali 1950) persists for long periods, even for samples immersed in water. The X-ray powder pattern of the modified chlorite structure is characterized by an increased intensity of the (001) peak and a general loss in intensity of higher order (00*l*) peaks relative to untreated chlorite. The chlorite to modified chlorite reaction is commonly utilized by clay mineralogists to identify Fe,Mg-rich chlorite in a clay where kaolinite or serpentine peaks are superposed on the higher order 00*l* chlorite peaks and where the 001 peak of the chlorite is weak. Heating at 550°C in air for one hour (e.g., Moore and Reynolds 1989) causes the low-intensity 14-A peak to increase by a factor of 2–5, thus revealing the presence of chlorite.

Dehydroxylation temperature is dependent on crystallinity, grain size, and composition (Caillère and Hénin 1960, Brindley and Chang 1974). The near Fe^{2+} end-member interlayer of chlorite typically dehydroxylates at about 450°C and a near Mg end-member interlayer at about 640°C. Above 750°C, the talc-like layer de-hydroxylates, with the loss of long-range atomic periodicity. Finally, with prolonged heating, olivine and other stable phases are produced. Bai *et al* (1993) gave a complete description of the metastable phase relations involving a clinochlore and a Mg-rich chamosite at elevated temperatures and pressures. They found that the thermal decomposition of these chlorites is greatly affected by variations in water fugacity.

Brindley and Chang (1974) re-examined the modified chlorite structure derived by heat-treatment of Mg, Al and Fe-rich clinochlores (using current nomenclature) in air. By using an X-ray powder diffractometer and an oriented aggregate to enhance the 00*l* series of reflections, Brindley and Chang (1974) found that a 27-A spacing occurs and that the peak width of the *l* = odd reflections (e.g., 001 at $d = 27$A; 003 at $d = 9$A) is different from the *l* = even reflections (e.g., 002 at $d = 14$A). In addition, they found that the (001) reflection is not an exact multiple of $d = 14$A. To account for the 27-A spacing, they postulated that the modified chlorite structure is similar to the chlorite structure but with two different interlayers: (1) an interlayer with Mg cations located between two oxide planes and (2) an interlayer with two (Mg + O) planes. To account for differences in peak width and the non-exact multiple of 14A for the (001) reflection, Brindley and Chang

Table 1. Weight-percent oxides of samples studies.

Oxide	Clinochlore[1]	Chamosite[2]	Sudoite[3]	Cookeite[4] Londonderry	Cookeite[5] Arkansas	B-rich Chlorite[6]	Nimite[7]	Chlorite-Ib(90°)[8]
SiO_2	32.20	24.30	32.90	37.28	34.7	25.20	28.2	25.16
Al_2O_3	15.23	21.30	35.40	43.90	48.4	47.80	11.2	18.81
Cr_2O_3	3.16	na[9]	na	na			na	na
MgO	35.56	13.78	14.73	0.01	0.05		12.8	9.38
TiO_2	0.03	0.060	0.06	bd			1.0	na
MnO	bd[10]	0.366	0.01	bd			na	0.76
FeO	1.19[11]	26.0	bd	0.29[11]			20.2[11]	34.54[11]
Fe_2O_3		3.50	2.69		0.1		na	na
NiO	0.24	na	na	na	na		14.6	na
Li_2O	na	na	0.04	na	2.45	3.97	na	na
P_2O_5	na	0.022	na	na	na	na	na	na
CaO	na	0.005	bd	na	0.12		na	na
Na_2O	na	<0.001	0.01	na	0.01	0.48	na	na
BaO	na	<0.001	0.03	na	na	na	na	na
K_2O	na	0.021	na	na		0.20	na	na
H_2O^+	12.39[12]	11.80	14.13[12]	na	14.1	14.10	12.00[12]	11.35[12]
Total	100.00	101.13	100.00		99.93	100.22	100.00	100.00

[1] Analysis from Phillips et al (1980).
[2] Analysis from Saccocia and Seyfried (1994).
[3] Analysis from Lin and Bailey (1985) and Fransolet and Bourguignon (1978).
[4] Analysis (partial) from Guggenheim et al (1983).
[5] Analysis from Miser and Milton (1964) as reported (averaged) in Cerný (1970).
[6] Analysis from Lacroix (1922). $B_2O_3 = 9.25$.
[7] Analysis from Guggenheim et al (1983).
[8] Analysis from Guggenheim et al (1983).
[9] na = not analyzed.
[10] bd = below detection.
[11] All iron present given as FeO.
[12] Computed by difference.

(1974) suggested a model involving an imperfect alternation of the two different interlayers.

Recently, Villieras et al (1994) found that modified chlorite samples have micropores filled with atmospheric H_2O and other gasses. Based on spectroscopic results, they proposed a model with one interlayer containing residual Al_p and oxygen (+micropores) and a second containing a central Al_p plane between two (Mg + O) planes.

Both the models of Brindley and Chang (1974) and Villieras et al (1994) do not account well for the X-ray data. Brindley and Chang (1974) and Villieras et al (1994) simulated 00l diffraction patterns and although the model of Villieras et al produced a better fit of data, neither model is convincing. In addition, the model of Villieras et al implies a diffusion of cations through the cation-rich 2:1 layer and the formation of a high-density interlayer at elevated temperatures; both possibilities are unlikely to occur on crystal chemical grounds.

The assumption of both models (above) is that the diffraction pattern implies a single phase. An alternate explanation is that a second phase, with a 27-A spacing, is intergrown topotactically with a phase having a 14-A spacing. In this model, the two phases have a different mosaic character (i.e., crystallinity) to produce some reflections that are relatively sharp (i.e., from the high-crystallinity phase) and reflections that are broad (i.e., from the low-crystallinity phase). The purpose of this paper is to examine both powder and single crystal X-ray data to test these models. In addition to clinochlore-IIb and chamosite-IIb, which contain a trioctahedral sheet in both the 2:1 layer and the interlayer, we examined three varieties of di,trioctahedral chlorite, sudoite-IIb, cookeite-Ia, and an ill-defined B-rich (Ia) variety. These di,trioctahedral chlorites contain an Al-rich dioctahedral sheet in the 2:1 layer. Cookeite and the B-rich chlorite are Li-rich, and sudoite is Li-poor. In addition, we examined nimite, a Ni-rich chlorite, and an Fe-rich chlorite, both tri,trioctahedral chlorites, but with a Ia stacking sequence.

EXPERIMENTAL AND RESULTS

Single-crystal X-ray data of heat-treated clinochlore

Figure 1 shows the h0l Buerger precession pattern of a chromian clinochlore-IIb crystal from the Day Book Body, North Carolina, USA (Phillips et al 1980, Nelson and Guggenheim 1993) after the crystal was heated in a Pt crucible at 650°C in air for about 24 hours. All heating experiments, including those described below, started with a cold furnace. The furnace usually required about an hour or more to reach equilibrium, depending on the set-point temperature. The
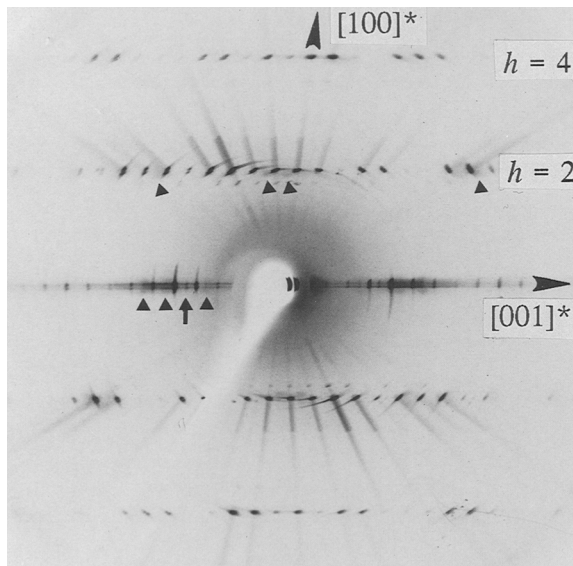
Figure 1. Buerger precession camera photograph taken for about 50 hours with Mo radiation, Zr filter, showing the $h0l$ pattern of a heat-treated chromian clinochlore. Triangles indicate the presence of broad and diffuse reflections. These reflections are attributed to the 27-A phase. Note that reflections indicated by triangles near the $h = 2$ row (where h indices refer to the 14-A phase) do not lie exactly on the layer line of the 14-A phase. The beam stop prevents the recording of the lowest order reflections, such as the spacings at $d = 27A$ and 9A. The (009) peak of the 27-A phase (note arrow) is very weak, but superimposes over the stronger K_β peak of the (0, 0, 10), where indexing is based on 27-A cell. Thus, in this reproduction, the composite peak appears relatively strong and sharp due to the K_β of the (0, 0, 10).

chemical analysis prior to heating is given in Table 1 and the structural formula is $(Mg_{2.97}Al_{0.03})(Si_{3.02} \cdot Al_{0.98})O_{10}(OH)_2 \cdot (Mg_{1.98}Al_{0.69}Cr_{0.23}Fe^{3+}_{0.04}Fe^{2+}_{0.04} \cdot Ni_{0.02})(OH)_6$. Based on mosaic character, two types of reflections occur in the pattern. The triangles on Figure 1 mark broad, diffuse reflections that indicate a large mosaic spread. The other reflections, not indicated by triangles, are sharper and are consistent with the spacing and characteristics of a chlorite-like (14A) structure. Note that the diffuse reflections along the $h = 2$ row do not lie on the layer line. In total, we could locate only about 15 diffuse reflections from both zero and upper level precession photographs.

For reasons given below (see *Topotaxy* section) and for simplicity in the description of the X-ray results, we describe the X-ray data as two superimposed diffraction patterns originating from a 14-A phase that produces sharp reflections and a 27-A phase that produces diffuse reflections. We refer to the phase with the 14-A spacing as the "14-A phase" or the "modified chlorite" structure and the phase producing the 27-A spacing as the "27-A phase."

The 00*l* reflections (*l* = odd) of the 27-A phase (Fig-

ure 1) may be compared to the diffractometer trace of Brindley and Chang 1974 (Figure 2). Because of the beam stop in the precession method, the lowest order peaks [e.g., (001) at $d = 27A$] cannot be observed in Figure 1. Diffuse peaks occur with d-spacings of approximately 4.01, 3.18, 2.58, and 2.19A, which represent the (007), (009), (0,0,11) and (0,0,13) indices respectively. Brindley and Chang (1974) reported d-spacings corresponding to l = odd reflections at 2θ values (Cu radiation) of approximately 3° (001), 9.5° (003), 22.4° (007, $d = 3.96A$), and 28.7° (009, $d = 3.10A$); higher order reflections were not given by Brindley and Chang 1974 (Figure 2).

Buerger precession photographs indicate unit spacings of the 27-A phase of approximately $a = 2.72A$, $b = 3.19A$, $c = 27.4A$, $\alpha = 90°$, $\beta = 98°$, $\gamma = 90°$. However, these are preliminary results because of the difficulty in examining large regions of reciprocal space for weak and diffuse reflections. In addition, however, with the phase so poorly organized and the diffraction data so limited, cell spacings as described may be unjustified. For example, this phase may be related to poorly developed domains within the 14-A phase. Unit cell parameters for the 14-A phase based on least-squares refinement of Picker four-circle (Mo radiation, graphite monochromator) data of thirty reflections are $a = 5.368(1)A$, $b = 9.297(2)A$, $c = 14.215(6)A$, $\alpha = 89.86(3)°$, $\beta = 97.15(3)°$, $\gamma = 89.98(2)°$. An X-ray data set involving one-half of the reciprocal sphere in $C\bar{1}$ space group symmetry was collected to $2\theta = 60°$. The model was refined by least-squares after a starting model was derived by Fourier methods. The final residual (R) factor was R = 0.055 for 934 reflections. Two major features of the refinement results important to this paper are: (1) The interlayer consists of two planes containing $(M + O)$, where M is equal to the interlayer cation species (e.g., Mg, Al, Cr) of the parent phase. There is no evidence for scattering material centered at $z = 0.5$ between the two 2:1 layers. (2) The two planes of $(M + O)$ show positional disorder along the [001] direction of about ±0.5A. A complete accounting of the structure refinement and results will be presented at a later time.

Powder diffraction data of various heat-treated chlorite (di,trioctahedral and tri,trioctahedral) polytypes

Sudoite. About 40 mg of sudoite-*IIb* from Ottré, Belgium was gently crushed to pass a 325 mesh sieve. The structural formula for this sample (Table 1) is $Al_{2.009}(Si_{2.999}Al_{1.001})O_{10}(OH)_2 \cdot (Mg_{2.002}Al_{0.82}Fe^{3+}_{0.184}Li_{0.015}Ti_{0.004}Mn_{0.001})(OH)_6$. The sample was heated to 575°C for two hours in air in a Pt crucible. A Siemens D-5000 diffractometer (Cu radiation, graphite monochromator) was used to examine the specimen prior to, and after, heat treatment. The sample was prepared by sedimentation in water on a "backgroundless" quartz plate.
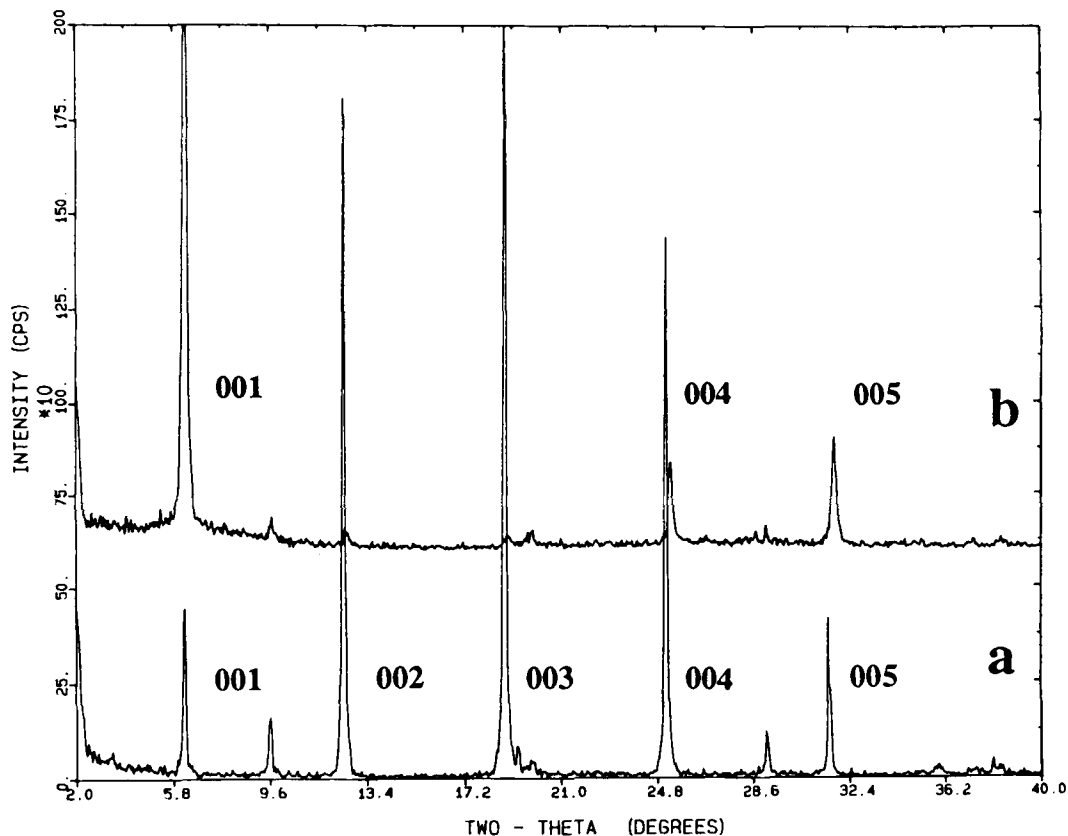
Figure 2. Sudoite 00l diffraction pattern (a) before and (b) after heat treatment (untreated sample: about 40 mg.; heat-treated sample: 575°C in air, 2 h). Patterns were taken with graphite monochromatized Cu radiation, 2 mm slit system, step scans at 0.02° at 0.5 s. Any unlabeled peaks are caused by pyrophyllite and other impurities.

Similar to heated-treated clinochlore, the 001 reflection increases in intensity and the other 00l reflections generally decrease (Figure 2). Note, however, that there is no 27-A phase. These results were confirmed also by using sudoite from the Oishizawa deposit, Hanaoka mine, Odate Shi, Akita, Honshu, Japan (U.S. Museum #151952) heated to 625°C for four hours in air and by Buerger precession single crystal examination of large flakes of Ottré sudoite.

Cookeite. Approximately 6 mg of cookeite, Londonderry, Western Australia (Guggenheim *et al* 1983, Bailey 1980) and 250 mg of cookeite (Clay Minerals Society Special Clay CAr-1), Jeffrey Quarry, North Little Rock, Arkansas (Miser and Milton 1964 as reported in Cerný 1970) were each heated to 625°C for 10 hours in a Pt crucible in air. Each sample was identified as a *Ia* polytype and consisted of single crystals 0.2–2 mm in size. Partial analysis of the Londonderry sample and a complete analysis of the Little Rock sample are given (Table 1). The structural formula of the latter is approximately $Li_{0.86}Al_{4.02}(Al_{0.96}Si_{3.04})O_{10}(OH)_8$. The samples were prepared for X-ray work in a similar

fashion as was done for sudoite, except that the crystals were not crushed. The results were similar to sudoite in that no 27-A phase was observed, and the 001 reflection increased in intensity and the other 00l reflections generally decreased.

B-rich chlorite. Approximately 18 mg of B-rich chlorite (Harvard #104797), Sahatany Valley, Madagascar (referred to as "manandonite" by Cerný 1970, Lacroix 1922, and Guggenheim *et al* 1983, but this name is now reserved for the 7-A, B-rich serpentine, see Ranorosoa *et al* 1989) was heated to 625°C for 10 hours in a Pt crucible in air. It has a structural formula of approximately $Li_{1.35}Al_{4.13}(B_{1.35}Al_{0.53}Si_{2.13})O_{10}(OH)_8$, and it is a *Ia* polytype. This sample was treated in a fashion similar to cookeite for X-ray diffraction analysis. In contrast to either sudoite or cookeite, however, this sample produced a 27-A phase after heating, along with an increase in the 14-A peak and a general decrease in intensity of higher order peaks of the 14-A phase.

Nimite. Approximately 25 mg of nimite-*Ia* crystals, Woodline Well, near South Windarra, Western Australia, was heated for 20 hours at 550°C in a Pt crucible
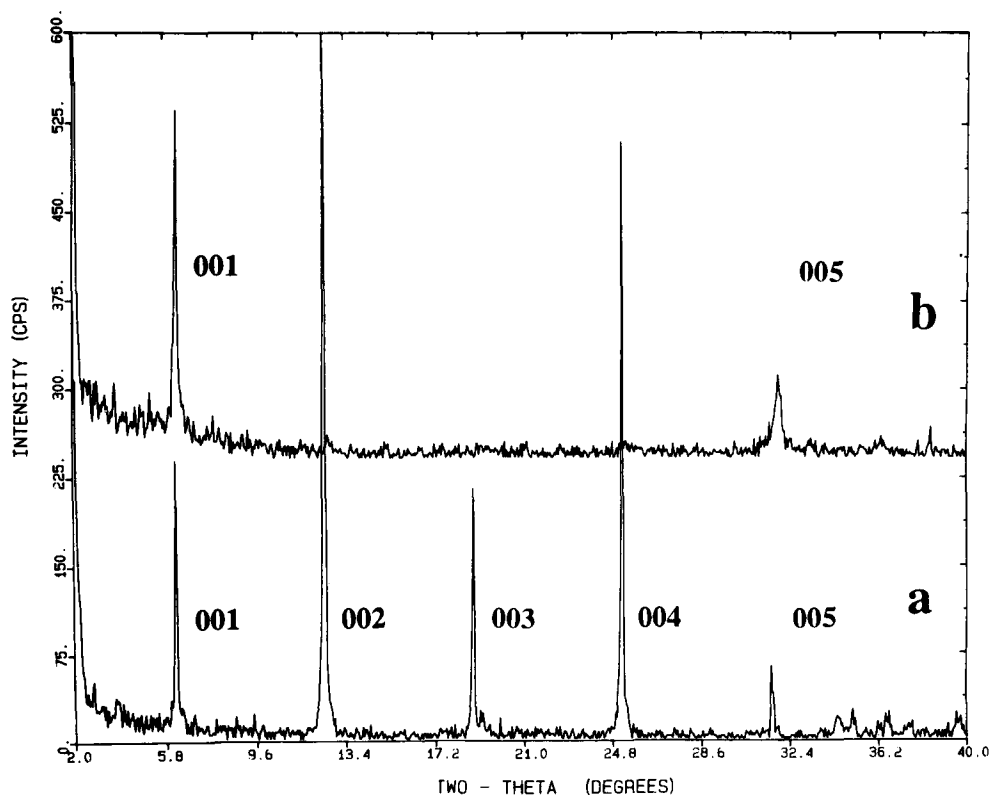
Figure 3. Chamosite 00l diffraction pattern (a) before and (b) after heat treatment (untreated sample: 20 mg.; heat-treated sample: 1 bar Ar pressure in presence of graphite, 550°C, 16 h, 15 mg). Diffractometer conditions same as for Figure 2.

in air, examined as single crystals in the powder diffractometer, and then re-heated at 600°C for an additional 16 hours to assure dehydroxylation. The structural formula (Guggenheim *et al* 1983) is approximately $Ni_{1.22}Mg_{1.98}Fe_{1.75}Al_{0.30}(Si_{2.93}Al_{1.07})O_{10}(OH)_8$. Crystals were crushed after heating for final powder X-ray examination (diffractometer conditions same as above). The X-ray pattern was similar to that of heat-treated sudoite (Figure 2): there was no evidence of a 27-A phase, the (001) peak increased in intensity, and the higher-order peaks generally decreased in intensity.

*Iron-rich tri,trioctahedral chlorite-*Ib*(90°).* Approximately 25 mg of an iron-rich chlorite-*Ib*(90°) from Arakawa Mine, Japan was heated and examined in a manner similar to nimite. The structural formula (Gugheim *et al* 1983) is approximately $Mg_{1.53}Fe_{3.18}$-$Al_{1.21}Mn_{0.07}(Si_{2.77}Al_{1.23})O_{10}(OH)_8$. X-ray powder data was similar to that of heat-treated sudoite (Figure 2), and there was no evidence of the 27-A phase, the (001) peak of the 14-A phase increased in intensity relative to the unheated sample, and there was a general decrease in intensity of the higher-order reflections. In contrast to heat-treated sudoite, however, the (005) peak was unobserved.

Additional heating experiments

A Mg-rich chamosite-*IIb* from Burke Mountain, Vermont, was abraded with an iron file to pass a 325 mesh sieve and heated to 550°C under reducing conditions in Ar in the presence of graphite at 1 bar. This heating procedure, although not discussed extensively by Bai *et al* (1993), is identical to the technique used in that study, since graphite was used as packing material near the sample. The chemical analysis of this sample (Saccocia *et al* 1994, Bai *et al* 1993) is given in Table 1. The dehydroxylation reaction was sluggish, requiring about 16 hours for 15 mg of sample to react, and the sample color became a darker shade of green. Figure 3 shows an X-ray diffractogram (same instrumental details as above) of the reactant (a) and product (b). Note that there is no 27-A phase present. The (001) and the (005) peaks (14-A cell) remain similar in intensity (Figures 3a and 3b), whereas other (00l) peaks are not observed for the pattern from the heat-treated sample. These results are in sharp contrast to Fe-rich clinochlores and chamosites heated in air (=oxidizing conditions), where there is a color change to reddish brown, along with the formation of a 27-A phase.

A second set of heating experiments identical to the

above were made using Burke Mountain chamosite, except that the graphite packing material was removed. The resulting product was reddish brown, indicating oxidizing conditions. However, unlike chamosite heated in air, no 27-A phase was observed in the X-ray diffractogram.

DISCUSSION

Topotaxy

The two different types of mosaic character of the hkl-type reflections in precession photographs of heat-treated clinochlore (Figure 1) are strongly suggestive of two separate phases, one with a 14-A spacing, the other with a 27-A spacing along the c axis. Furthermore, the difference in lateral spacings [a = 2.70A vs 5.366(2)A, b = 3.22A vs 9.304(4)A] and the non-exact multiples of corresponding spacings are further evidence for the presence of two phases. Finally, the results of the thermal experiments on chamosite, shown in Figure 3, indicate that the 14-A phase can be maintained without the presence of a 27-A phase. Thus, it is concluded that the transformation involves two phases, in those cases where both a 27-A and a 14-A peak occur in the diffraction pattern. Additional comments are given below (see the Brindley and Chang (1974) model) concerning the possible interstratification of two-layer phases.

Because reflections of the 27-A phase of the type hkl are present with lateral (a, b) spacings clearly different than the 14-A phase, these reflections suggest an incoherency between the intergrown phases in these directions. The few reflections from the 27-A phase and the broad mosaic character of these reflections suggest that the phase is poorly crystallized (Figure 1). As the intergrowth of the 27-A phase is crystallographically oriented with respect to the 14-A phase (Figure 1), the intergrowths are topotactic in nature. Furthermore, the c-axis cell length of 27-A suggests that the formation of the 27-A phase involves both the interlayer and the octahedral sheet of the 2:1 layer. Presumably, both phases make use of portions of the parent chlorite to minimize structural reorganization and the energetics of transformation.

Effect of iron content and water fugacity on the dehydroxylation mechanism

The heat-treatment of a chamosite under reducing conditions did not produce evidence of the 27-A phase (Figure 3). In addition, however, oxidizing conditions did not always produce the 27-A phase. For example, heat-treatment in air produces a 27-A phase for chamosite, whereas heat-treatment in a closed reaction vessel, even under oxidizing conditions, does not produce the 27-A phase. Thus, iron content and its potential for oxidation does not appear to be an important aspect for the formation of the 27-A phase. The significant

difference between an open system and a closed system is the H_2O content of the environment around the sample as dehydroxylation occurs, with the open system having a lower water fugacity than a closed system. Thus, we conclude that the formation of the 27-A phase in the clinochlore/chamosite series is at least partly dependent on the H_2O content of the surrounding environment. This interpretation is consistent with the study by Bai et al (1993).

Effect of 2:1 layer octahedral occupancy and polytypism on the dehydroxylation mechanism

In general, both the octahedral nature (dioctahedral vs trioctahedral) of the 2:1 layer and the stacking sequence (polytype) affects the formation of the 27-A phase, although neither of the trends are universal. Of the three di,trioctahedral chlorites examined (sudoite-IIb, cookeite-Ia, B-rich chlorite-Ia), only the B-rich chlorite-Ia sample produced a 27-A phase upon heating in air. Likewise, of the four Ia polytypes examined [cookeite-Ia, B-rich chlorite-Ia, nimite-Ia, Fe-rich chlorite-Ib(90°)], the 27-A phase was produced by the B-rich sample upon heating in air. Brindley and Chang (1974) noted also that heat-treated Fe-rich Ia and Ib chlorite polytypes (tri,trioctahedral chlorites) did not produce the 27-A phase. The samples they examined were very poorly crystallized and few details were given.

The B-rich chlorite-Ia sample showed the presence of the 27-A phase after heat treatment, and this sample breaks the observed trends for both octahedral "type" and polytype. The composition of this sample is unusual, and it may be an additional parameter in the formation of the 27-A phase. Excluding the B-rich chlorite-Ia sample, all Ia,b samples examined here and by Brindley and Chang (1974) do not produce the 27-A phase upon heating in air. Although the clinochlore-chamosite (IIb) series produced the 27-A phase upon heating in air, we note also that the heat-treated sudoite-IIb sample did not exhibit the 27-A phase, although this may be because sudoite is di,trioctahedral. In summary, with the limited data currently available, both stacking sequence and di,trioctahedral character may be important parameters in the formation of the 27-A phase in heat-treated chlorites, but the data are equivocal.

If the di,trioctahedral arrangement of chlorite is an important parameter in the formation of the 27-A phase, this would imply that (a) the dioctahedral sheet of the 2:1 layer in the Al-rich chlorites inhibits the transformation and conversely, (b) the trioctahedral sheet of the 2:1 layer in the Mg,Fe-rich chlorites promotes the transformation. If this is the case, it cannot be assumed that OH-loss at near 550°C is a result of dehydroxylation of the interlayer alone for those chlorites where a 27-A phase forms. For those reactions involving chlorites where a 27-A phase forms, partial OH-loss

from the 2:1 layer may occur simultaneously with the formation of the 27-A phase. Therefore, the interpretation of thermal analysis (e.g., TGA) data in which the peak at near 550°C is generally considered to be a result of the dehydroxylation of the interlayer only must be re-examined. A careful spectroscopic study may be useful to determine if such OH-loss occurs and whether the nature of octahedral occupancy is an important parameter in this transformation.

If the stacking sequence (*I* vs *II*) is an important parameter to consider in the transformation, then the slant of the interlayer octahedral sheet, based on the set of octahedral cation positions occupied in the interlayer, is an important structural feature determining if the transformation occurs. Interestingly, the results based on stacking sequence (*I* vs *II*) imply the importance of the interlayer configuration, whereas octahedral occupancy (dioctahedral *vs* trioctahedral occupancy of the 2:1 layer) suggests the importance of the 2:1 layer. Perhaps optimum conditions in both regions of the structure are necessary to produce the long spacing.

The Brindley and Chang model

The results of the structural refinement indicating that there is no scattering material centered between adjacent 2:1 layers (e.g., at $z = 0.5$) precludes the possibility that the Brindley and Change model is correct, since one of the two interlayers in their model requires scattering material at this location. Such scattering material would be evident in electron density maps of our one-layer structure as a superposition of both layers of the Brindley and Chang model, which is not observed. Thus, the most straightforward explanation is the presence of two intergrown topotaxial phases, one with a 14-A spacing and the other with a 27-A repeat as discussed above.

Because the refinement indicates also that there is positional disorder of the interlayer along the [001] direction, the Brindley and Chang model may be modified so that the 27-A phase results from the interstratification of interlayers displaced by ±0.5A along the [001] direction to produce a two-layer interstratification. We have produced models following this type of disorder, but in each case the agreement between the calculated and observed structure factors are very poor ($R > 0.40$) for the data. By calculation, all such models produce many intense reflections of the type 0*kl* and *h*0*l* with *l* = odd (based on $c = 27A$), which are absent on precession photographs. In addition, such models cannot explain the different lateral (*a, b,*) spacings observed in precession photographs.

The model of Villieras et al

The model of Villieras et al 1994, like the Brindley and Chang model, requires scattering material centered between adjacent 2:1 layers, which is contrary to the structure refinement. Thus, the model of Villieras et al 1994 cannot be correct.

The heat-treatment of clinochlore to produce a dehydroxylated interlayer involves a partial misalignment of the layers of the 14-A phase, which is evident in the structure refinement by positional disorder as described above. In our experience of examining many single crystals of both the original chlorite and the heat-treated product, the mosaic spread of the 14-A product is always greater than the original chlorite, as indicated by a visual inspection of the peak width of the reflections. We interpret this effect as a partial "delamination" or "exfoliation" of the layers, in which the layers slightly separate from each other during the process of dehydroxylation, as well as a loss of some crystallinity due to defects created by the dehydroxylation process. We minimized these effects by heating the single crystals gently over time, starting our heating experiments in a cold furnace. Villieras et al 1994 placed chlorite in a preheated furnace, thereby maximizing the thermal shock. We believe that the microporosity observed by Villieras et al is related to the partial delamination of layers. Alternatively, however, pores may form at the juncture between the two product phases present or by other mechanisms not yet understood, such as the introduction of additional defects. Regardless of the mechanism for the development of micropores, however, an explanation cannot be based on a two-layer modified chlorite structure.

SUMMARY AND CONCLUSIONS

Single crystal X-ray diffraction data are presented that indicate the existence of two phases in heat-treated clinochlore/chamosite chlorites that have undergone dehydroxylation under oxidizing conditions in air. These phases show topotaxy, with parallel *c* axes and a fixed orientation of lateral axes. One of these phases has a 14-A repeat and the other has a 27-A repeat. Previous researchers were unable to recognize such an intergrowth because their data set consisted only of spectroscopic data or powder diffraction data of oriented aggregates.

The 14-A phase, which most closely approximates the early concept (Brindley and Ali 1950) of the modified chlorite structure, is relatively well-crystallized and maintains the 2:1 layer of the parent phase. A preliminary report of the structure is presented; a major structural feature is that the interlayer consists of only two planes, each containing both cations and oxygen. In contrast, the 27-A phase is poorly crystallized with few reflections which are very diffuse.

The limited data on polytypic effects on the formation of the 27-A phase and the effect of whether the octahedral sheet in the 2:1 layer is either dioctahedral or trioctahedral are equivocal. Evidence suggests the importance of these parameters, but there are excep-

tions, as is the case for the B-rich chlorite. However, the B content may also affect the transformation. It is clear, however, that oxidation/reduction and the Fe content is not an important parameter in the formation of the 27-A phase, whereas water fugacity is important.

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