

Metastable phase relations in the chlorite-H₂O system

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ABSTRACT

The dehydroxylation reactions of Mg-rich chlorite-*I1b* (clinochlore) and Fe,Mg-rich chlorite-*I1b* (i.e., Mg-rich chamosite) were determined by using high-pressure differential thermal analysis (HP-DTA) to pressures of about 770 bars and temperatures of about 900 °C. These reactions may be described in the metastable binary system chlorite-H₂O. All experiments were reducing, with the Fe remaining in the Fe²⁺ state for all Fe-containing phases. For conditions involving open capsules and $P_{\text{H}_2\text{O}} < P_{\text{tot}}$, the chlorite phase undergoes the dehydroxylation of the interlayer to form a modified chlorite structure (MC) + vapor (V). Above about 100 bars, this reaction is nearly isothermal (clinochlore at about 690 °C, chamosite at near 670 °C). For conditions involving closed capsules and $P_{\text{H}_2\text{O}} = P_{\text{tot}}$, the reaction involving clinochlore occurs at the same P - T conditions as for open-capsule experiments. However, chamosite does not show an apparent reaction, although it is interpreted that such a reaction occurs over a large temperature range and thus the reaction is not detectable on the DTA thermogram. At higher pressures (e.g., 500 bars), a back reaction occurs when chlorite is formed from dehydroxylated chlorite during the quench in the presence of H₂O. This back reaction complicates the interpretation of the phases present in both open- and closed-capsule experiments where H₂O vapor is present, either as H₂O added initially or as H₂O generated during the reaction.

From a metastable invariant point at about 855 °C and 50 bars (clinochlore) and about 776 °C and 30 bars (chamosite) four reactions emanate: (1) MC = A + V, (2) A + V = L, (3) MC = L + V, and (4) MC + A = L, where MC is a modified chlorite structure with an oxide-like interlayer, A is a postulated anhydrous metastable phase, and V and L refer to vapor and a liquidlike phase, respectively. Reaction 1 is located at 817 (clinochlore) and 740 °C (chamosite) at 1 bar. Reaction 3 terminates in a singular point at slightly higher and unknown temperatures and pressures above the invariant point. Two other reactions, MC + V = L and MC = L, originate at the singular point. At a given pressure, the Fe-rich MC phase thermally decomposes at a much lower temperature than the Mg-rich MC phase, perhaps suggesting that the oxide interlayer in the Mg-rich MC phase is different from the Fe-rich MC phase.

INTRODUCTION

A fundamental problem in mineralogy and petrology is the role of H₂O and OH⁻ in reactions involving phyllosilicates. Clay interactions with H₂O and OH⁻ are important in many geologic environments, as well as in many industrial applications. Furthermore, the role of $f_{\text{H}_2\text{O}}$ can be particularly interesting and potentially significant if comparisons can be made between Fe-rich and Mg-rich systems. Often, the oxidation of Fe²⁺ is coupled with these

reactions. Understanding and, ultimately, predicting how such materials may act and interact as environmental conditions change require thermodynamic, kinetic, and atomistic knowledge of the materials and the reactions.

The reaction of chlorite under varying conditions of $f_{\text{H}_2\text{O}}$ is of fundamental interest in understanding fluid-rock interactions in hydrothermal (volcanogenic) deposits (e.g., see Appleyard and Guha, 1991) and the role of dehydration as a response to subduction processes at convergent plate boundaries (e.g., see Anderson et al., 1978; Tatsumi, 1989) and in determining pressures and temperatures of metamorphic processes. Both metastable and stable reactions are of interest, especially if reactions pro-

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ceed through transformations of the metastable phases before the stable assemblages are obtained.

Upon heating in air, chlorite undergoes dehydroxylation of the interlayer, where half or more of the OH groups are lost as H₂O and the interlayer cations move away from the center plane of the interlayer (Brindley and Ali, 1950). This structure was called the modified chlorite structure by Brindley and Ali (1950) and appears to persist in this state for long periods, even when immersed in H₂O. It is characterized by X-ray powder diffraction by an increase in the intensity of the (001) peak by a factor of 2–5 and a general loss in intensity of higher order (00 l) peaks relative to chlorite. The dehydroxylation temperature is dependent on crystallinity, grain size, and composition (Caillère and Hénin, 1960), with a Fe²⁺-rich interlayer typically dehydroxylating near 450 °C and a Mg-rich interlayer near 640 °C. At temperatures above 750 °C, dehydroxylation of the talc-like layer occurs first, followed by recrystallization to olivine.

Chlorite was first studied by DTA at various H₂O vapor pressures by Stone and Weiss (1956). They used a dynamic gas method, in which they forced steam through 0.45 g of coarsely ground (<0.5 mm) chlorite powder during the DTA procedure. At steam pressures of ≤3 atm, they observed that (1) an endothermic peak is replaced by two or more peaks at higher pressures, (2) an exothermic peak at near-vacuum conditions is suppressed at 1 atm, and (3) an endothermic peak decreased in size at 3 atm relative to 1 atm. These remarkable changes are difficult to evaluate. The use of such coarsely ground samples, although necessary to facilitate steam migration through the sample, was shown by Shirozu (1980) to affect DTA curves adversely by producing extra endotherms, changing the size ratio between two peaks, increasing the number or shape of exotherms, etc.

This paper reports on high-pressure DTA experiments of Mg-rich and Fe²⁺, Mg-rich chlorite. It is a companion paper to a Mössbauer study of the experiment products of the Fe, Mg-rich chlorite (Rancourt, unpublished manuscript) and to a high-temperature single-crystal study of clinocllore (Nelson and Guggenheim, 1993). Equilibrium experiments, which are not a topic of this paper, are summarized by Chernosky et al. (1988).

EXPERIMENTAL PROCEDURE

Starting materials

Three chlorite samples were used in the HP-DTA study, two Mg-rich end-member clinocllore samples and a Mg-rich chamosite sample. Chemical analyses are given in Table 1. The Mg-rich clinocllore is from West Town, Chester County, Pennsylvania, and Långban, Sweden. The West Town sample (Harvard no. 102181) is from a large (15 cm) plate, light green in color. Single-crystal X-ray analysis indicates that it is very crystalline; it is a two-layer, chlorite-*I1b* polytype. The Långban sample (Harvard no. 116353) is composed of orange plates ranging in size from 0.2 to 1.5 cm in calcite. Single-crystal X-ray

studies show variability in crystallinity, with most crystals as semirandom stacking of *I1b* polytypes. About 5% of the crystals studied are well-ordered one-layer *I1b* polytype. Crystals were acid-leached from the sample with a very dilute solution of HCl.

The chamosite sample is from Burke Mountain, in northeastern Vermont. The dark green sample is from an altered basalt dike. Although the crystals are small (about 0.2–0.5 mm in size), the sample is a pure aggregate. Single-crystal X-ray analysis indicates that all crystals are a semirandom stacking of *I1b* polytypes. The chemical analysis (Table 1) shows that the chamosite is nearly midway in solid solution between clinocllore and chamosite, with a slight predominance of Fe²⁺ over Mg. This sample was used in solubility studies by Saccocia and Seyfried (1993).

The distributions of elements of high atomic number, essentially Fe and Mn, of the chamosite octahedral sheets (interlayer and 2:1 layer) may be determined approximately by using X-ray powder diffraction data, as discussed by Petruk (1964) and Brown and Brindley (1984). The procedure uses the ratios of the integrated intensities of $I(003)/I(005)$ to determine the degree of asymmetry of the Fe and Mn content between the two octahedral sheets. With the assumption that trivalent cations in the interlayer order into M4, the M4 content is Fe_{0.28}³⁺, Al_{0.72}, and M3 sites contain (Mn_{0.03}, Fe_{0.87}²⁺, Mg_{1.10}); the elements of higher atomic number thus total to 1.18, as determined by the Petruk method. This allows the determination of the structure formula for chamosite, with a small adjustment of vacancies to the interlayer, as [(Mg_{1.08}, Fe_{0.86}²⁺, Fe_{0.28}³⁺, Al_{0.71}, Mn_{0.03})(OH)₆]·[(Mg_{1.08}, Fe_{1.43}²⁺, Al_{0.49})(Si_{2.56}, Al_{1.44})O₁₀(OH)₂].

Apparatus and procedures

The HP-DTA system (Koster van Groos, 1979) consists of a Cu sample holder accommodating three sample capsules. Capsules were made by an extrusion technique using Au foil. Capsules were 7 mm in length, 3 mm in diameter, and 110 mg in weight, with a reentry well 1 mm deep at the base of each capsule to position the Pt-Pt₉₀Rh₁₀ thermocouple at the center of the sample volume. The central capsule in the holder contained about 18 mg of reference material (α -Al₂O₃) and 2 mg of pure quartz (St. Peter Sandstone), and the other two capsules each contained about 20 mg of chlorite. The quartz was added as an internal temperature standard using the low-high quartz inversion (Koster van Groos and ter Heege, 1973). The chlorite was abraded with an Fe file to reduce its grain size without compromising its structural integrity (Guggenheim et al., 1982) and passed through a 325 mesh sieve. Samples were stored in a desiccator over a saturated solution of Mg(NO₃)₂·6H₂O (55% R.H.).

Each cell in the Cu holder is coated with TiO₂ to insulate the holder electrically and thermally from the capsules. The completed assembly was sealed within an internally heated pressure vessel, similar to the one described by Holloway (1971), and mounted horizontally.

TABLE 1. Chemical analyses of the studied chlorite samples

Oxide	Clinochlore ^a Långban		Clinochlore ^b West Town, PA		Mg-rich chamosite ^c Burke Mountain, VT	
	EMPA	Wet	EMPA	Wet	EMPA	Wet
SiO ₂	33.02 ± 0.19	28.35	29.81 ± 0.17	24.30	24.57 ± 0.16	
Al ₂ O ₃	14.50 ± 0.10	20.11	18.32 ± 0.11	21.30	21.04 ± 0.12	
TiO ₂	0.1 ± 0.01	0.10	0.06 ± 0.02	0.060	0.05 ± 0.03	
Fe ₂ O ₃		1.30		3.50		
FeO	0.09 ± 0.02 ^d	2.16 ^e	3.36 ± 0.06 ^d	26.00	27.87 ± 0.22 ^d	
MnO	0.73 ± 0.03	bd ^f	0.02 ± 0.01	0.366	0.36 ± 0.02	
MgO	36.84 ± 0.16	32.82	32.92 ± 0.16	13.78	14.11 ± 0.08	
CaO	bd		bd	0.005	bd	
Na ₂ O	0.15 ± 0.01		bd	bd	0.01 ± 0.01	
K ₂ O	0.01 ± 0.01		bd	0.021	0.01 ± 0.01	
P ₂ O ₅	bd		bd	0.022	0.02 ± 0.01	
H ₂ O ⁺		13.02		11.80		
H ₂ O ⁻		1.23				
CO ₂				0.005		
Total	85.35	99.09	84.49	101.13	88.02	
Formula based on 28 positive charges						
Si	3.14	2.74	2.89	2.56	2.61	
¹⁴ Al	0.86	1.26	1.11	1.44	1.39	
¹⁶ Al	0.76	1.03	0.98	1.20	1.24	
Ti	0.00	0.01	0.00	0.00	0.00	
Fe ³⁺		0.09	0.09 ^g	0.28	0.26 ^g	
Fe ²⁺	0.01	0.17	0.17 ^g	2.29	2.18 ^g	
Mn	0.06	0.00	0.00	0.03	0.03	
Mg	5.21	4.74	4.76	2.16	2.23	
Ca	0.00			0.00	0.00	
Na	0.03			0.00	0.00	
K	0.00			0.00	0.00	
¹⁶ Σcharge	12.87	13.22	13.07	13.40	13.38	
¹⁶ Σ	6.07	6.04	6.00	5.96	5.94	

^a Clinochlore, Långban, Sweden (Harvard no. 116353), D. Lange, analyst, Cameca MBX electron microprobe analysis (EMPA) using WDS; stds. used: Si, magnesium enstatite; titanium rutile; aluminum kyanite; iron fayalite; manganese rhodonite; calcium wollastonite; sodium albite; potassium microcline; phosphorus apatite. Beam voltage of 15 keV, beam current of 15 nA, beam size 16 × 16 μm, using BA85 matrix correction. Analysis is the average of five points.

^b Clinochlore, West Town, Pennsylvania (Harvard no. 102181), Jun Ito, wet-chemical analyst, D. Lange, EMPA chemical analyst; see probe details above.

^c Mg-rich chamosite, Burke Mountain, Vermont, R. Knurr, wet-chemical analyst by DCP, FeO by titration, and H₂O⁺ by weight change. D. Lange, EMPA chemical analyst; see probe details above.

^d All Fe assumed FeO.

^e Possible hematite contamination noted by analyst.

^f Below detection.

^g Where possible, Fe²⁺ and Fe³⁺ values calculated in EMPA analysis by using Fe₂O₃/(Fe₂O₃ + FeO) ratios determined from wet analysis.

Experiments were made between 50 and 900 °C with a heating rate of 20 °C/min. The temperature of the sample was obtained from the reference capsule thermocouple and corrected for deviations by using the differential temperature (ΔT). The correction was usually 1–2 °C, with corrected temperatures accurate to ± 1 °C. The HP-DTA signals were recorded on the 50- μ V range of a Kipp recorder, resolving ΔT to 0.05 °C. Ar was used as the pressure medium, which was measured by calibrated Bourdon-type Heise gauges accurate to within 0.5%. Separate gauges covered ranges of 0–68 bars and 0–1000 bars, respectively. Samples were subjected to several conditions to establish the effect of H₂O vapor pressure on the dehydroxylation reaction. About 30 experiments were made with open-system conditions, $P_{\text{H}_2\text{O}} < P_{\text{tot}}$. Up to 15 wt% H₂O was added to some of these experiments; see Table 2. Capsules for these latter experiments were loosely packed with silica wool filler to minimize convection. Because the molar volume of H₂O is high, H₂O vapor displaced the Ar in these experiments, and $P_{\text{H}_2\text{O}}$ approached P_{tot} . A second series of 40 experiments was made

with H₂O added to the sample and the capsule welded shut, so that $P_{\text{H}_2\text{O}} = P_{\text{tot}}$. Closed-capsule experiments cannot be made at very low pressures, and, even for higher pressures, almost half of the closed-capsule experiments failed because of the high molar volume of H₂O and capsule leakage. Peak temperature, defined as the temperature at the maximum deflection of the dehydroxylation endotherm, was used to define the temperature of the reaction.

The effect of the heating rate was determined by comparing experiments described above with experiments made at 10 °C/min and 1 bar for each of the chlorite samples studied. The heating rate did not seriously affect the peak temperatures.

Experimental products

Selected experiments were halted immediately before and after DTA peak temperatures, so that products could be examined by petrographic methods, Debye-Scherrer X-ray, and X-ray diffractometer methods (Siemens D-5000, graphite monochromatized Cu radiation). In ad-

TABLE 2. Results from the high-pressure differential thermal analysis experiments

Expt.	%H ₂ O	First peak [T(P)]			Second peak [T(P)]		
		Onset	Peak	Return	Onset	Peak	Return
Chamosite (open)							
C-1A	dry	520 (1)	595 (1)	615 (1)	710 (1)	738 (1)	750 (1)
N-4A	dry	542 (1)	588 (1)	613 (1)	—	743 (1)	749 (1)
N-5A	dry	532 (1)	595 (1)	619 (1)	—	—	—
N-14A	15	567 (18.5)	643 (18.8)	680 (18.9)	740 (19.3)	772 (19.4)	793 (19.6)
N-36A	15	595 (25)	659 (25)	690 (25)	750 (25.5)	780 (26)	796 (26)
N-29A	15	570 (31)	657 (33)	699 (34)	723 (34)	782 (35)	793 (35)
N-38A	15	590 (56)	660 (57)	730 (58)	752 (59)	782 (60)	—
C-2A	10	580 (57)	655 (58)	720 (59)	756 (60)	777 (60)	791 (60)
N-18A	15	592 (94)	661 (95)	724 (95)	726 (95)	770 (95)	793 (96)
N-37A	15	570 (91)	675 (95)	717 (96)	735 (96)	778 (97)	800 (97)
C-3A	10	610 (174)	672 (178)	720 (179)	740 (181)	780 (182)	798 (183)
N-53A	dry	—	675 (421)	—	—	780 (435)	—
C-4A	10	—	686 (444)	725 (446)	—	778 (456)	791 (457)
S-131A	10	—	669 (620)	—	—	802 (634)	—
Chamosite (closed)							
S-7B*	5	639 (432)	768 (451)	—	—	—	—
S-4B*	dry	—	765 (461)	—	—	—	—
C-5A*	5	740 (463)	768 (470)	—	—	—	—
N-52A*	dry	—	770 (515)	—	—	—	—
S-124B*	dry	710 (518)	767 (520)	—	—	—	—
S-123B*	dry	694 (522)	767 (529)	—	—	—	—
S-10B*	5	—	750 (598)	—	—	—	—
S-8B*	5	708 (698)	747 (708)	—	—	—	—
S-6B*	5	675 (752)	740 (768)	—	—	—	—
Clinochlore (open)							
N-7A	dry	595 (1)	650 (1)	680 (1)	780 (1)	815 (1)	—
N-11B	dry	590 (1)	638 (1)	667 (1)	797 (1)	817 (1)	—
C-1B	10	592 (1)	645 (1)	677 (1)	776 (1)	818 (1)	—
S-112A	dry	640 (1)	667 (1)	708 (1)	—	—	—
S-112B	dry	610 (1)	670 (1)	706 (1)	—	—	—
N-15A	8	629 (12)	678 (12)	740 (12)	790 (12)	818 (12)	830 (12)
N-36B	15	664 (25)	685 (25)	718 (25)	—	—	—
N-29B	dry	—	690 (34)	—	—	—	—
N-38B	15	—	694 (60)	762 (61)	—	—	—
C-2B	10	638 (58)	688 (59)	750 (60)	850 (60)	863 (60)	876 (61)
S-97A	dry	—	710 (79)	—	825 (79)	848 (80)	—
S-97B	dry	—	—	—	815 (79)	850 (80)	865 (80)
N-37B	15	—	695 (95)	716 (95)	855 (98)	869 (98)	884 (99)
S-98B	dry	—	705 (123)	—	—	840 (125)	857 (126)
C-3B	10	—	688 (179)	—	852 (184)	865 (185)	877 (186)
C-4B	10	—	686 (444)	—	841 (464)	855 (466)	874 (468)
Clinochlore (closed)							
S-119A*	dry	650 (276)	693 (283)	713 (285)	—	—	—
S-119B*	dry	660 (276)	682 (283)	700 (284)	—	780 (303)	796 (304)
S-113B*	6	—	700 (400)	720 (402)	731 (403)	762 (407)	791 (409)
S-120A*	dry	650 (438)	677 (441)	—	—	—	—
S-124A*	dry	650 (488)	667 (490)	681 (492)	720 (514)	744 (517)	758 (519)
S-116A*	dry	—	681 (538)	—	—	752 (566)	—
S-116B*	dry	—	686 (538)	—	—	745 (566)	—
S-127A*	dry	649 (535)	676 (538)	—	—	—	—
S-118A*	dry	638 (541)	674 (552)	706 (554)	738 (558)	755 (572)	771 (575)
S-118B*	dry	660 (548)	682 (552)	718 (557)	—	—	—
S-115A*	dry	663 (561)	680 (572)	708 (578)	—	757 (593)	—
S-122A*	8	—	691 (628)	710 (633)	—	740 (669)	—
S-122B*	10	675 (625)	688 (628)	—	—	—	—

Note: clinochlore samples with numbers beginning with S are from West Town, PA. All others from Långban, Sweden.

dition, products were examined in a Jeol JEM 35C scanning electron microscope (SEM) to obtain particle size information.

RESULTS AND DISCUSSION

Identification of the phases

Table 2 shows a tabulation of the DTA results. The physical appearance of products of low-pressure experi-

ments (near 1 bar) with both Mg- and Fe-rich chlorite samples in open capsules show little change after the first (endothermic) peak, except for a slight change in color to lighter greens and a slight compactness of the sample. On the basis of the X-ray results and the work of Brindley and Ali (1950), this phase represents the modified chlorite (MC) phase. Although the physical appearance changed little, the X-ray patterns show a strong 001 peak and weaker higher order peaks. At higher temperatures

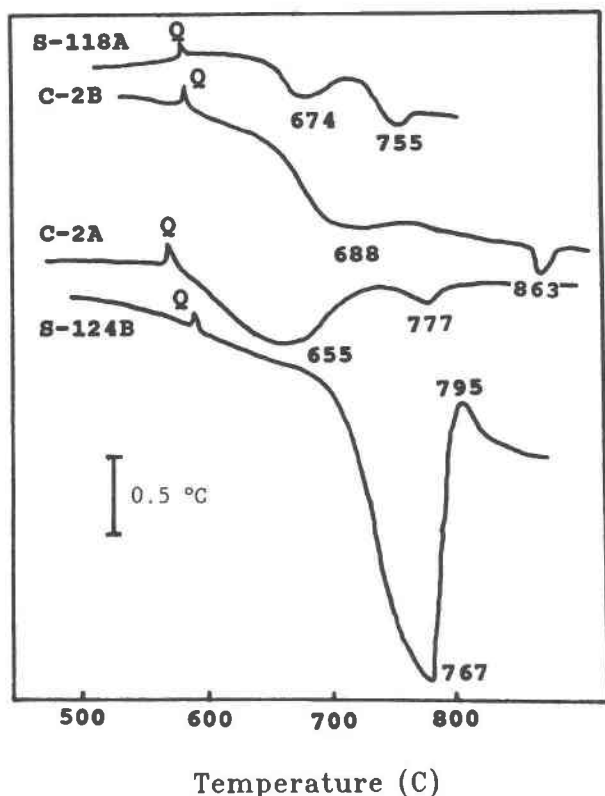


Fig. 1. HP-DTA curves of selected experiments, with peak temperatures provided. The top two thermograms are for clinocllore, and the bottom two are for chamosite. Conditions of experiments: S-118A, about 562 bars; C-2B, about 60 bars with 10 wt% H₂O added; C-2A, about 59 bars with 10 wt% added; S-124B, about 520 bars. Q = quartz.

after the second (endothermic) peaks, both compositions produced compact, uniform glassy products. The Fe-rich chlorite was slightly lighter in color. This glassy phase is liquidlike (L).

HP-DTA curves of selected representative open- and closed-capsule experiments for each sample are shown in Figure 1 for higher pressures. The illustrated open-capsule experiments were made at 60 bars and involve 20 mg of sample with 10 wt% H₂O added. The Fe-rich sample has a low-temperature, broad endotherm at 655 °C, compared with 688 °C for the clinocllore. Experiment products for both compositions remain powderlike, much like the starting material but more compact, and are interpreted to be the MC phase. At higher temperatures, both thermograms for open-capsule experiments show endotherms: at 777 °C (Fe) and 863 °C (Mg). The experiment products for both compositions were compact and glassy (L).

Closed-capsule experiments for the two compositions are very different. For chamosite, there is only a single endotherm. Immediately before the peak, the product looks similar to the starting material, although slightly more compact. After the peak, the color is much lighter,

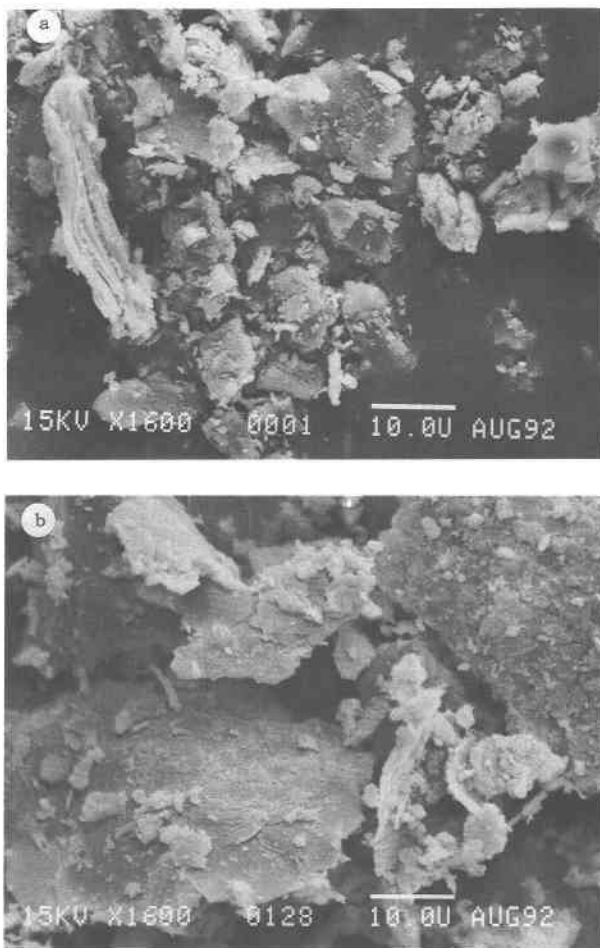


Fig. 2. SEM photographs showing grain-sized variations of chamosite starting material (a) and product (b) at the same magnification (white bar indicates 10 µm). Product is the result of a quench from about 500 bars and 680 °C, which is just above the interlayer dehydroxylation temperature. See text for discussion.

and the sample appears glassy (L). There were some crystalline grains (1–2%) present in the glassy matrix, but these could not be identified. For clinocllore, the product after the first endotherm was similar to the open-capsule experiment (MC). After the second endotherm, the products were glassy, compact, and without a color change (L). The bulk chemistry of the glass (L) phase reflects the composition of the parent, but little is known about the H₂O content. However, it may be inferred in part from the metastable phase relations and the reaction curves (see below). Presumably, there was a vapor phase (V) present as well. Thus, there are four phases readily identified or assumed to be present: C (chlorite), MC, L, and V.

Particle size and back reactions

SEM photographs of the experiment product of samples of chamosite treated at just above the interlayer dehydroxylation reaction (e.g., 680 °C) at about 500 bars indicate a significant change in grain size, with grain sizes

up to a factor of four larger than the original (Fig. 2). These experiments, which were under open-capsule conditions, were evolving H₂O by interlayer dehydroxylation. Although the temperature above the interlayer-dehydroxylation endotherm was reached, the experiment products were chlorite, rather than the expected modified chlorite structure. Grain sizes were affected by annealing or higher temperatures. For example, experiments made to 740 °C produced smaller particle sizes than experiments at 680 °C. In addition, samples brought to 680 °C but annealed for 10–20 min before quenching also had smaller grain sizes. Thus, the results suggest that chlorite was formed from partially dehydroxylated chlorite during quenching in the presence of H₂O (= back reaction), with variations in grain size determined by the amount of H₂O vapor present. Similar results were observed for clinocllore under analogous conditions (open capsules, above the interlayer dehydroxylation temperature), although the grain sizes of the examined quenched products are not as large.

Debye-Scherrer X-ray powder patterns of the quench products for both chamosite and clinocllore indicated that the grains (overgrowths?) were similar to the reactants, consisting of chlorite-*Ib* polytypes, and not the *Ia* or *Ib* polytypes typical of low temperatures or metastability (see Bailey and Brown, 1962). Given the rapidity of the quench of a couple of minutes and the fact that the experiments were open capsule, the grain size changes are remarkable. A similar, remarkable growth of a phyllosilicate during a rapid quench was found in experiments with vermiculite, where very large crystals (2 mm) formed from a fine-grained vermiculite reactant in the presence of H₂O.

***PT* relations**

Thermograms involving closed capsules of the Fe and Mg forms show considerable differences. For example (Fig. 1), the clinocllore thermograms (closed and open capsule) have two endothermic peaks (e.g., at 674 and 755 °C). Both peaks are broad and small in size for the closed-capsule experiments, whereas the open-capsule lower-temperature peak for clinocllore differs somewhat by being larger (medium size but still broad). Open-capsule experiments involving chamosite have peak characteristics similar to those of the open-capsule experiments for clinocllore.

In contrast, however, there is only one endotherm for the closed-capsule experiments involving Fe-rich chlorite (at 767 °C), followed by an exothermic peak (at 795 °C). The endotherm is large, although still broad. Thus, under conditions of $P_{\text{tot}} = P_{\text{H}_2\text{O}}$, Fe-rich chlorite thermally decomposes directly to a liquid phase without an apparent intermediate MC phase with a dehydroxylated interlayer. At slightly higher temperatures, recrystallization occurred, as shown by the exothermic peak. The recrystallization products included olivine solid solution and hematite. There were also several unidentified lines in diffraction patterns of products. Olivine and hematite are

stable phases involved in the decomposition of chlorite (Chernosky et al., 1988) and do not play a role in the metastable equilibria. Rancourt (unpublished manuscript) determined by Mössbauer studies that the chlorite did not oxidize. Thus, the Fe is all Fe²⁺, except for the small amount of Fe³⁺ present in the original material. The Mössbauer results confirm similar work by Dyar et al. (1992).

The presence of C, MC, L, and V is obvious from the nature of the reactions described (see above). The lower temperature reaction involves the interlayer dehydroxylation of chlorite ($C = MC + V$), whereas the high-temperature reactions primarily involve the modified chlorite phase. The positions of the apparent reactions in *P-T* diagrams are illustrated in Figure 3. These diagrams have close topological similarities to the previously determined *P-T* relationships of dioctahedral phyllosilicates such as kaolinite (Yeskis et al., 1985), Na-rich and K-exchanged montmorillonite (Koster van Groos and Guggenheim, 1987), and Ca-exchanged montmorillonite (Koster van Groos and Guggenheim, 1989). These previous studies have modeled the phase relations on a phyllosilicate-H₂O binary system.

Two observations may be made with respect to the topology of the observed reactions and the possibility of a chlorite-H₂O binary system. Under conditions of $P_{\text{H}_2\text{O}} = P_{\text{tot}}$, the Mg-rich chlorite has a DTA signature for an interlayer OH-loss reaction, but there is no apparent peak indicating a similar reaction in the Fe-rich chlorite. At higher temperatures, both the Mg-rich and the Fe-rich systems have peaks indicating a loss in crystallinity (e.g., both near 750 °C at 600 bars). Two interpretations are possible: (1) the Fe-rich chlorite does not produce a modified chlorite structure phase under closed-capsule conditions, or (2) the reaction occurs but was not detected in our experiments, because OH loss is slow and occurs over a large temperature interval. The latter interpretation cannot be easily tested because back reactions would be expected for closed-capsule experiments where H₂O vapor is present. In fact, for chamosite, experiments were made to 710 °C at 469 bars and then quenched, and the products were examined by X-ray methods. It was found that the product was chamosite and not the modified chlorite structure, but SEM photographs indicated a larger grain size than that of the original starting material. Therefore, there is strong evidence that a back reaction had occurred. Thus, it appears likely that the chlorite to modified chlorite reaction exists for chamosite, although OH loss is relatively slow and not detectable by our DTA.

The other observation relates to the topology of the binary system. As with the dioctahedral phyllosilicates studied previously, another phase is required. In systems containing dioctahedral phyllosilicates (e.g., Na or K-rich montmorillonite: Koster van Groos and Guggenheim, 1987), this phase was a dehydroxylate (e.g., montmorillonite dehydroxylate). In contrast to trioctahedral phyllosilicates, the vacant site in dioctahedral phyllosilicates allows the reorganization of the structure without a major

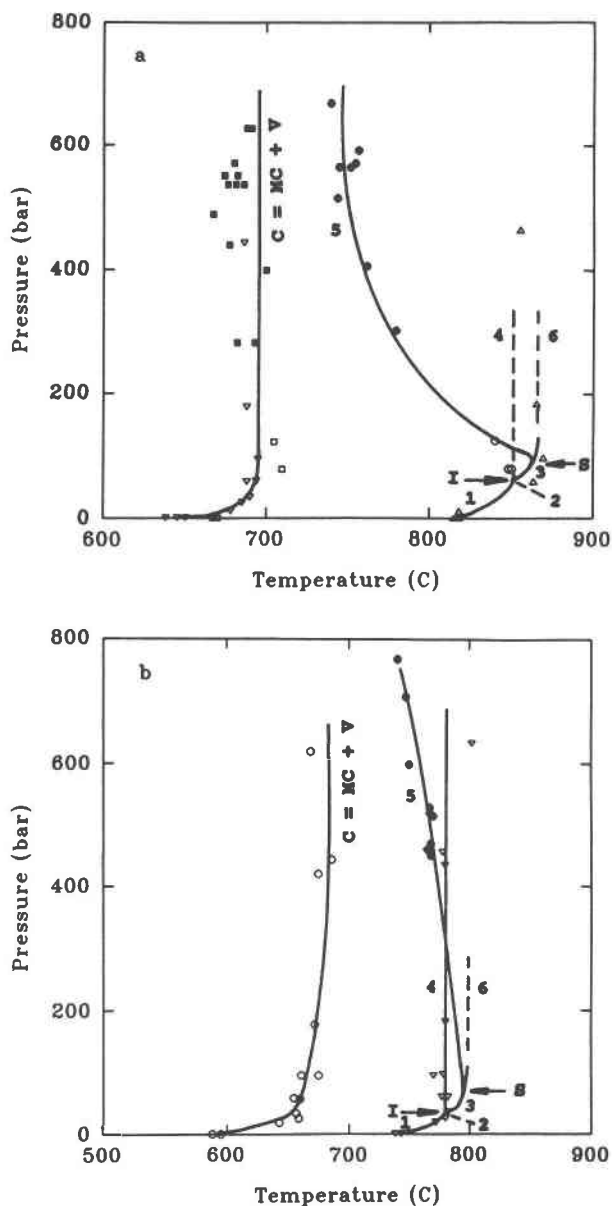


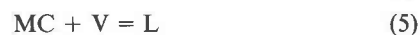
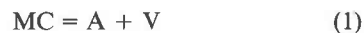
Fig. 3. *P-T* relations in the clinocllore-H₂O (a) and the Mg-rich chamosite-H₂O (b) systems. Reaction $C = MC + V$ in a occurs at the same conditions for both open and closed experiments. The points represent the maximum temperature possible for this reaction. This reaction, $C = MC + V$, is apparently missing for chamosite (b) for closed experiments. Reactions labeled 1–6 are defined in the text. The invariant (I) and singular (S) points are labeled. Solid and open symbols are closed and open experiments, respectively. In a, triangles are from West Town and all others are from Långban. In b, open circles and triangles indicate first and second peaks from open-capsule experiments, respectively.

reconstructive transformation (Guggenheim et al., 1987), thereby producing a metastable dehydroxylate structure. There are strong diffraction and other data to support the observation of these phases. However, there are no anal-

ogous data to support a trioctahedral analogue, such as a modified chlorite dehydroxylate phase. In fact, Brindley and Ali (1950) showed that chlorite apparently transforms topotactically to olivine, and they proposed a mechanism to explain this transformation.

The observation of the stable phase (olivine) instead of a metastable phase suggests that the metastable phase is short-lived. How short-lived this phase may be is not consequential. Brindley and Ali (1950, p. 28–29) noted the possibility of a short-range ordered, transitional form between the modified chlorite structure and the formation of olivine, if account is taken of the replacement of some Al by Si to form olivine. The transformation mechanism, thus, must be complex and multisteped, with the formation of a transitional phase. For convenience, we call this phase the MC-anhydrous phase (A); it is not analogous in structure to the dehydroxylate phases common among the dioctahedral phyllosilicates. Thus, it is now possible to place the metastable phase assemblages into a phase-equilibrium framework using the binary chlorite-H₂O system. In summary, there are five phases: chlorite (C), modified chlorite (MC), liquid (L), an aqueous vapor (V), and MC-anhydrous (A) phases, the last four involved in a Schreinemaker's bundle at higher temperatures.

At higher temperatures, the following reactions (Fig. 3) occur:



Reactions 1–4 form a Schreinemaker's bundle around an invariant point, which is determined to be 846 ± 15 °C at approximately 50 bars for the West Town clinocllore, 863 ± 15 °C at approximately 50 bars for the Långban clinocllore, and 776 ± 15 °C at 30 bars for chamosite. Several reactions are inferred from the phase relations. For example, there are no experimental data for Reaction 2 because the A phase is transitional and short-lived. Therefore, this reaction is appropriately placed topologically in Figure 3 but cannot be defined more accurately. Inferred reactions are shown as dashed lines. The composition of each phase is believed constant, with the exception of L, which has a variable H₂O content, as indicated by the negative slope of Reaction 5. Reaction 3 terminates in a singular point, S, at higher pressures and temperatures, which cannot be defined by the data. At this point, the H₂O content of the MC phase is equal to that of the liquid. At higher pressures Reactions 5 and 6 occur. No direct evidence for Reaction 6 is available, but it is required from the phase relations.

The enthalpy of interlayer dehydroxylation and 2:1 lay-

er dehydroxylation may be calculated (e.g., Anderson, 1977; Koster van Groos and Guggenheim, 1986) from the *P-T* relations of each of the dehydroxylation reactions, respectively. For clinocllore, the enthalpy of dehydroxylation of the interlayer is approximately 610 ± 70 kJ/mol for Långban, 850 ± 40 kJ/mol for West Town, and 380 ± 50 kJ/mol for chamosite. Although the difference between the enthalpy of dehydroxylation for the two clinocllore samples is high (230 kJ/mol), the uncertainties for both values are high also. The large magnitudes of the uncertainties occur because of the experimental conditions for the 1-bar data; even very small overpressures produce considerable variations in the temperature of dehydroxylation because of the low slope of the reaction in *P-T* space near 1 bar.

For Reaction 1, the enthalpy of 2:1 layer dehydroxylation is 930 ± 20 kJ/mol for the Långban clinocllore and 860 ± 120 kJ/mol for chamosite. These values are consistent with the large amount of H₂O in the structure. The lack of 1-bar data prevents a determination of enthalpy of 2:1 layer dehydroxylation for Reaction 1 for the West Town clinocllore.

Implications regarding the structure of modified chlorite

Both the chamosite and the clinocllore open-capsule experiments show interlayer OH loss ($C = MC + V$) at lower temperatures followed by a loss in crystallinity at higher temperatures. The low-temperature interlayer-OH loss reaction for the chamosite occurs at about 20 °C lower than for the clinocllore at pressures of near 400 bars. Thus, at least for dynamic experiments involving small grain size, the chemical composition of the chlorite does not greatly affect the thermal stability of chlorite under conditions of $P_{\text{H}_2\text{O}} < P_{\text{tot}}$. These results are in sharp contrast to the 1-bar experiments. Interlayer H₂O-loss in clinocllore occurs at about 654 °C at 1 bar, whereas it occurs at about 592 °C in Fe-rich samples, a difference of about 60 °C. However, this difference is nowhere near as large as the difference of 190 °C reported by Caillère and Hénin (1960) in their heating experiments.

The thermal extent of the modified chlorite phase field is greatly reduced for the more Fe-rich samples. Note, for example, that the Fe-rich modified chlorite structure decomposes at about 770 °C above about 100 bars, whereas the Mg-rich modified chlorite structure persists to 855 °C. This large difference suggests that the nature of the interlayer oxide sheet in the modified chlorite structure between Mg- and Fe-rich compositions is sufficiently different to account for the temperature variations.

Variations in DTA results of the clinocllore

Ignoring small differences in composition, the Långban sample, which has substantial stacking disorder, would be expected to have lower thermal stability than the West Town clinocllore. This is consistent with the open-capsule experiments, which show that the loss of interlayer OH of the Långban sample occurs at a temperature about

20 °C below that of the West Town sample. There was an insufficient amount of the Långban sample to compare reactions for closed-capsule experiments.

In preliminary experiments, Guggenheim (unpublished manuscript) found that the same polytype occurs for the derived modified chlorite structure regardless of the polytype of the original chlorite, although it is unknown if regularity in stacking is inherited from the parent. It is noteworthy, however, that the thermal decomposition of the modified chlorite structure occurs about 20 °C lower for the West Town sample than for the Långban sample, in contrast to expectations based on the crystallinity of the parent chlorite. Chemical composition of the modified chlorite structure, however, plays a very important role in the extent of its phase field, as discussed above.

CONCLUSIONS

The results presented here establish that the metastable phase relations of chlorite may be placed within a phase-equilibria framework, whereas previously, the metastable phase relationships of only dioctahedral phyllosilicates were recognized. The chlorite-H₂O binary, however, requires the recognition of a transitional phase, the significance of which has not been recognized formerly. All the dioctahedral phyllosilicates thus studied appear to have similar metastable-phase topologies. Therefore, if the analogy to the dioctahedral phyllosilicates holds, it is likely that many, if not all, trioctahedral phyllosilicate minerals can be treated in a similar way. The results suggest also that the modified chlorite structure may have a different interlayer configuration for Fe²⁺ vs. Mg varieties because the temperatures of thermal decomposition of the two phases are so different, although cation size and charge of the interlayer cations are similar.

The experimental data for chlorite (and vermiculite) show that back reactions are common at higher pressures and where a hydrous vapor is present. Thus, the large smectite crystals observed in the quench products of the high-pressure (5.5 GPa, 1600 °C) studies of Nakazawa et al. (1992) are probably a result of a back reaction, rather than the stability of montmorillonite at high pressures.

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REFERENCES CITED

- Anderson, G.M. (1977) Fugacity, activity and the equilibrium constant. In H.J. Greenwood, Ed., *Applications of thermodynamics to petrology and ore deposits*, p. 17–37. Mineralogical Association of Canada, Vancouver.
- Anderson, R.N., DeLong, S.F., and Schwarz, W.M. (1978) Geophysical and geochemical constraints at converging plate boundaries. II. A thermal model for subduction with dehydration in the downgoing slab. *Journal of Geology*, 86, 731–739.

- Appleyard, E.C., and Guha, J. (1991) A special issue on applications of hydrothermal alteration studies to mineral exploration. *Economic Geology*, 86, 461–465.
- Bailey, S.W., and Brown, B.E. (1962) Chlorite polytypism. I. Regular and semi-random one-layer structures. *American Mineralogist*, 47, 819–850.
- Brindley, G.W., and Ali, S.Z. (1950) X-ray study of thermal transformations in some magnesium chlorite minerals. *Acta Crystallographica*, 3, 25–30.
- Brown, G., and Brindley, G.W. (1984) X-ray diffraction procedures for clay mineral identification. In G.W. Brindley and G. Brown, Eds., *Crystal structures of clay minerals and their X-ray identification*, p. 305–360. Mineralogical Society of Great Britain, London.
- Caillère, S., and Hénin, S. (1960) Relation entre la constitution cristallographique des phyllites et leur température de déshydratation application au cas des chlorites. *Bulletin Société Française Céramiques*, 48, 63–67.
- Chernosky, J.V., Jr., Berman, R.G., and Bryndzia, L.T. (1988) Stability, phase relations, and thermodynamic properties of chlorite and serpentine group minerals. *Mineralogical Society of America Reviews in Mineralogy*, 19, 295–346.
- Dyar, M.D., Guidotti, C.V., Harper, G.D., McKibben, M.A., and Saccoccia, P.J. (1992) Controls on ferric iron in chlorite. *Geological Society of America Abstracts with Programs*, 24, A130.
- Guggenheim, S., Bailey, S.W., Eggleton, R.A., and Wilkes, P. (1982) Structural aspects of greenalite and related minerals. *Canadian Mineralogist*, 20, 1–18.
- Guggenheim, S., Chang, Y.-H., and Koster van Groos, A.F. (1987) Muscovite dehydroxylation: High temperature studies. *American Mineralogist*, 72, 537–550.
- Holloway, J.R. (1971) Internally heated pressure vessels. In G.C. Ulmer, Ed., *Research for high pressure and temperature*, p. 217–258. Springer-Verlag, New York.
- Koster van Groos, A.F. (1979) Differential thermal analysis of the system NaF-Na₂CO₃ to 10 kbar. *Journal of Physical Chemistry*, 83, 2976–2978.
- Koster van Groos, A.F., and Guggenheim, S. (1986) The dehydration of K-exchanged montmorillonite at elevated temperatures and pressures. *Clays and Clay Minerals*, 34, 281–286.
- (1987) Dehydration of a Ca- and a Mg-exchanged montmorillonite (Swy-1) at elevated pressures. *American Mineralogist*, 72, 292–298.
- (1989) Dehydroxylation of Ca- and Mg-exchanged montmorillonite. *American Mineralogist*, 74, 627–636.
- Koster van Groos, A.F., and ter Heege, J.P. (1973) The high-low quartz transition up to 10 kilobar pressure. *Journal of Geology*, 81, 281–286.
- Nakazawa, H., Yamada, H., and Fujita, T. (1992) Crystal synthesis of smectite applying very high pressure and temperature. *Applied Clay Science*, 6, 395–401.
- Nelson, D.O., and Guggenheim, S. (1993) Inferred limitations to the oxidation of iron in chlorite: A single-crystal high-temperature X-ray study. *American Mineralogist*, 78, 1197–1207.
- Petruk, W. (1964) Determination of the heavy atom content in chlorite by means of the X-ray diffractometer. *American Mineralogist*, 49, 61–71.
- Saccoccia, P.J., and Seyfried, W. (1993) The solubility of chlorite solid solution in 3.2 wt. % NaCl fluids from 300–400°C, 500 bars. *Geochimica et Cosmochimica Acta*, in press.
- Shirozu, H. (1980) Variations of DTA and TG curves for Mg-chlorites. *Clay Science*, 5, 237–244.
- Stone, R.L., and Weiss, E.J. (1956) Examination of four coarsely crystalline chlorites by X-ray and high-pressure D.T.A. techniques. *Clay Minerals Bulletin*, 3, 214–222.
- Tatsumi, Y. (1989) Migration of fluid phases and genesis of basalt magmas in subduction zones. *Journal of Geophysical Research*, 94, 4697–4704.
- Yeskis, D., Koster van Groos, A.F., and Guggenheim, S. (1985) The dehydroxylation of kaolinite. *American Mineralogist*, 70, 159–164.

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