SYNTHESIS OF CLINOCHLORE AT HIGH PRESSURES

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Abstract

The behavior of the clinochlore composition was investigated in the Griggs-Kennedy piston-anvil apparatus. The 7 Å aluminous serpentine and the 14 Å chlorite structures were readily synthesized at pressures up to 20 kilobars. At 15 kilobars and 830°C. clinochlore dissociated to talc+forsterite+spinel+vapor.

Introduction

The chlorites form an extensive series of minerals with a high degree of isomorphous substitution. They occur naturally under a wide variety of geological conditions ranging from unconsolidated clays to highly metamorphosed schists, and may form as alteration products of many minerals such as biotite and garnet. Hey (1954) made a survey of these naturally occurring chlorites and brought a good deal of order into their classification and relationships. A knowledge of their stability relationships over a wide range of temperature and pressure is therefore of importance in petrogenesis. The magnesian end-member of the group is clinochlore, $Mg_5Al_2Si_3O_{10}(OH)_8$, which may occur in the almost pure state in nature (Loughnan and See, 1958). Its stability at high pressures has been studied in this work. The experimental work was carried out while the author was a Research Associate at the Institute of Geophysics, University of California, Los Angeles.

Previous Work

The stability curve of clinochlore was determined in the range 2000 psi to 30,000 psi by Yoder (1952) as part of an investigation into the system $MgO-Al_2O_3-SiO_2-H_2O$. He showed that the reaction clinochlore→forsterite+cordierite+spinel+vapor took place at 2000 psi, 630° C., and at 30,000 psi, 720° C. At temperatures below 520° C., irrespective of pressure, he found a new phase of clinochlore composition with a 7 Å type structure and termed it aluminous serpentine. The transition point from one to the other was poorly defined. Aluminous serpentine changed slowly to clinochlore above 520° C., but the reverse change did not take place. Roy and Roy (1955) obtained similar results, but synthesized clinochlore as low as 450° C. They also found that the transition aluminous serpentine→clinochlore was enhanced by increasing pressure. They suggested that the sluggish conversion was probably due to the energy barrier involved in the transfer of each alternate Si-O sheet on changing from one form to the other.

Nelson and Roy (1958) showed that, at low temperatures, there was a continuous replacement of $Si^{4+}+Mg^{2+}$ by $2Al^{3+}$ from the antigorite, $Mg_6Si_4O_{10}(OH)_6$, through clinochlore to amesite, $Mg_4Al_2Si_2O_{10}(OH)_8$; at higher temperatures there is a similar series for the 14 Å structure, but stopping somewhat short of the aluminum-free end-member.

Gillery (1959) made a detailed study of the synthetic compounds and showed that the 7 Å structure formed both a one-layer and a six-layer polymorph in the syntheses.

Experimental Procedure

Mixtures of kaolin, hydrated silica and magnesium hydroxide in the correct proportions to form clinochlore or amesite were subjected to pressures ranging from 6 to 30 kilobars at temperatures up to 865° C. in the piston-anvil device of Griggs and Kennedy (1956). These mixtures contained an excess of water over that needed to form chlorite; furthermore, this water was retained to a sufficiently high temperature under pressure for reaction to take place. Reaction was generally complete within 30 minutes if water was successfully retained, which was generally the case at 10 kilobars and higher. At six kilobars water was more easily lost, although some successful runs were made. The resulting sample was a thin flake approximately $\frac{3}{16}$ inch in diameter, and this was examined, without crushing, on a Norelco diffractometer using Cu k radiation. The very fine grained or flaky nature of the products made microscopic identification unsatisfactory.

Nature of the Crystalline Phases

Clinochlore and aluminous serpentine. The flakes resulting from the high pressure runs appeared to be single crystals of clinochlore, aluminous serpentine or a mixed phase structure. Under the microscope cleavage laminations were distinct, and the flakes gave a centered uniaxial interference figure. Although this is not unequivocal evidence of true structural orientation of all the layers of the flake, it does seem that single crystals of layer structure minerals form readily in the piston-anvil high pressure apparatus. Segnit and Kennedy (1961) formed muscovite crystals giving centered biaxial interference figures under similar conditions.

The flakes gave strong, sharp peaks corresponding to the basal spacings of the minerals on the *x*-ray diffractometer. The absence of peaks for other compounds such as periclase was an indication of the completeness of the reaction.

Other phases. Talc, forsterite, and spinel were identified as the breakdown products of clinochlore. Talc, like the other layer structure minerals,

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TABLE 1. RESULTS OF HIGH PRESSURE RUNS

(a) Clinochlore Composition

Pressure Kilobars	Temperature ° C.	Phases	Relative[2] Intensity 002/003
6	760	clinochlore	nr.
6	770	clinochlore	nr.
6	780	talc, forsterite, spinel	—
6	790	talc, forsterite, spinel	—
10	510	aluminous serpentine	∞
10	595	aluminous serpentine	∞
10	625	mixed phase	—[1]
10	655	mixed phase	3.2
10	670	mixed phase	5.0
10	690	mixed phase	—[1]
10	708	mixed phase	9.6
10	725	mixed phase	7.5
10	765	mixed phase	3.6
10	777	clinochlore	2.0
10	780	clinochlore, talc, sm. amt. forsterite and spinel	1.7
10	797	clinochlore	nr.
10	797	talc	—
10	800	talc, forsterite, spinel sm. amt. clinochlore	—
10	810	talc, forsterite, spinel	—
10	865	talc, forsterite, spinel	—
15	700	mixed phase	3.0
15	725	mixed phase	—[1]
15	760	mixed phase	2.8
15	800	clinochlore	1.0
15	820	clinochlore	1.7
15	825	clinochlore	1.1
15	830	talc, forsterite, spinel	—
20	550	aluminous serpentine	∞
20	555	aluminous serpentine	∞
20	600	mixed phase	—[1]
20	610	mixed phase	—[1]
20	660	mixed phase	—[1]
20	700	mixed phase	3.5
20	730	mixed phase	—[1]
20	750	mixed phase	4.6
20	760	mixed phase	6.8

[1] Peak at $2\theta = 18.6°$ very weak and diffuse.
[2] Ratio of heights of 002 and 003 peaks in chlorite-aluminous serpentine structures.
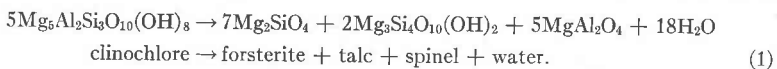nr. not recorded.

TABLE 1—*Continued*

Pressure Kilobars	Temperature ° C.	Phases	Relative[2] Intensity 002/003
		(b) Amesite composition	
10	580	mixed phase	—[1]
10	600	aluminous serpentine	∞
10	702	aluminous serpentine	∞
10	715	mixed phase	3.2
10	725	mixed phase	—[1]
10	748	mixed phase	2.3
10	755	mixed phase, talc, spinel	3.5
10	763	mixed phase, sm. amt. talc	nr.
10	800	clinochlore, talc, spinel	1.1
15	725	aluminous serpentine	∞
15	750	mixed phase	5.3
25	700	mixed phase	2.1
30	700	mixed phase	2.7

gave very strong x-ray patterns. Forsterite and spinel gave less strong but nevertheless well defined patterns.
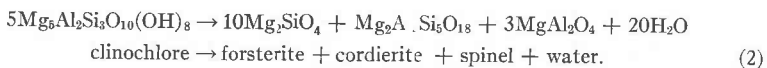
RESULTS

Clinochlore dissociation curve. Results of the experimental runs are given in Table 1. Most were carried out on the clinochlore, and a few were done on the amesite composition. From the former results a curve representing the limits of formation of clinochlore under these conditions can be constructed (Fig. 1). The curve is sensibly a smooth continuation of the low pressure data of Yoder (1952), from which the lower part of the curve of Fig. 1 has been taken. Inferred boundaries are shown as broken lines. In the present work, however, it was not possible to demonstrate reversibility of the reaction, so that the curve presented cannot be considered without question to be the true vapor pressure curve of clinochlore.

The reaction at high pressure at the dissociation temperature was:

$$5Mg_5Al_2Si_3O_{10}(OH)_8 \rightarrow 7Mg_2SiO_4 + 2Mg_3Si_4O_{10}(OH)_2 + 5MgAl_2O_4 + 18H_2O$$

$$\text{clinochlore} \rightarrow \text{forsterite} + \text{talc} + \text{spinel} + \text{water.} \tag{1}$$

At lower pressures (up to two kilobars) Yoder found the following reaction:

$$5Mg_5Al_2Si_3O_{10}(OH)_8 \rightarrow 10Mg_2SiO_4 + Mg_2A . Si_5O_{18} + 3MgAl_2O_4 + 20H_2O$$

$$\text{clinochlore} \rightarrow \text{forsterite} + \text{cordierite} + \text{spinel} + \text{water.} \tag{2}$$
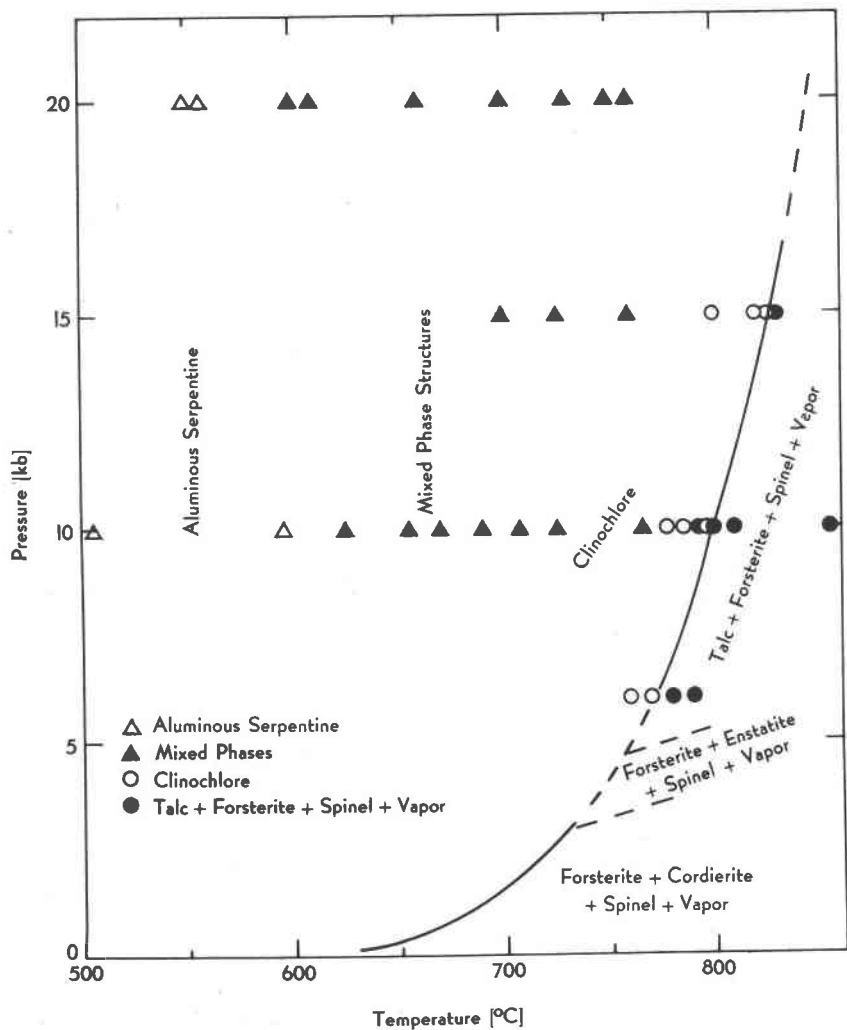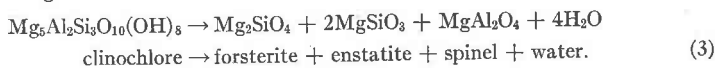
Fig. 1. Pressure-temperature plot of aluminous serpentine-clinochlore syntheses. Curve indicates the pressure-temperature limits of synthesis of clinochlore in the piston-anvil apparatus. Lower part of curve is from hydrothermal data of Yoder; broken boundaries inferred.

The pressure range between two and six kilobars remains unexplored, but somewhere in this region clinochlore presumably breaks down to a further assemblage:

$$Mg_5Al_2Si_3O_{10}(OH)_8 \rightarrow Mg_2SiO_4 + 2MgSiO_3 + MgAl_2O_4 + 4H_2O$$
$$\text{clinochlore} \rightarrow \text{forsterite} + \text{enstatite} + \text{spinel} + \text{water}. \qquad (3)$$

This assemblage would form when, with increasing water vapor pressure, cordierite itself is replaced by talc, sillimanite, and quartz. In nature, the forsterite-enstatite-spinel assemblage is represented by olivine-hypersthene-spinel (Friedman, 1954). Figure 2 shows the assemblages of minerals obtained from the clinochlore composition at 800° C., with the
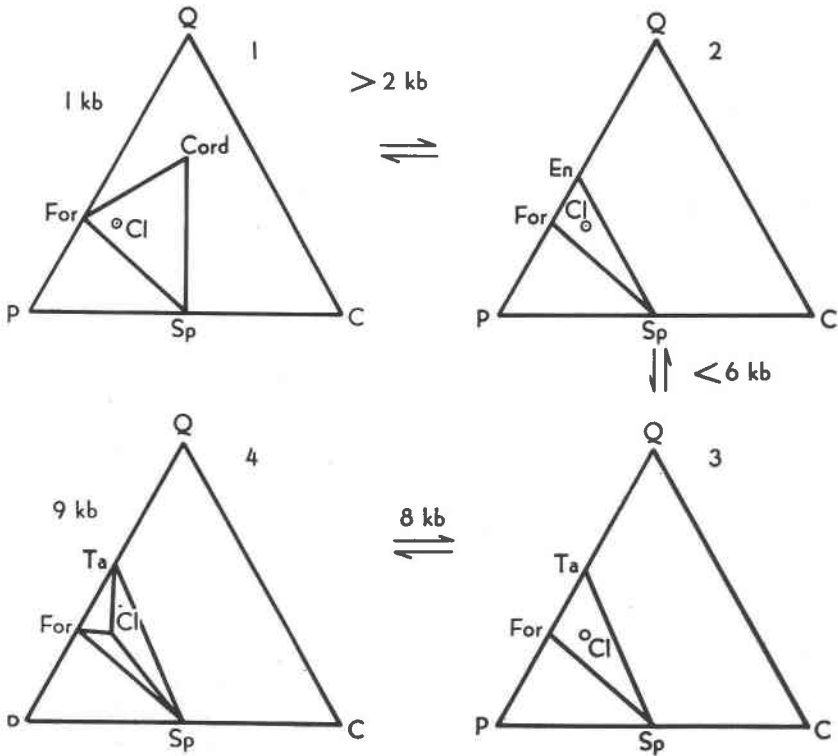

Fig. 2. Assemblages formed from the clinochlore composition at 800°C. Assemblage 2 inferred Q=quartz, P=periclase, C=corundum, Ta=talc, For=forsterite, Sp=spinel, En=enstatite, Cord=cordierite, Cl=clinochlore.

approximate pressure ranges, assemblage 2 being inferred. The breaks in the curve of Fig. 1 corresponding to these changes would be largely imperceptible under experimental conditions, as the slopes of each part of the curve are chiefly controlled by the volume changes of the vapor phase. No change in the free water content is involved in the change from reaction (3) to (2), and only a 10 per cent decrease in free water content occurs in the change to assemblage (1).

Clinochlore-aluminous serpentine relationships. Under the experimental conditions the 7 Å structure was readily formed and occurred at higher temperatures than has previously been reported. Strong, sharp diffraction patterns from the basal flakes were obtained, with no trace of a peak
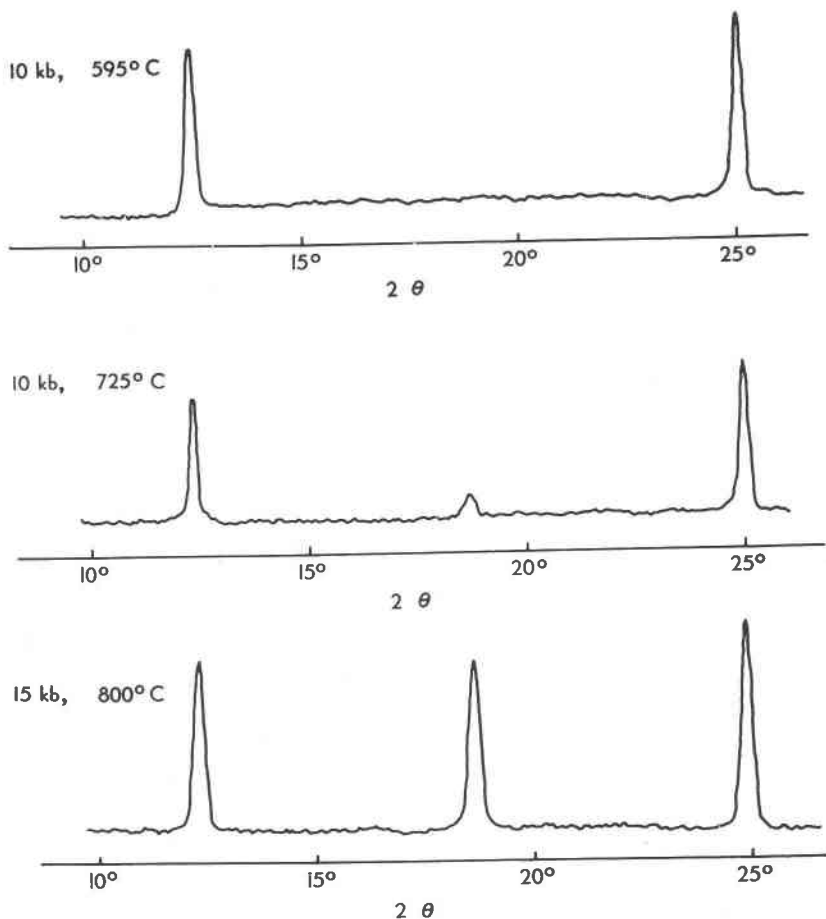

Fig. 3. X-ray diffraction patterns, Cu-Kα radiation from basal flakes of clinochlore composition.

in the 18.7°[1] region from runs below 600° C. Above this temperature, however, a diffuse peak usually began to appear in the diffraction pattern between 18° and 19° ($\sim$4.6 Å), its strength tending to increase with

[1] Angles refer to 2θ. Unfortunately, the diffractometer available at the time the experiments were carried out would not record angles below about 8° 2θ.

higher temperatures of preparation (Fig. 3). This is further illustrated in Fig. 4 where the ratios of the intensities of the 022 and 003 reflections are plotted against the temperature of formation. Variation in starting composition had no effect on the distribution of the points. Although there is considerable scatter at any given temperature, a statistical analysis of their distribution shows that there is a highly significant positive trend in the data. The calculated trend is indicated by the straight line drawn through the points.

The suggested interpretation of these data, bearing in mind the single crystal-like nature of the products, is that, at approximately 600° C.,
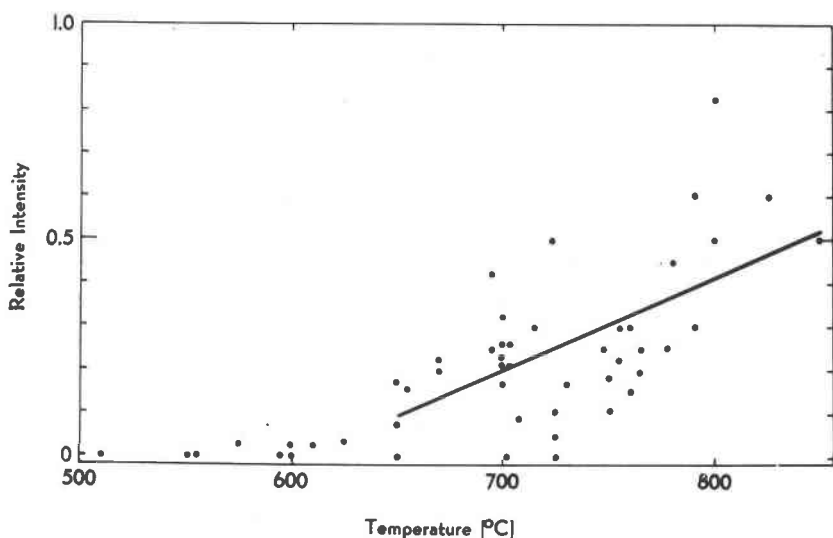

FIG. 4. Relative intensity of 18.7° (003):12.5° (002) diffraction peaks plotted against temperature of formation of serpentine-chlorite structures.

14 Å layers began to form in the charge producing a type of mixed phase structure. As the temperatures of the runs were increased the proportion of the 14 Å layers in the crystal increased until, at about 780° C., it became the dominant or sole form. The evidence is insufficient to determine whether a true mixed layer structure was formed. The transformation sequence described by Brindley and Gillery (1954) for an iron-rich mixed layer natural chlorite could, however, offer an explanation for the changes observed in these experiments.

The scatter of the points strongly suggests that the mixed phase structure in these syntheses is a metastable formation. High pressure runs on hydrothermally prepared clinochlore at lower temperatures might dem-

onstrate whether the reaction aluminous serpentine→clinochlore is reversible.

Gillery (1959) found two polymorphs of the 7 Å structure, a one-layer form with a basal (001) spacing of 7.22 Å, and a six-layer form with a basal (006) spacing of 7.08 Å. In the present work the corresponding aluminous serpentine spacing was in the region 7.06–7.10, suggesting the six-layer polymorph. The corresponding spacing for clinochlore is 7.20 (Yoder, 1952). The smaller spacing for the six-layer aluminous serpentine suggests therefore that its formation may be favored by higher pressures, and that a corresponding stable range might be possible. A search amongst high grade metamorphic chloritic schists which have been subjected to high pressures without excessive temperatures might reveal the presence of aluminous serpentines in nature. At low pressures, however, the 14 Å structure may well be the stable form at low temperatures, as Loughnan and See (1958) describe an almost pure clinochlore occurring in close association with montmorillonite, vermiculite, and other layer minerals. The assemblages appear to be derived from the hydrothermal alteration of an albitite at relatively low temperatures.

Results of runs with the amesite composition at high pressures were somewhat different from those of Nelson and Roy (1958) at 1000 bars. They found continuous replacement of $Mg^{2+}+Si^{4+}$ by $2Al^{3+}$ (see above). In a series of runs at 10 kilobars in the present work, a mixture of the amesite composition yielded well-crystallized aluminous serpentine at 550° C., 700° C., and 725° C., with no other phases, while at 750° C. a mixed phase structure, and at 800° C. a 14 Å form crystallized, both the latter being accompanied by talc and spinel. In runs at 700° C. at 25 and 30 kilobars, a mixed phase structure alone formed.

Conclusions

Both the 14 Å clinochlore and the 7 Å aluminous serpentine structures can be readily synthesized at high pressures in the Griggs and Kennedy piston-anvil apparatus from a mixture of kaolin, silicic acid and magnesium hydroxide. In runs from 10 to 20 kilobars aluminous serpentine was obtained below 600° C., and clinochlore above 780° C. Between these temperatures, the change in intensity of the x-ray diffraction peak corresponding to the basal spacing of 4.6 Å indicated that some type of mixed phase structure was formed. The ready synthesis of well-crystallized aluminous serpentine at high pressures and moderately high temperatures suggests the possibility of its occurrence in high grade metamorphic chlorite schists.

Clinochlore itself dissociated under these conditions to forsterite, talc, spinel, and vapor at 10 kilobars, 800° C., and 15 kilobars, 830° C.

Similar high pressure runs on hydrothermally prepared clinochlore and aluminous serpentine should give direct evidence on the stability of the latter structure.

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