

AN EXPERIMENTAL STUDY OF THE EQUILIBRIUM: GROSSULAR + CLINOCHLORE = 3 DIOPSIDE + 2 SPINEL + 4 H₂O

XIAOMIN WANG* AND HUGH J. GREENWOOD

Department of Geological Sciences, University of British Columbia, Vancouver, British Columbia, V6T 2B4

ABSTRACT

The equilibrium grossular + clinocllore = 3 diopside + 2 spinel + 4 H₂O was investigated using cold-seal pressure vessels from 500 to 700°C at 0.5 to 4.0 kbars. Reversals with stable assemblages diopside + spinel or grossular + clinocllore were obtained at *P-T* conditions far from the equilibrium. However, aluminous diopside + clinocllore were produced at conditions close to the equilibrium over the entire pressure range. The aluminous diopside is inferred to be metastable. The experimental results from this study are shown by linear programming to be consistent with both UBCDATA (Berman *et al.* 1986a) and the database of Helgeson *et al.* (1978). The diopside formed was extensively examined by X-ray diffraction, scanning-electron microscopy and electron microprobe. It contains up to 11 wt.% Al₂O₃, which can be interpreted in terms of Ca-Tschermak and Mg-Tschermak substitutions. Natural diopside found in similar assemblages inferred to have formed under *P-T* conditions similar to the experiments contains little aluminum.

Keywords: grossular, clinocllore, diopside, spinel, thermodynamics, experimental equilibrium, petrology, metamorphism, rodingite.

SOMMAIRE

Nous avons étudié l'équilibre grossulaire + clinocllore = 3 diopside + 2 spinelle + 4 H₂O à l'aide d'autoclaves à joint froid entre 500 et 700°C, à une pression variant de 0.5 à 4.0 kilobars. Les assemblages stables diopside + spinelle et grossulaire + clinocllore sont renversés à des conditions *P-T* éloignées de l'équilibre. Toutefois, l'assemblage diopside alumineuse + clinocllore est formé à des conditions proches de l'équilibre, quelle que soit la pression. On considère la diopside alumineuse comme étant métastable. Une analyse par programmation linéaire montre que nos résultats expérimentaux concordent avec la banque de données UBCDATA (Berman *et al.* 1986a) et celle de Helgeson *et al.* (1978). On a étudié la diopside en détail par diffraction X, microscopie électronique à balayage et microsonde électronique. Elle contient jusqu'à 11% Al₂O₃ (en poids), ce qui peut s'expliquer par une substitution des pôles Ca-Tschermak et Mg-Tschermak. La diopside des assemblages naturels semblables, qui aurait cristallisé à des conditions *P-T* similaires à celles des expériences, contient très peu d'aluminium.

(Traduit par la Rédaction)

Mots-clés: grossulaire, clinocllore, diopside, spinelle, thermodynamique, équilibre expérimental, pétrologie, métamorphisme, rodingite.

INTRODUCTION

Thermodynamic calculations of equilibria among minerals commonly found in metarodingites have been reported by Rice (1983). In that paper, the stable $\mu(\text{CO}_2) - \mu(\text{H}_2\text{O})$ topologies relating minerals were established according to observed parageneses. Thermodynamic data of Helgeson *et al.* (1978) were used to calculate the principal equilibria resulting in a petrogenetic model in agreement with observed natural assemblages in both low- and high-pressure terranes.

This study reports experimental work related to metarodingite equilibria chosen so as to test or enhance the strength of the UBC database UBCDATA. Phases considered in this study are grossular, clinocllore, diopside, spinel and H₂O, in the system CaO-MgO-Al₂O₃-SiO₂-H₂O. These phases are related through the equilibrium: grossular + clinocllore = 3 diopside + 2 spinel + 4 H₂O which has been studied and experimental reversibility demonstrated. Experiments near the equilibrium commonly concluded with diopside + clinocllore instead of either diopside + spinel or grossular + clinocllore. Mass-balance constraints from chemistry and phase proportions suggest this to be caused by the metastable growth of aluminous clinopyroxene, a suggestion confirmed by microprobe analysis.

EXPERIMENTAL PROCEDURES

All experiments were carried out using standard cold-seal pressure vessels of either Stellite K-25 or Rene 41 alloys. Temperature was measured by sheathed chromel-alumel thermocouples mounted in an external well. Calibrations of the thermocouples were made between 400 and 800°C at one atmosphere for each furnace with specific bomb and thermocouple. Temperature gradients were less than $\pm 1^\circ\text{C}$ over the two- to three-centimeter length of the sample capsule. During the experiments, temperatures were controlled to within $\pm 1^\circ\text{C}$ by fully proportional controllers. Temperature was measured

*Present Address: Department of Geology, Stanford University, Stanford, California 94305, U.S.A.

daily with a digital thermometer checked occasionally by potentiometer and recorded every half hour by an automatic data-recording system using an IBM-XT computer and DAS A/D interface. No systematic difference in temperature was noticed among measurements taken with digital thermometer, potentiometer, or computer. Temperatures reported here are the averages of the daily measurements. The total cumulative errors, including calibration, measurement, and variation are estimated to be less than $\pm 5^\circ\text{C}$.

Pressure was measured daily with a Bourdon tube gauge. If the pressure dropped more than 3% the experiment was repeated. The pressures reported here are the averages of daily measurements and are estimated to be precise to within ± 20 bars and accurate to ± 40 bars.

Most experiments were performed with two adjacent capsules of starting mixtures having different proportions of low- and high-temperature assemblages (80–20 and 20–80% reactants and products). The exceptions are those having experimental conditions quite far from equilibrium, where only one capsule was used. For each capsule, approximately 20 mg of starting mixture were sealed with excess distilled water (30 wt. %) and leak-tested in an oven at 100°C . Thirty to sixty minutes were required to heat the vessels and about five minutes to cool them to below 100°C . Because most of the experiments showed incomplete reaction, an XRD intensity technique was used to estimate the extent and direction of reaction. Standard curves were made as follows.

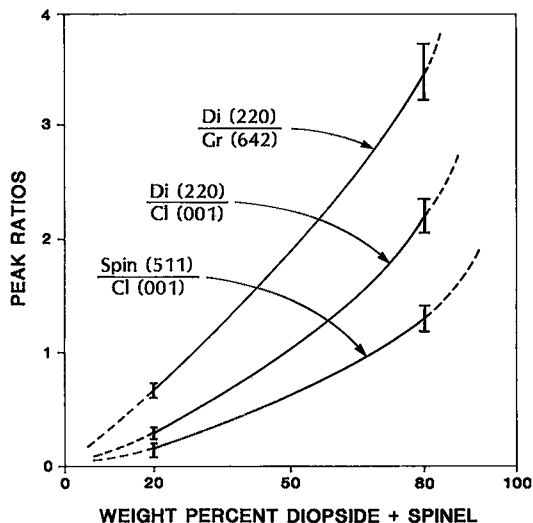


FIG. 1. Calibration of peak-height ratios from starting material XRR (80 wt. % grossular + clinocllore and 20 wt. % diopside + spinel) and XRE (80 wt. % diopside + spinel and 20 wt. % grossular + clinocllore). Vertical bars show one standard deviation of mean from 6 measured ratios.

Mixtures with different phase proportions were prepared. Each mixture was then used to make six independent XRD mounts and the intensities measured. Only the experiments with large ratio changes (greater than 30%) were considered to have reacted (Fig. 1). The (201) peak of chlorite showed intensity changes similar to those of (001), giving us a measure of confidence that we were not simply observing preferred orientation or progressive recrystallization.

STARTING MATERIALS

All phases considered in this study were synthesized from oxide mixtures. Periclase was prepared by baking MgO (Fisher Certified Reagent Lot #741694) for 24 hours at 800°C and 1 hour at 1000°C . Cristobalite (SiO_2) was made from $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ by baking at 1300°C for 24 hours and recrystallizing for another 24 hours at 1200°C . Al_2O_3 was prepared from aluminum chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) (Fisher Certified Reagent Lot #429332) by heating in a fume hood using a gas burner for 1 hour and then baking at 650°C for 96 hours. Lime was made from calcium carbonate by baking at 500°C for 24 hours, followed by calcination at 800°C for 12 hours.

Each prepared oxide was ground, under alcohol, in an agate mortar by hand for several hours to make sure that the grain size was less than $1 \mu\text{m}$ for enhanced reactivity during synthesis. The oxide was then dried in a furnace at 110°C and stored in a desiccator for further use.

SYNTHESIS OF PHASES

All the phases were synthesized individually on their theoretical end-member compositions. Spinel was synthesized at two different conditions: at 1000°C for 1 hour and 1200°C for 24 hours at one atmosphere, and hydrothermally at 795°C and 1.0 kbar for 12 days. Both syntheses were successful and spinel synthesized by both methods is identical with respect to optical properties, XRD, and SEM. The synthetic spinel typically crystallized as euhedral crystals, 2 to $10 \mu\text{m}$ across, with well-developed (111) and (110) faces (Fig. 2A).

Diopside was synthesized at 795°C and 1 kbar $P(\text{H}_2\text{O})$ for 15 days. The synthetic diopside is subhedral to euhedral, with a grain size of $0.5 \times 3 \mu\text{m}$ (Fig. 2B). Results of unit-cell parameter refinement with 11 diffraction maxima using the program of Evans *et al.* (1963) are shown in Table 1. Also shown in this table are cell-refinement results of synthetic diopside from Nolan & Edgar (1963) and a diopside standard from JCPDS #11-654. Table 2 shows cell parameters of diopside as refined by various authors.

Clinocllore was synthesized at 680°C and 4.0

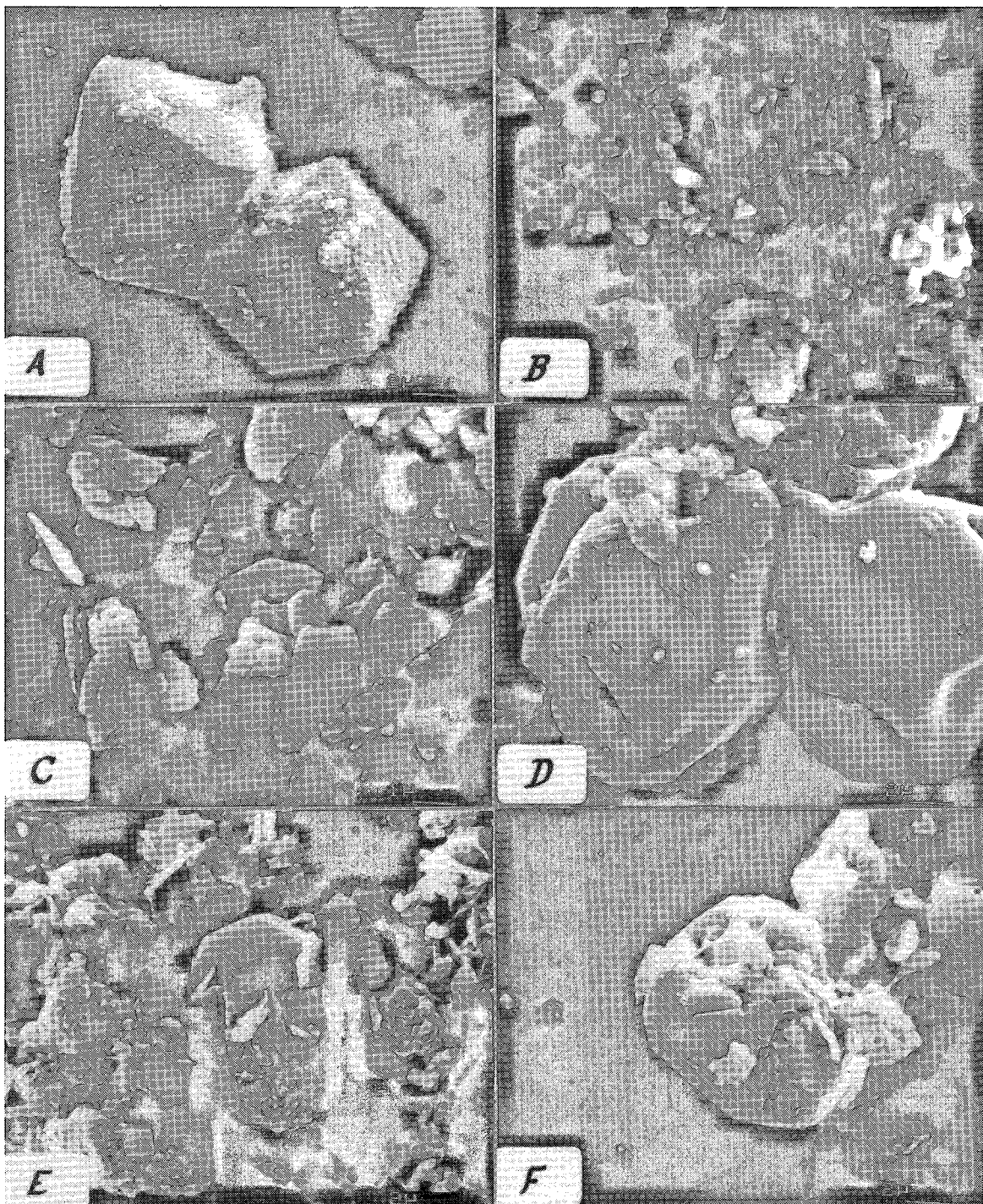


FIG. 2. Electron photomicrographs of experimental products. A. Euhedral crystals of synthetic spinel with (111) and (110) faces. B. Subhedral to euhedral crystals of synthetic diopside. C. Subhedral crystals of synthetic clinocllore. D. Close view of synthetic grossular crystals with some unidentified inclusions. E. Low-temperature stable assemblage of clinocllore + grossular. Note the euhedral grossular crystals showing (110) and (111) faces. F. Grossular crystal growing near crystals of spinel which show signs of dissolution during the run (Gr, grossular; Sp, spinel).

TABLE 1: *d*-VALUES AND CELL PARAMETERS OF SYNTHETIC DIOPSIDE

h k l	1/100	(A)	(B)	(C)	(D)	(E)	(F)
0 2 1	15	3.344	3.344	3.340	3.338	3.350	-----
2 2 0	30	3.232	3.234	3.222	3.222	3.230	3.160
2 2 $\bar{1}$	100	2.990	2.991	2.984	2.985	2.991	-----
3 1 0	32	2.949	2.952	2.943	2.942	2.952	2.904
3 1 $\bar{1}$	37	2.892	2.894	2.889	2.889	2.893	-----
1 3 $\bar{1}$	25	2.564	2.565	2.558	2.558	2.566	-----
3 1 1	20	2.303	2.302	2.297	2.297	2.304	2.274
3 3 0	12	2.156	2.156	-----	-----	2.157	2.106
3 3 $\bar{1}$	20	2.134	2.133	-----	-----	2.134	-----
4 2 $\bar{1}$	12	2.109	2.108	-----	-----	2.109	-----
0 4 1	$\bar{c}2$	-----	2.041	-----	-----	2.043	1.991
1 3 $\bar{2}$	$\bar{c}2$	1.970	1.968	-----	-----	1.970	-----
1 5 0	$\bar{c}2$	-----	-----	-----	-----	1.755	1.703
5 3 $\bar{1}$	$\bar{c}2$	-----	-----	-----	-----	1.625	-----
a(A)		9.755(4)		9.725(3)		9.761	9.619
b(B)		8.928(6)		8.891(5)		8.926	8.659
c(C)		5.247(7)		5.257(5)		5.258	5.278
β		105°52'		105°58'		105°47'	106°8'
V(A ³)		439.51(45)		437.13(30)		440.80	

(A) • Synthetic end-member diopside CaMgSi₂O₆ (observed)

(B) • Synthetic end-member diopside (calculated)

(C) • Al-bearing diopside from run XRR-3 (observed)

(D) • Al-bearing diopside from run XRR-3 (calculated)

(E) • Diopside standard from Mineral Powder File, JCPDS (1980)

(F) • Calcium Tschermak pyroxene CaAl₂Si₂O₆ standard from Mineral Powder File, JCPDS (1980)

kbars for 21 days. Synthetic clinocllore is platy and fine grained, with its size ranging from 1 to 4 μm (Fig. 2C), and is similar in appearance to the chlorite of Cho & Fawcett (1986). The results of cell-parameter refinement using a silicon internal standard are listed in Table 3 along with refinement

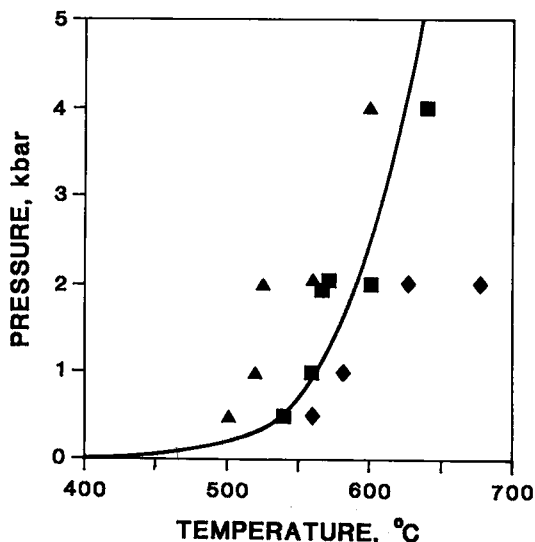


FIG. 3. Equilibrium curve for grossular + clinocllore = 3 diopside + 2 spinel + 4H₂O. Calculated with PTSYSTEM using phase properties from UBCDATA database and the experimental brackets of this study. Triangles: assemblage grossular + clinocllore increased at the expense of diopside + spinel. Diamonds: assemblage diopside + spinel increased at the expense of grossular + clinocllore. Squares: metastable assemblage aluminous diopside + clinocllore.

results of synthetic clinocllore by Chernosky (1974).

Grossular was synthesized under two different conditions: at 745°C and 1 kbar *P*(H₂O) for 17 days, and at 680°C at 4.0 kbar for 21 days. Both synthesis products contain minor additional amounts of wollastonite estimated to be less than 5% by volume. The mass-balance implied by this could not be attributed to unreacted Al₂O₃ in the grossular as no such inclusions were found in SEM examination. The extraneous phase was so minor that we consider the grossular to be of stoichiometric end-member composition. Synthetic grossular was subhedral to euhedral and ranged in size from 2 to 10 μm (Fig. 2D).

Hydrogrossular is common in rodingites, and may be the most abundant mineral in volcanic rocks altered to rodingite (Coleman 1966). Hydrogrossular with formula Ca₃Al₂(SiO₄)_{3-x}(H₄O)_x was found to be the result of a continuous solid solution between Ca₃Al₂Si₃O₁₂ and Ca₃Al₂(H₄O)₃ at low temperature (Flint *et al.* 1941). Silica-free Ca₃Al₂(H₄O)₃ decomposes above approximately 250°C. Yoder (1950) reported that hydrogrossular is stable only below about 600°C. Shoji (1974) found that the hydrogen content in the grossular-hydrogrossular series decreases with increasing temperature and the value of *d*(420) can be used to determine the H₂O content in hydrogrossular: *d*(420) varies from about 2.650 for grossular, to 2.680 Å for hydrogrossular. The grossular synthesized in this study has a value of 2.6498 Å, in good agreement with the value reported by Shoji (1974) and with the observations of Huckenholz & Fehr (1982). We conclude, therefore, that our synthetic grossular has no hydrogrossular component.

EXPERIMENTAL RESULTS

Experimental reversals of the equilibrium grossular + clinocllore = 3 diopside + 2 spinel + 4 H₂O were made at pressures of 0.5, 1.0, 2.0 and 4.0 kbars. The experimental conditions and results are listed in Table 4 and illustrated in Figure 3. Experiments far from equilibrium achieved complete reaction (100% grossular + clinocllore or 100% diopside + spinel). When experiments were conducted at conditions close to the equilibrium, the final assemblage was clinocllore + diopside instead of clinocllore + grossular or diopside + spinel. This was first found in experiments at 2.0 kbar, and repeated experiments at 0.5, 1.0, 2.0, and 4.0 kbar showed the same results. Thus the reversal brackets are wider than we would have liked, owing to the persistence of the assemblage diopside + clinocllore near the equilibrium boundary.

Special experiments were conducted to test whether the occurrence of diopside + clinocllore was caused by errors in bulk composition. One

TABLE 2: CELL PARAMETERS OF SYNTHETIC AND NATURAL DIOPSIDE

Samples	Reference	a (Å)	b (Å)	c (Å)	β	V (Å ³)
Synthetic	Rutstein, et al. (1969)	9.752(2)	8.926(2)	5.246(2)	105°50'	439.68(15)
Synthetic	Present study	9.754(4)	8.927(5)	5.246(7)	105°52'	439.51(45)
Synthetic	Clark, et al. (1962)	9.745(1)	8.925(1)	5.248(1)	105°52'	
Synthetic	Sakata, (1957)	9.743	8.923	5.251	105°56'	
Synthetic	Nolan and Edgar, (1963)	9.748	8.924	5.251	105°47'	439.5
Natural	Viswanathan, (1966)	9.754(14)	8.916(8)	5.24(9)	105°49'	
Natural	Clark et al. (1969)	9.746(4)	8.899(5)	5.251(6)	105°39'	438.6
Run Diop	This study	9.725(4)	8.891(5)	5.260(5)	105°55'	437.13(31)
Syn. CaTs	Okamura et al. (1974)	9.609	8.652	5.274	106°3'	421.35

experimental product (XRR-3) containing only diopside + clinocllore was used as new starting material. Relative proportions of diopside and clinocllore were estimated according to XRD peak intensities and appropriate amounts of spinel and grossular were then added to the mixture for a 1:1 ratio of product and reactant and ground under alcohol for 2 hours. This experiment (XR-20, 552 hrs, 2kbars, 600°C) was converted to 100% diopside + clinocllore (see Table 4).

Ten synthesis experiments were made to test the role of bulk composition. New mixes of oxides were prepared as starting materials for the compositions shown in Figure 4. Two sets of conditions were used for the special synthesis runs (see Table 4, XRBULK1-10). All concluded with either diopside + clinocllore or the low-temperature assemblage grossular + clinocllore. One run (XRBulk-4) showed three unidentified peaks in the XRD patterns.

TABLE 3: d-VALUES AND CELL PARAMETERS OF SYNTHETIC CHLORITE

h k l	(1) d(calc)	(1) d(obs)	I(/100)	(2) d(obs)	(3) d(obs)
0 0 1	14.299	-----	**	14.132	-----
0 0 2	7.149	-----	**	7.135	-----
0 0 3	4.766	4.771	**	4.757	4.752
0 2 0	4.609	-----	---	-----	4.592
1 1 0	4.581	4.587	40	4.588	-----
1 1 1	4.505	-----	---	4.493	4.500
0 2 1	4.387	-----	---	4.373	4.384
1 1 1	-----	-----	---	4.242	-----
0 2 2	3.874	-----	---	3.883	3.862
1 1 2	3.682	-----	---	3.674	-----
0 0 4	3.575	3.577	**	3.572	3.560
0 0 5	2.860	2.860	60	2.864	2.846
1 1 4	2.682	-----	---	2.691	-----
2 0 1	2.655	2.653	12	2.656	2.653
2 0 2	2.582	2.581	45	2.584	2.579
2 0 1	2.541	2.540	100	2.540	2.538
2 0 3	2.440	2.440	75	2.441	2.437
0 0 6	2.383	2.383	36	2.385	2.380
2 0 4	2.261	2.261	28	2.260	2.258
1 3 4	2.071	2.071	11	-----	-----
0 0 7	2.043	2.042	18	2.041	2.034
2 0 4	2.008	2.009	58	2.008	2.004
2 0 6	1.889	1.889	20	1.889	1.885
2 0 5	1.830	1.830	20	1.831	1.826
0 0 8	1.787	-----	---	-----	1.781
2 0 7	-----	-----	---	1.724	-----
2 0 6	1.669	1.670	11	1.671	-----
2 0 8	1.573	1.573	32	1.573	1.568
0 6 0	1.536	1.536	53	1.539	1.532
0 6 2	1.502	1.502	15	1.502	1.501
0 6 3	1.462	1.463	18	1.463	-----
1 1 9	1.454	-----	---	1.455	-----
0 0 10	1.430	1.430	10	-----	1.424
3 3 3	1.411	-----	---	1.412	-----
2 0 8	1.402	1.402	24	1.402	1.397
a(Å)	5.320(1)	-----	---	5.324(1)	5.317(1)
b(Å)	9.218(1)	-----	---	9.224(3)	9.192(2)
c(Å)	14.409(2)	-----	---	14.420(5)	14.349(2)
β	97°5'(1')	-----	---	97°6'(1')	97°8'(1')
V(Å ³)	701.26(16)	-----	---	702.69	695.83

- (1) Synthetic clinocllore from this study. $Mg_{0.5}Al_{0.5}Si_2O_{10}(OH)_2$
 (2) Synthetic clinocllore from Chernosky, (1974) $Mg_{0.5}Al_{0.5}Si_2O_{10}(OH)_2$
 (3) Synthetic chlorite from McPhail, $Mg_{0.5}Al_{0.5}Si_2O_{10}(OH)_2$ (1985)

** Peak intensity more than 100 renormalized.

TABLE 4: EXPERIMENTAL RESULTS

Experimental results for the equilibrium
 Grossular + Clinocllore = 3 Diopside + 2 Spinel + 4 H₂O

Run #	P(bar)	T(°C)	Duration	Results
XRR-1	2000	678	384(hrs)	100% Di + Sp
XRR-1	2000	525	336	80% Gr + Clino
XRR-2	2000	627	360	mainly Di + Sp, minor Clino
XRR-2	2000	566	504	no reaction
XRR-3	2000	601	552	Di + Clino
XRR-3	2000	601	552	Di + Sp stable
XRR-4	2000	580	588	mainly Di + Clino, minor Gr
XRR-4	2000	580	588	Di + Sp stable
XRR-5	2000	561	552	Gr + Clino stable
XRR-5	2000	561	552	Gr + Clino grow 40%
XRR-7	2000	570	576	Gr + Clino stable
XRR-7	2000	570	576	mainly Di + Clino, minor Gr
XRR-6	1000	560	600	no obvious reaction
XRR-6	1000	560	600	Gr + Clino grow
XRR-9	1000	520	384	80% Gr + Clino
XRR-9	1000	520	384	60% Gr + Clino
XRR-10	1000	581	720	Di + Sp grow
XRR-10	1000	581	720	Di + Clino
XRR-8	500	502	840	100% Gr + Clino
XRR-8	500	502	840	95% Gr + Clino, minor Di
XRR-11	500	540	672	Di + Sp grow
XRR-11	500	540	672	Mainly Gr + Clino
XRR-17	500	560	648	Mainly Di + Clino
XRR-17	500	560	648	Mainly Di + Sp
XRR-18	4000	600	600	Mainly Gr + Clino
XRR-18	4000	600	600	Mainly Gr + Clino
XRR-19	4000	640	672	Mainly Di + Clino
XRR-19	4000	640	672	Mainly Di + Clino
XR-13*	2000	600	672	Mainly Di + Clino
XR-14*	1000	570	672	Mainly Di + Clino
XR-20	2000	600	552	Mainly Di + Clino
XRBulk-1	1000	590	1152	Mainly Di + Clino
XRBulk-3	1000	590	1152	Mainly Di + Clino
XRBulk-5	1000	590	1152	Mainly Di + Clino
XRBulk-7	1000	590	1152	Mainly Di + Minor Clino
XRBulk-9	1000	590	1152	Mainly Di + Minor Clino
XRBulk-2	1000	530	1152	Mainly Gr + Clino + Minor Di
XRBulk-4	1000	530	1152	Mainly Di + Clino + Gr + ?
XRBulk-6	1000	530	1152	Mainly Gr + Clino + Minor Di
XRBulk-8	1000	530	1152	Mainly Gr + Di + Minor Clino
XRBulk-10	1000	530	1152	Mainly Gr + Di + Minor Clino

* Runs with starting material of 50 wt% reactant and 50 wt% product
 All others began with 20-80 and 80-20 mixtures.
 Reaction progress estimated from XRD intensities, and SEM

XRR = 20% (Di + Sp) 80% (Gr + Clino) (Stoich. Diops.)
 XRE = 80% (Di + Sp) 20% (Gr + Clino) (Stoich. Diops.)
 XRBulk - runs were syntheses of long duration, from oxides.

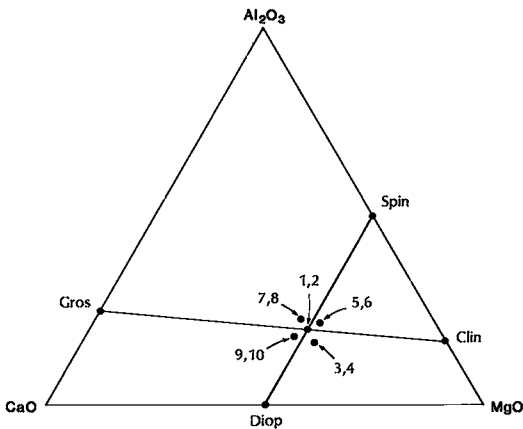


FIG. 4. Starting bulk compositions for experiments XRBulk-1 to XRBulk-10. Solid lines within the triangle are the tie-lines for the stoichiometric reaction; their intersection represents the bulk composition for the balanced reaction.

These results suggest that nonstoichiometric behavior may occur in one or more of the phases. Spin is the only phase that may not exhibit solid solution in the chemical system studied.

Ca-Mg-Al stoichiometry of grossular

Grossular was treated as stoichiometric $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ although pyrope-grossular solution can be complete at very high temperature and pressure. The mixing properties of grossular-pyrope solid solution have been discussed by various authors: *e.g.*, Chinner *et al.* (1960), Saxena (1968), Boyd (1970), Wilken (1977), Ganguly & Kennedy (1974), Hensen *et al.* (1975). At 29 kbars and 1250°C, a complete range of solid solution can be crystallized (Yoder & Chinner 1960), but at 10 kbars water pressure and 950°C, only garnets within the narrow range $\text{Gr}_{100}\text{-Gr}_{94}\text{Py}_6$ are stable. The synthetic grossular in this study is anhydrous and stoichiometric as shown from the value of $d(420)$.

Chlorite stoichiometry

Changes in chlorite composition with increasing pressure were reported by Fawcett & Yoder (1966) and more recently by Jenkins & Chernosky (1986) and Cho & Fawcett (1986). It was concluded that the composition of chlorite coexisting with other phases varies with pressure, becoming more aluminous at higher pressure. McPhail (1985) detected no shift in the basal peaks of chlorite coexisting with forsterite and spinel. Chernosky (1974) and Jenkins & Chernosky (1986) showed that clinocllore from different temperatures and pressures show no nonstoichio-

metric phenomena. In this study, the same observation that basal peak positions do not shift indicates that clinocllore in this study has the composition $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$ throughout the course of the experiments.

Diopside stoichiometry

Chemographic and mass-balance considerations coupled with observations of phase proportions have been cited above as evidence that the diopside formed during equilibration experiments may contain aluminum. These possibilities have been pursued by calculation from existing thermodynamic data and by direct analysis. Briefly, existing experimental and thermodynamic data indicate that the clinopyroxene in our experiments should be pure diopside, whereas the chemographic relations and direct microprobe analysis of the diopside grains indicate the reverse.

Thermodynamic evidence

Existing data on aluminum in clinopyroxene indicate mostly that high Al content is the result of high pressure. In this section we calculate from existing thermodynamic models what composition of clinopyroxene we would expect under our experimental conditions. We conclude that the pyroxene should be almost pure end-member diopside.

Wood & Holloway (1984) have discussed the solid solution of pyroxenes and their mixing properties. In the four-component system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$, orthopyroxene compositions can be represented in the ternary $\text{CaMgSi}_2\text{O}_6$, $\text{Mg}_2\text{Si}_2\text{O}_6$ and $\text{MgAl}_2\text{SiO}_6$. Clinopyroxene compositions may readily be represented by the compositions $\text{CaMgSi}_2\text{O}_6$, $\text{Mg}_2\text{Si}_2\text{O}_6$ and $\text{CaAl}_2\text{SiO}_6$.

Using the Margules parameters from Wood & Holloway (1984), thermodynamic calculation was made of the equilibrium grossular + clinocllore = 3 diopside + 2 spinel + 4 H_2O considering solid solution along the joins orthopyroxene $\text{CaMgSi}_2\text{O}_6\text{-Mg}_2\text{Si}_2\text{O}_6$, and clinopyroxene $\text{CaMgSi}_2\text{O}_6\text{-Mg}_2\text{Si}_2\text{O}_6\text{-CaAl}_2\text{SiO}_6$. The program THERIAK by C. Decapitani (pers. comm.) was used for the calculation. This program is a free-energy minimization algorithm that accepts UBCDATA thermodynamic parameters, including Margules parameters for solid solutions, and computes the proportions and compositions of all coexisting phases for a given bulk composition at any chosen pressure and temperature. The reaction was examined, allowing for solid solution in pyroxene as outlined above. This resulted in determining the equilibrium temperatures to be 583°C and 558°C at 2000 bars and 1000 bars, respectively. These temperatures are almost identical to those found from the calculation without considering solid solution in

pyroxenes. On the low-temperature side, the compositions obtained are the ideal stoichiometric formulae for grossular and clinocllore. The mineral assemblage for the high-temperature side consists of clinopyroxene and spinel. Composition of clinopyroxene depends on temperature and pressure, but diopside is the main component of the pyroxene, comprising more than 98 mol%. The activity of the Di-component is more than 0.96. The remaining 2 mol% are made up of clinoenstatite and Ca-Tschermak. We conclude that all existing thermodynamic data imply that the equilibrium pyroxene should be nearly pure diopside, with very little aluminum.

The synthetic stoichiometric end-member diopside was very well crystallized, with peak positions and intensities comparable with standard diopside. Cell-parameter refinements were made with eleven peaks using the program of Evans *et al.* (1963) (see Table 1; A,B,E). These were done on equilibrated diopside to trace any variation of composition. The products usually contain four phases (owing to incomplete reaction), which results in many peak overlaps. Consequently, only seven peaks could be measured precisely for cell refinement (see Table 1; C,D.) The results show that the cell parameters of the diopside produced are well within the range between diopside and Ca-Tschermak pyroxene as reported by Clark *et al.* (1962) (see Table 1,F). XRD is thus inadequate to detect the compositional variation which has been deduced to be present.

Scanning electron microscopy

All examinations were carried out using a SEMCO Nanolab-7 scanning electron microscope with Kevex E.D.S. operated at 15 kV at a working distance of 15–18mm. Samples were ultrasonically dispersed, mounted on polished graphite stubs, and coated with carbon or gold depending on whether composition or morphology was being studied.

The synthetic end-member diopside grains are euhedral to subhedral prismatic crystals. Although the EDS was not used for quantitative analysis, the following features may be noted. The chemical spectra (Fig. 5) show that the diopside is very uniform in composition with all grains having very similar spectra. The peak ratios of Mg/Si and Ca/Si are very similar from one grain to another and no Al peak is visible.

Diopside from equilibration experiments was easily identified by crystal shape, morphology, and chemical analysis on the basis of results on end-member synthetic diopside. Grains of diopside at least 4 μm apart from other grains of any phase were chosen for chemical examination. It was found that if any other phase lay within 4 μm of the diopside, its chemical spectrum would show the effects of the neigh-

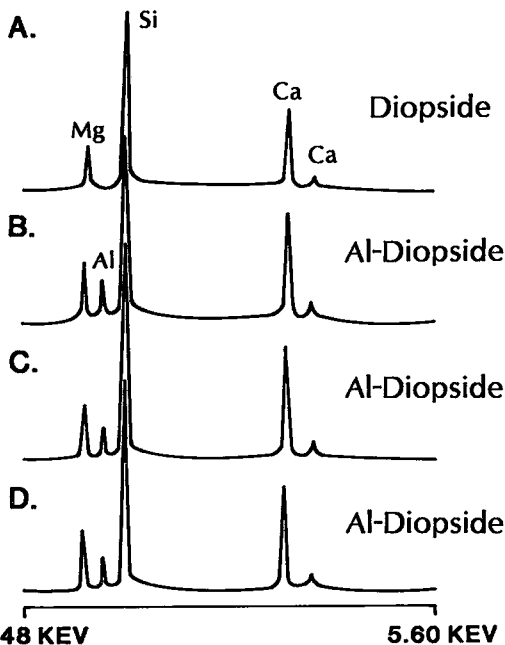


FIG. 5. Scanning electron microscope E.D.S. chemical spectra of synthetic end-member diopside and diopside produced near the equilibrium boundary; (15 kv accelerating voltage).

bor. The chemical spectra show clearly that some diopside grains contain aluminum. A reproducible aluminum peak was obtained from most of these grains (Fig. 5).

Electron-microprobe analysis

Samples were prepared for microprobe analysis using graphite stubs of 0.25-inch diameter on which

TABLE 5: MICROPROBE ANALYSES OF SYNTHETIC CLINOPYROXENES

Duplicate of the microprobe analyses of standard diopside						
	Ca	Mg	Al	Si	Cation Total	Wt%total
Grain A						
#1	1.0433	.9957	.0037	1.9773	4.0211	97.96
#2	1.0231	.9933	.0034	1.9891	4.0093	104.36
Grain B						
#1	1.0063	.996	.0057	1.9944	4.0029	112.49
#2	.9753	1.051	.0051	1.9828	4.0146	115.36
#3	.9782	1.020	.0041	1.9975	4.0005	110.94
n ¹	1.006	1.011	.0044	1.988	4.010	
σ^2	.026	.022	.0008	.007	.007	
¹ means, 5 analyses						
² standard deviation, 5 analyses						
Microprobe analyses from run diopsides and mass balance						
	Ca	Mg	Al	Si	Cation Total	Wt%total
n ¹	0.8840	0.9198	0.4546	1.7486	4.0231	94.72
σ^2	0.1393	0.0650	0.1251	0.0698	0.0270	10.14
¹ means for 58 analyses						
² standard deviation for 58 samples						

the charge was dispersed and carbon-coated to a thickness of 25 nm. An A.R.L. SEMQ microprobe was used, with specimen current at 40 nA on aluminum at an accelerating potential of 15 kV with a 300 μm aperture. Counting time for both background and peak was 10 seconds. Analyses using the minimum size beam were unsatisfactory because of Na loss in standardization on jadeite, and beam instability on the small grains available. A small raster of about 2 μm was successfully used.

Oxides determined in the analyses were Al_2O_3 , SiO_2 , CaO and MgO . Standardization was made on synthetic phases of similar size and shape to the unknown. Synthetic end-member jadeite prepared at 20 kbars and 600°C, and synthetic end-member diopside were used as standards. Because the grains of synthetic standard minerals and run-products were all very small (less than the X-ray excitation volume), the shape and the size of the grains selected were very important factors in achieving good analyses. To reduce the effect of grain size and orientation, grains of similar shape, orientation and size were chosen. Both standard and unknown mineral grains had to be well separated from other grains. Even with all precautions weight-percent totals vary from less than 80% to more than 120%. Results are given in Table 5. Pure end-member diopside is close to the theoretical composition, lending some confidence to the technique.

No differences were noticed from data obtained on different days. Table 5 shows the duplicate analyses of standard synthetic end-member diopside in which the same grain was analyzed repeatedly.

Oxides were normalized to a pyroxene formula using 12 oxygen atoms. Table 5 shows the analyses of diopsides from different run-products. Al_2O_3 in run-product clinopyroxene varies from 0.3 to 0.7 per formula unit, whereas the diopside standard has none.

The presence of aluminum and the deficiencies of magnesium and calcium in clinopyroxene indicate that the solution can be described by a Tschermak substitution. If only Ca-Tschermak substituted for diopside then calcium should not change from a value of 1.0 atom per formula unit, and Mg and Si would decrease as aluminum increases. The deficiencies in both magnesium and calcium suggest that substitutions involve both Ca-Tschermak and Mg-Tschermak.

In an attempt to see more clearly the relations between elements, all possible pairs of elements were plotted against one another. Of these, the following pairs showed scatter without any convincing trend (Al-Ca, Al-Mg, Ca-Si, Mg-Si, Ca-Mg). In Figure 6 are plotted Al-Si and Al-(Ca + Mg), which show well-defined trends. Theoretically, if an experiment reached equilibrium at a particular pressure and temperature and the analytical errors could be eliminated, all the analyses should plot at one point. The differences in composition seen here are certainly beyond analytical error, and can be attributed either to various mixtures of diopside and Al-rich pyroxene or to a range of nonequilibrium solid solutions. Although the data for aluminum and silicon vary from one analysis to another, the plot of Al versus Si (Fig. 6) shows that the data can be well fitted by a linear equation. Also shown in the Figure is the

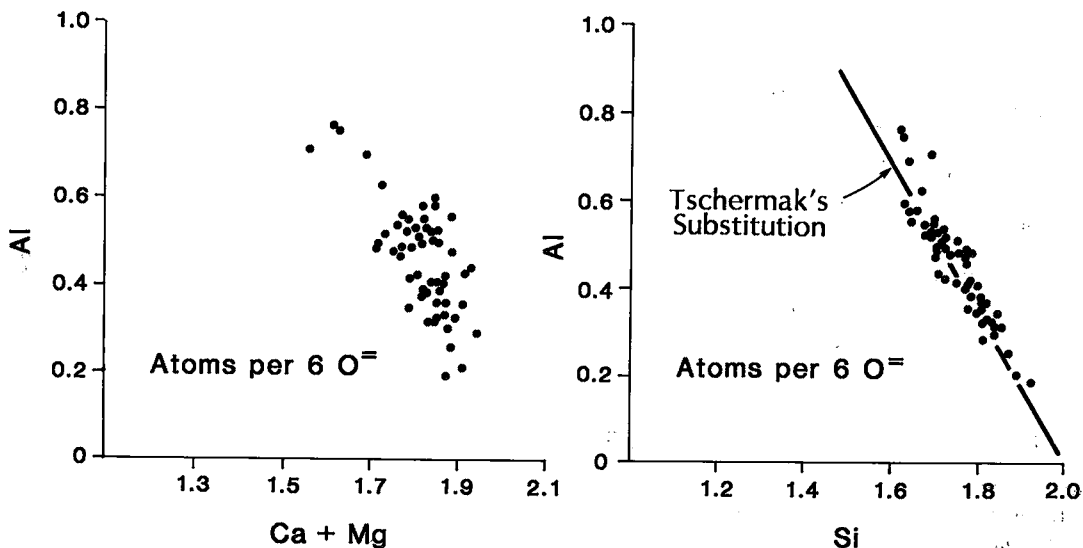


FIG. 6. The relation between Al and (Ca + Mg) atoms per formula unit (left) and between Al and Si (right) in diopside produced in equilibration experiments (microprobe data). The straight line in the right-hand plot is the theoretical relation between Al and Si for a Tschermak-type substitution.

line of theoretical variation that would result from perfect Tschermak's substitution.

The question arises as to the relative proportion of Ca-Tschermak and Mg-Tschermak molecule substitution. All the oxides have been partitioned and balanced between the components Ca-Tschermak, Mg-Tschermak, and diopside. The analytical data show that the average calcium deficiency may be slightly greater than that of magnesium. If real, this could be caused by more Mg-Tschermak than Ca-Tschermak substituting for diopside.

It has been reported (Gasparik & Lindsley 1980) that aluminous pyroxenes are very difficult to equilibrate and may form inhomogeneous crystals because of the slow diffusion of aluminum. It would not be surprising, according to their results, to find an aluminum-free center of diopside seed-crystals with an aluminum-rich clinopyroxene overgrowth. Fujii (1977) found that, in homogenization experiments at 16 kbars and 1100 to 1375°C, the pyroxene grains were not completely equilibrated. Large grains were cored by compositions close to that of the starting material, but the small grains were similar to the rims of large grains. Although an examination of such zoned grains was impossible in the present study because of the small grain size, zonation may be the reason for the variation of aluminum content.

Evidence from natural assemblages

Clinopyroxene compositions from rodingite have been reported by Bell *et al.* (1911), Challis (1965), Frost (1975), Evans *et al.* (1979), Wares & Martin (1980), and Rawson (1984, J.M. Rice, pers. comm.). Rawson (1984), studying rodingites from the north-central Klamath Mountains, California ($P = 5$ to 7 kbars), found that clinopyroxene in rodingite is a complex but dilute solid solution of Mg, Mn, Fe and Al in diopside. Ca contents range from 0.931 to 0.993 cations per formula unit. Mg contents range between 0.94 and 0.81 per formula unit. Tschermak's substitution of aluminum, ferric iron, and titanium appears to increase with metamorphic grade. Aluminum is the only cation substituting in the tetrahedral site in these pyroxenes. The average value of Al_2O_3 is about 2 to 3 wt.%. Wares & Martin (1980) reported small amounts of aluminum in clinopyroxene from rodingite. It seems clear that diopside from natural rodingites metamorphosed under conditions similar to those in the experiments reported here contains much less aluminum than the experimentally produced diopsides.

THERMODYNAMIC PROPERTIES

Critically-limiting experimental results were selected for the purpose of constraining sets of ΔS° ,

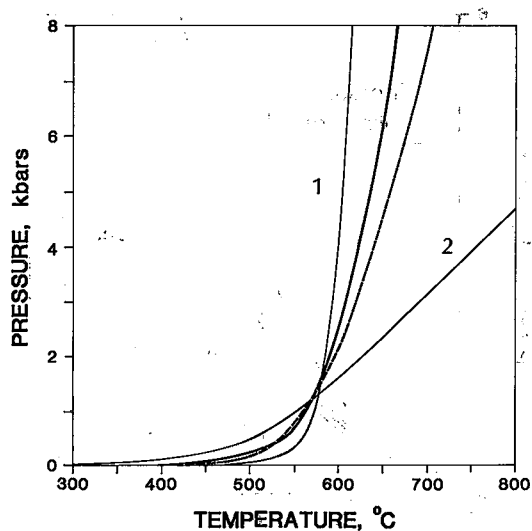


FIG. 7. The upper (#1) and the lower (#2) limits of possible equilibrium curves derived from linear programming analysis of the new experimental results without reference to other constraining data. The heavy solid curve is the equilibrium calculated using PTSYSTEM and UBCDATA, and the heavy dashed curve is calculated using the database of Helgeson *et al.* (1978).

TABLE 6: THERMODYNAMIC PROPERTIES, UBC DATA

Phase	ΔH_f° (J)	S° (J/K)	V (cm ³)
Clinoclchlore	-8921085	429.77	209.82
Mg ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈	K_0 1214.28	K_1 -11217.13	K_2 0.0
			K_3 -1256253184
Diopside	ΔH_f° (J)	S° (J/K)	V (cm ³)
	-3201898	142.50	66.18
CaMgSi ₂ O ₆	K_0 305.41	K_1 -1604.93	K_2 -7165973
			K_3 921837568
Grossular	ΔH_f° (J)	S° (J/K)	V (cm ³)
	-6632395	255.00	125.30
Ca ₃ Al ₃ Si ₃ O ₁₂	K_0 573.43	K_1 -2039.41	K_2 -18887168
			K_3 2319311872
Spinel	ΔH_f° (J)	S° (J/K)	V (cm ³)
	-2302436	83.67	39.74
MgAl ₂ O ₄	K_0 235.90	K_1 -1766.58	K_2 -1710415
			K_3 40616928
Water H ₂ O	ΔH_f° (J)	S° (J/K)	V (cm ³)
	-241816	188.72	24450.30

$$C_p = K_0 + K_1/T^{0.5} + K_2/T^2 + K_3/T^3$$

TABLE 7: THERMODYNAMIC PROPERTIES AS CONSTRAINED BY THE EXPERIMENTS

Clinoclchlore		Reaction	
maximum S°	627.77(J/K)	maximum ΔS°	466.99(J/K)
minimum S°	65.42(J/K)	minimum ΔS°	1029.34(J/K)
maximum ΔH_f°	-8755376.(J)	maximum ΔH_r°	209941.(J)
minimum ΔH_f°	-9233983.(J)	minimum ΔH_r°	688548.(J)

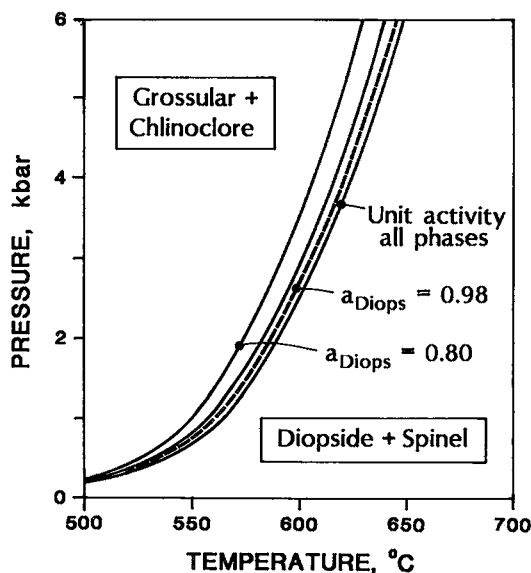


FIG. 8. The equilibrium curve displaced by various amounts of solid solution in diopside. The heavy dashed line is the equilibrium with diopside activity of 0.98 as calculated with program THERIAK. The curve at highest temperature is the equilibrium calculated with stoichiometric phases of unit activity, and the low-temperature curve was calculated with diopside activity of 0.8 corresponding to the analyzed composition of the aluminous diopside.

(298, 1 bar) and ΔH°_f (298, 1 bar). These data were analyzed by linear programming (Berman *et al.* 1986b). Linear programming solutions to problems of this kind can result from optimizing some objective function, which may be any linear combination of the thermodynamic properties of the phases. For example, one may find the maximum or minimum of the S° and ΔH°_f of any phase, or the ΔS° and ΔH°_f of the reaction. The limits on ΔS° and ΔH°_f for the reaction that are consistent with the experiments are listed in Table 7.

Both types of constraints are illustrated in Table 7. In one, the properties of the other reacting phases were held constant and the S° and ΔH°_f of clinocllore were both maximized and minimized. In the other, the Δ 's for the entire reaction were maximized and minimized while maintaining consistency with the new experiments. The new experiments are consistent with UBCDATA (Table 6) and with the data of Helgeson *et al.* (1978), and do not narrow those limits for clinocllore.

The reaction curves were calculated and plotted using programs from Perkins *et al.* (1987) (Fig. 7) using these two sets of ΔS° (298, 1 bar) and ΔH°_f (298, 1 bar) values. Also shown are the equilibrium calculated with coefficients from UBCDATA

(Table 6) and the curve calculated by Rice (1983) using the database of Helgeson *et al.* (1978). Figure 7 indicates that the experimental results from this study are consistent with UBCDATA and the database of Helgeson *et al.* (1978).

Diopside activity and displaced equilibrium

In the reaction: grossular + clinocllore = 3 diopside + 2 spinel + 4 H₂O, the equilibrium will be displaced from the pure end-member reaction if any phase is not a pure end-member. The experimental evidence is that all phases are of end-member composition except diopside produced by reaction with spinel, clinocllore and grossular. The substitution of Al in diopside reduces the free energy of diopside by an amount $\Delta\mu_{Di}$, where

$$\Delta\mu_{Di} = RT \ln a_{Di}^{Cpx}$$

in which a_{Di}^{Cpx} is the activity of diopside in clinopyroxene. This reduction in free energy of diopside component would be expected to stabilize the high-temperature assemblage, displacing the "equilibrium" curve to lower temperature. We have calculated the position of the equilibrium curve with P - T system and UBCDATA with different diopside activities as shown in Figure 8. The displacement of equilibrium curves with different diopside activity values is significant. Equilibrium temperature decreases as the diopside activity values decrease.

The equilibrium curve with diopside activity value of 0.96 which is derived from the calculation using program THERIAK is also shown in Figure 8. Diopside activity in clinopyroxene from experiments has been calculated from $a_{Di}^{Cpx} = Ca^{2+}(M2) * Mg^{2+}(M1)$ as Si (T) is not independent of Al ($M1$ and $M2$) assuming $M2$ is filled by Ca and Al is equally distributed between $M1$ and T (see Table 5). Because the aluminum values vary rather widely, the diopside activities also vary. The average value, however, is close to 0.8. In Figure 8, it may be seen that a diopside activity of 0.8 should displace the equilibrium to lower temperature from the stoichiometric equilibrium curve (18°C at 1000 bars and 20°C at 2000 bars).

The position of the equilibrium displaced as it should be by aluminum in diopside is still within the brackets of reversals obtained in the equilibration experiments, so that we are unable to use the precise location of a displaced equilibrium curve to confirm or deny the presence of a contaminant in the diopside.

We tentatively explain the formation of the Al-bearing diopside in the experiments as follows. First, we assume that the existing thermodynamic data and data from natural assemblages reflect the equilibrium condition, and that the stable clinopyroxene is almost

pure diopside. This requires that the synthetic aluminous diopside coexisting with spinel and clinocllore be metastable and thus have a higher free energy than pure diopside (see Fig. 9).

We can only suppose that the Al-bearing diopside is formed during the reaction that breaks down clinocllore plus grossular. Either the tetrahedral groups of the clinocllore are not destroyed in the process or the aluminum is derived from the destroyed grossular. The lack of tetrahedral aluminum in grossular suggests clinocllore as the source, which would result in an 'inherited' tetrahedral-Al content of the new clinopyroxene, which, though metastable, is more stable than the alternative low-temperature assemblage of grossular + clinocllore. However, chlorite remains and grossular is reduced, favoring grossular as the source.

At the lowest temperatures (1 in Fig. 9) and at the highest temperatures (4 in Fig. 9) the assemblages found experimentally would be unambiguous and would contain stoichiometric phases. However, at intermediate temperatures just above the true equilibrium, where kinetics are slow, metastable Al-rich diopside would form first and would persist, producing the observed relations.

Because of the very small grain sizes and the insensitivity of the clinopyroxene cell parameters to Al content, we are unable to prove that this explanation is correct, but it seems consistent with all of our data and with the data of others.

CONCLUSIONS

Experimental results show that the low-temperature assemblage grossular + clinocllore is stable below 502°C at 500 bars, 520°C at 1000 bars, 561°C at 2000 bars, and 600°C at 4000 bars. The high-temperature assemblage diopside + spinel is stable at temperatures higher than 560°C at 500 bars, 581°C at 1000 bars, and 627°C at 2000 bars. Between these brackets there is a pressure-temperature region in which the metastable assemblage aluminous diopside + clinocllore seems always to be found.

Diopside from the experimental assemblage diopside + clinocllore was proven to contain aluminum and is interpreted to be consistent with Tschermak substitution. Aluminum content varies greatly from one analysis to another. Zonation of aluminum in diopside is probably the main cause for this variation, although no zonation could be seen with SEM, microprobe, or optical microscope.

Theoretical thermodynamic prediction of the equilibrium allowing for solid solution in pyroxene indicates that diopside should be the dominant component, as high as 98 mol%. Ca-Tschermak molecule and clinoenstatite should make up the remaining 2 mol%. Activity of diopside in the pyroxene thus should be very close to 1.0. The average of diopside

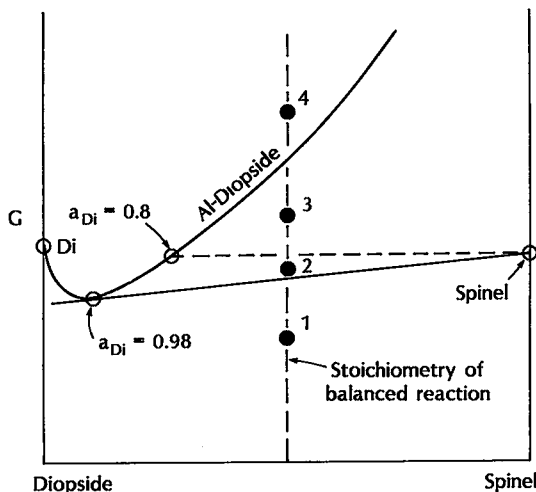


FIG. 9. Diagrammatic sketch of free-energy relations to explain the occurrence of metastable aluminous diopside. The composition axis is taken along the diopside-spinel join, and the total free energy of the grossular + chlorite assemblage is shown as a piercing point at the stoichiometry of the balanced reaction. Points 1, 2, 3, and 4 represent the free energy of Gr + Cl relative to Di + Sp + H₂O at successively higher temperatures. (1) Low-temperature assemblage most stable. (2) Low-temperature assemblage more stable than metastable Di_{0.8} + Sp but less stable than Di_{1.0} + Sp. (3) Low-temperature assemblage more stable than aluminous diopside solid solution but less stable than any diopside-rich clinopyroxene + Sp. (4) Low-temperature assemblage less stable than either aluminous diopside solid solution or any linear combination of diopside pyroxene and spinel.

activities calculated from microprobe analyses, however, is about 0.8, which should lower the equilibrium temperature about 20°C from the calculated stoichiometric equilibrium. This calculated displacement is still within the experimentally reversed brackets. We infer that the Al-bearing diopside in a central 'zone of uncertainty' is metastable, and has derived its tetrahedral Al from the clinocllore- and grossular-bearing reactant assemblage.

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