

Phase changes

H. J. Hall

[AMERICAN JOURNAL OF SCIENCE, VOL. 258, APRIL 1960, PP. 247-257]

**STABILITY RELATIONS OF GROSSULARITE
AND HYDROGROSSULARITE
AT HIGH TEMPERATURES AND PRESSURES**

CARL W. F. T. PISTORIUS and GEORGE C. KENNEDY

STABILITY RELATIONS OF GROSSULARITE AND HYDROGROSSULARITE AT HIGH TEMPERATURES AND PRESSURES*

CARL W. F. T. PISTORIUS** and GEORGE C. KENNEDY

Institute of Geophysics, University of California, Los Angeles

ABSTRACT. The equilibrium relations between hydrogrossularite + quartz and anorthite + wollastonite + water have been determined to 15500 bars and 810°C by means of the "simple squeezer" high-pressure apparatus. There is a continuous solid-solution series from grossularite, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{SiO}_2$, through hydrogrossularite to hibschite, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$. The composition of hydrogrossularite, above 500°C and in equilibrium with quartz, is determined almost entirely by temperature. Grossularite is stable above 780° and 15 kilobars H_2O pressure in the presence of quartz.

INTRODUCTION

Pure grossularite garnet, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{SiO}_2$, is a very rare mineral in metamorphic rocks though members of the series grossularite-andradite are common, where some ferric iron replaces the aluminum. At modest temperatures and pressures in a hydrothermal environment hydrogarnets form (Yoder, 1950; Flint, McMurdie and Wells, 1941). Yoder succeeded in preparing hydrogrossularites of variable composition in hydrothermal experiments between 450°C and 750°C at pressures below 2000 bars. He failed to synthesize the dry end-member, grossularite, in the presence of water, and concluded that it could not exist in the presence of water at elevated temperatures. Later Coes (1954) synthesized grossularite at 600°C to 800°C and 15,000 bars. Yoder (1954) also prepared grossularite in the range below 750°C, 2000 bars and 1025°C, 10,000 bars. Unfortunately no further particulars are available.

Most naturally occurring hydrogrossularites form in metagabbros or in other rocks where silica is not present as a free phase. It seemed possible then that Yoder's earlier failure (1950) to synthesize the pure end-member, grossularite, was due to loss of silica to water vapor during the course of his hydrothermal run. This, indeed, was suggested by Yoder (1950) in his discussion of the results of his experiment. Fyfe and Turner (1958) found, however, that "if excess silica is present, grossularite will not form at low pressures between 450°C and 700°C, but that instead anorthite and wollastonite are the stable phases."

The present investigation was undertaken in the hope of clearing up some of these problems.

EXPERIMENTAL DETAILS

The majority of the experiments were carried out in the "simple squeezer" high-pressure apparatus designed by Griggs and Kennedy (1956). The confining pressure was produced by pressing two sintered carbide pistons together. The piston faces that come in contact had a diameter of approximately 6 mm. The finely ground sample, encapsulated in platinum foil was placed between the piston faces. The pistons were pressed together by a commercial 20-ton

* Publication No. 140, Institute of Geophysics, University of California.

** On leave from the National Physical Research Laboratory of the Council for Scientific and Industrial Research, Brummeria, Pretoria, South Africa.

hydraulic jack, supported by a framework of plates and tie rods. The sample was heated by an external furnace enclosing the sample and pistons. Temperature was measured by a chromel-alumel thermocouple placed in a hole in the top piston in such a way that the tip of the thermocouple was approximately a quarter of an inch from the sample. The difference between temperature at sample position and temperature at the thermocouple junction was independently determined by calibration runs. Temperatures are believed to be accurate to $\pm 7^\circ\text{C}$.

Sintered chromium carbide pistons in Blackalloy piston holders were used. The pressure was determined from the force applied to the pistons, assuming that the sample is approximately under hydrostatic pressure. The pressure, measured in this way, under favorable circumstances is accurate to approximately 5 percent.

The starting material in the majority of the runs was a finely ground mixture of Allied Co. Reagent grade silicic acid, $\text{SiO}_2 \cdot n\text{H}_2\text{O}$, Baker's analyzed aluminum hydroxide and Baker's analyzed calcium oxide, with a 40 percent excess of silicic acid over stoichiometric proportions of a 1:1 grossularite-quartz mixture. The calcium oxide contained less than 0.04 percent iron. No great care was taken in weighing out the calcium oxide, for the presence of a little excess calcium along with a good deal of excess silica only meant that a little wollastonite was present in the runs on the grossularite side of the boundary, and the position of the boundary was not influenced. The products were identified by comparing x-ray patterns obtained on a Norelco high angle diffractometer.

The samples were made up of the powder and mixed with distilled water to form a paste. However, the presence or absence of added water did not affect the position of the equilibrium curve or the reaction rate. Apparently the silicic acid yields a sufficient amount of water on heating for the reaction to proceed normally.

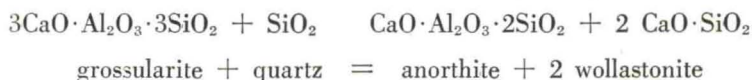
The pressure was first raised to the desired value and this sample then heated. This ensured that little water was lost, and that, consequently, the water vapor pressure was equal to the total pressure (Kennedy, 1959). The time required to bring the sample to the desired temperature ranged from 15 to 40 minutes. Only a few seconds were required to bring the sample to pressure. After the sample had been held at the required temperature and pressure for approximately one half hour, the sample was quenched in an air jet. Temperature dropped from 800°C to 200°C in 3 to 4 minutes.

Considerable experience with the piston anvil device has shown that the rate of attainment of equilibrium in this apparatus is many times the rate in conventional hydrothermal gear. Presumably the strain energy stored in the sample as it is taken to pressure promotes very rapid recrystallization. The initial reaction rate in the piston anvil device is exceedingly high. However, after the sample has been to pressures and temperatures for approximately a half hour, the reaction rate is decreased so markedly that longer times make little difference. It has been our experience in this device that runs of one half hour or several days give essentially the same results. In this particular system a few runs of 24 hours duration were made. The results of these were identical with

the runs of half hour duration. It must be emphasized that this is not true with conventional hydrothermal gear.

RESULTS

The boundary between grossularite-hydrogrossularite + quartz and anorthite + wollastonite first studied by Fyfe and Turner (1958) has been worked out in considerable detail by us. Anorthite and wollastonite are stable on the low-pressure and high-temperature side of the boundary, while grossularite or hydrogrossularite and quartz are the stable phases at high pressure and low temperature. The end-member reaction is given by



The results of 85 runs are summarized in table 1. This table lists the temperatures and pressures of the experiments, the starting materials, and the products. Quartz and small amounts of wollastonite were present among the products of all runs, and therefore these two products are not listed in table 1. Presumably wollastonite was formed directly from calcium oxide and silica, even though the run was not in the anorthite-wollastonite field. Further, a little excess calcium oxide was probably present. All runs were made at 500°C or higher temperatures, as reaction rates were very slow at lower temperatures.

The boundary curve, shown in figure 1, has been drawn on the basis of

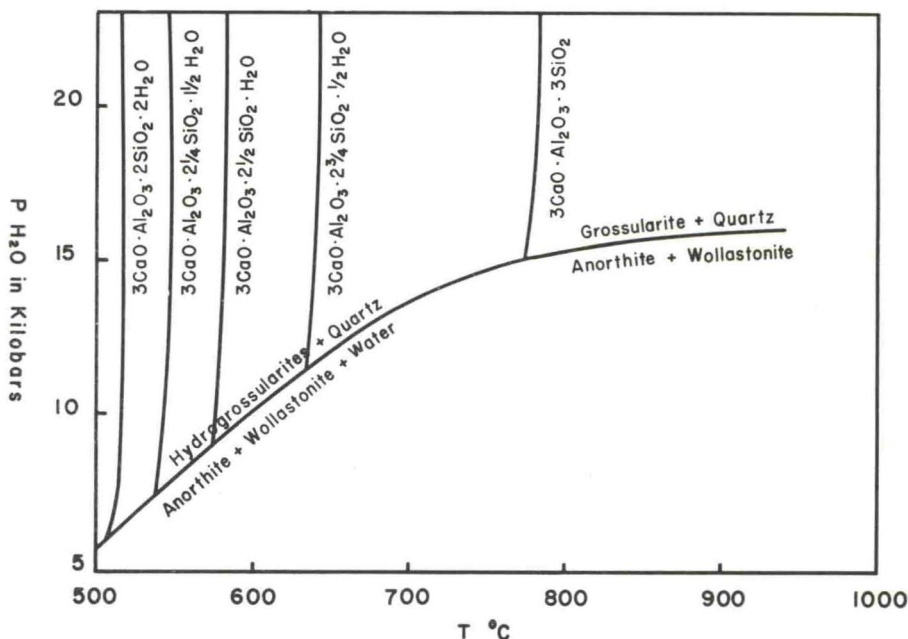


Fig. 1. Grossularite-hydrogrossularite relations at high temperatures and water pressures.

TABLE 1

Results

Run no.	Temp. °C ± 7°C	Pressure kb ± 1 kb	Time mins.	Unit-Cell of hydrogarnet A ± .012	Result of x-ray examination of products	Starting materials
1	720	27	30	11.857	Gr.	Oxides + H ₂ O
5	845	14.3	30	11.851	An. + Gr.	"
8	700	5.05	30	—	An.	"
9	744	10.1	30	11.858	An. + Gr.	"
10	792	10.2	30	11.847 ± .018	An. + minor Gr.	"
11	847	10.1	30	—	An. + minor Gr.	"
12	690	10.2	30	11.874	An. + minor Gr.	"
13	639	10.1	30	11.888	Gr. + minor An.	"
14	639	4.97	40	11.890	Gr. + minor An.	"
15	587	4.95	60	11.902 ± .027	An. + minor Gr.	"
16	691	5.01	30	11.878	An. + Gr.	"
17	742	5.11	30	11.864	An. + minor Gr.	"
18	585	5.05	60	11.932	An. + Gr.	"
19	384	5.03	45	—	Boehmite	"
20	606	15.0	35	—	Gr.	"
22	698	14.8	30	11.857	Gr.	"
23	808	14.8	25	11.851	Gr. + minor An.	"
24	695	12.5	30	11.868	An. + Gr.	"
25	756	12.4	30	11.851, 11.852	An. + Gr.	"
26	687	14.7	60	—	Gr.	"
27	596	7.28	35	11.904	Gr. + minor An.	"
28	605	9.84	35	11.899	Gr. + minor An.	"
29	657	10.1	30	11.873	An. + Gr.	"
30	702	10.0	30	11.862	An. + Gr.	"
31	642	7.4	35	11.879	An. + Gr.	"
32	712	9.0	360	—	No crystallization	Dry Oxides
33	647	16.4	40	11.878	Gr.	Oxides + H ₂ O
34	608	16.9	40	11.892	Gr.	"
35	657	12.9	35	11.877	Gr.	"
36	602	13.3	35	11.907	Gr.	Hydroxides
37	549	10.2	60	11.907	Gr.	Oxides + H ₂ O
38	503	10.6	60	11.988	Gr.	"
39	687	14.0	30	11.859	Gr.	"
40	708	14.4	30	11.867	Gr.	"
41	719	14.1	30	11.858	Gr.	"
42	754	14.3	30	11.855	Gr. + minor An.	"
43	697	10.6	30	11.884	An. + Gr.	Oxides + H ₂ O (insufficient silica)
44	620	10.8	30	11.925	Gr.	"
49	625	12.6	20	11.881	Gr.	Oxides + H ₂ O
52	615	13.1	30	11.895	Gr.	Oxides + H ₂ O (large excess silica)
53	625	13.2	30	11.912 ± .022	Gr.	"

TABLE 1 (Continued)

Run no.	Temp. °C ± 7°C	Pressure kb ± 1 kb	Time mins.	Unit-Cell of hydrogarnet Å ± .012	Result of x-ray examination of products	Starting materials
54	697	13.0	30	11.877	An. + Gr.	Oxides + H ₂ O
55	633	13.5	30	11.900	Gr.	"
56	595	20.9	30	11.909	Gr.	"
57	516	21.9	30	11.966	Gr.	"
58	573	21.0	40	11.912	Gr.	"
59	550	22.1	30	11.948	Gr.	"
60	570	17.9	30	11.924	Gr.	"
61	505	18.9	30	11.956	Gr.	"
62	576	15.3	30	11.916	Gr.	"
63	500	16.3	30	11.997 ± .022	Gr.	"
64	560	13.1	35	11.930	Gr.	"
65	502	14.0	35	12.019 ± .022	Gr. + Boehmite	"
66	555	7.9	40	11.948 ± .018	An. + Gr.	"
67	500	8.4	40	12.035 ± .031	Gr. + Boehmite	"
68	555	6.0	45	11.939 ± .037	An. + Boehmite + Gr.	"
69	500	6.4	45	12.045 ± .067	Boehmite + Gr.	"
70	666	10.7	30	11.872	An. + Gr.	"
71	600	11.4	30	11.903	Gr.	"
72	687	12.7	40	11.867	An. + Gr.	"
73	672	13.4	40	11.867	Gr.	"
74	819	16.6	25	11.851	Gr.	"
75	778	16.7	45	11.853	Gr.	"
76	803	15.6	35	11.853	Gr.	"
77	762	15.7	35	11.856	Gr.	"
78	826	5.3	45	11.856	Gr.	"
79	909	5.3	30	11.855 ± .022	An. + minor Gr.	"
80	610	10.5	30	11.898	Gr.	"
81	584	9.4	30	11.916	An. + Gr.	"
82	535	5.21	120	—	An. + Gr.	"
83	535	7.65	75	11.923 ± .022	Gr.	"
85	654	11.8	30	—	Gr.	"
86	510	5.4	120	11.973 ± .044	An. + Gr.	"
87	720	14.1	40	—	An. + Gr.	"
88	809	15.3	25	—	Gr.	"
89	677	13.0	30	—	An. + Gr.	"
90	514	6.1	120	12.021 ± .044	An. + Gr.	"
91	585	10.0	20	11.928	Gr.	"
92	585	10.0	20	11.930	Gr. + minor An.	Anorthite + Wol- lastonite + H ₂ O
93	622	10.0	20	—	An. + Gr.	Oxides H ₂ O
94	622	10.0	20	11.903	An. + Gr.	Anorthite + Wol- lastonite + H ₂ O
100	735	13.9	45	—	An. + minor Gr.	"
101	660	14.3	45	—	Gr. + minor An.	"
103	717	14.0	50	—	An. + Gr.	"
104	705	14.3	50	—	Gr. + minor An.	"

runs plotted in the p - t field in which anorthite formed and runs in which no anorthite formed. Runs of varied durations gave consistent results. All samples were quenched under pressure so that the sample remained on the grossularite side of the boundary during quenching.

An attempt was made to reverse the boundary by approaching equilibrium from the high temperature rather than the high pressure side. Runs 92, 94, 103 and 104 were made using a starting mixture of finely ground anorthite and wollastonite. Unfortunately, some grossularite was formed in these runs as the garnet stability field must be crossed while bringing the runs to temperature and pressure, so results were not clear-cut. However, runs made on the high pressure side of the boundary curve in the grossularite field showed a large yield of grossularite, while a much smaller yield of grossularite was obtained on the high-temperature side of the boundary curve. Thus the reversibility of the curve shown is believed established.

Yoder (1950) found that at very high temperatures grossularite breaks down to gehlenite, wollastonite and anorthite. Gehlenite was not detected in any of the present runs. Temperatures were not sufficiently high in the present experiments to be in the gehlenite stability field as extrapolated from Yoder (1950) and it is further unlikely that gehlenite has a stability field in the presence of free quartz, where the reaction gehlenite plus quartz equals wollastonite plus anorthite may be expected.

The crystals of grossularite-hydrogrossularite, formed by the reaction, were very small and it was impossible to determine their refractive indices accurately in order to establish the extent of substitution of water for silica in the grossularite-hydrogrossularite "molecule". Consequently, x-ray techniques were employed to measure the dimensions of the unit-cell of the "grossularite" obtained in each run.

Sodium chloride was standardized against diamond ($a_0 = 3.56680 \pm 0.0001 \text{ \AA}$). NaCl has a strong peak 2° from the strongest peak of grossularite for CuK_α radiation. The unit-cell size of the hydrogrossularite and grossularite formed in the various runs were measured by x-raying the samples on a Norelco diffractometer with a scanning of $1/8^\circ$ per minute, using the pre-calibrated sodium chloride as an internal standard. In all cases the (420) peak of the garnet was used for measurement. For any given run, the unit-cell edge obtained is reproducible to 0.004 \AA . However, a second run made at the same temperature and pressure did not usually yield exactly the same value. This was probably due to small differences in the conditions of the runs. However, in the majority of cases the a_0 -values given in table 1 are accurate to better than 0.012 \AA . There are exceptions for runs at very low temperatures (below 550°C), where the reaction rate was very slow, and for runs at very high temperatures but low pressures, where only a little metastable grossularite might be produced. In these cases a rather low yield of hydrogarnet is encountered, which makes an accurate determination of a_0 difficult. Furthermore, the peaks tended to broaden as lower temperatures were approached, suggesting a range of composition within a run or poor crystallization.

Pabst (1942) found that the hydrogrossularite, hibschite, is octahedral with a unit-cell edge of 12.0 \AA . The unit-cell edge of the dry end-member,

grossularite, is 11.851 Å (Skinner, 1956).

The composition of hydrogrossularite at a given temperature is, as a first approximation, nearly independent of pressure. Thus, under the conditions of our experiments, composition of garnet and unit-cell size can be closely correlated with temperature of formation. Variation of cell size as a function of temperature is shown in figure 2. The length of the vertical lines in figure 2

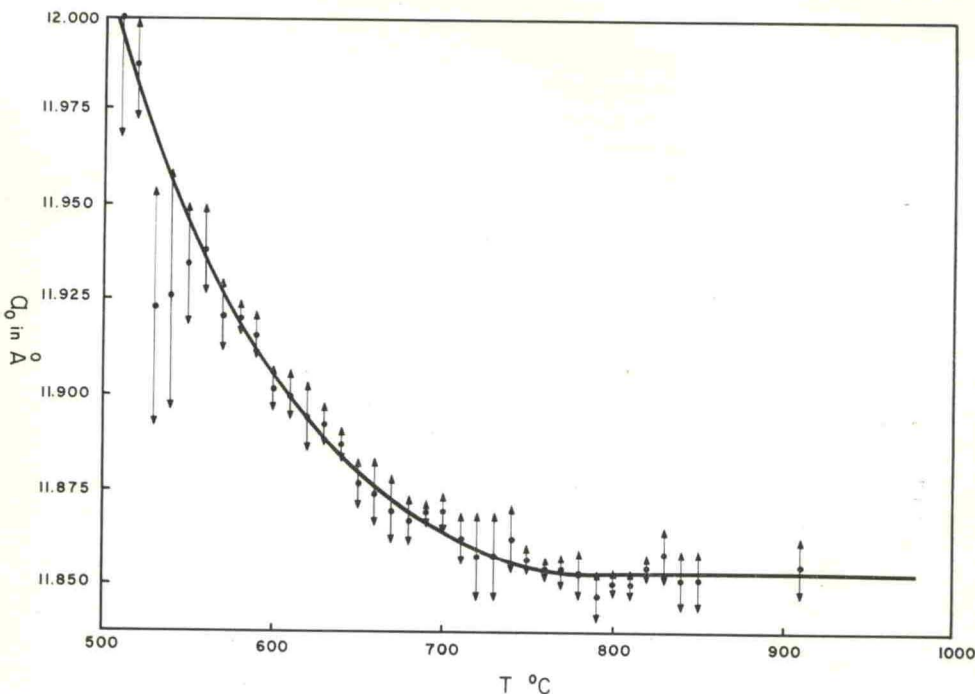


Fig. 2. a_0 of grossularite-hydrogrossularite, synthesized at various temperatures.

show the estimated uncertainty in cell sizes determined from all runs within 20° of the temperature plotted.

The curve separating the fields of grossularite-hydrogrossularite plus quartz and anorthite plus wollastonite plus water is not a straight line in the p - t plane, but its slope decreases with higher temperatures, for the composition of the hydrogrossularites changes regularly with temperature. Above 780° all grossularites formed had a cell of approximately 11.850 Å and were presumed to be pure dry end-members. The curve appears to be a straight line in this region within the limits of experimental error.

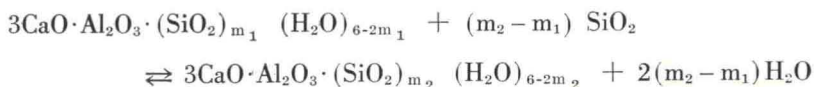
Composition boundaries of the various hydrogrossularites, shown in figure 1, have been plotted from the smoothed curve of figure 2 by use of Vegard's law (Vegard, 1927) and by assuming that the value 12.0 Å (Pabst, 1942) is correct for pure hibschite. There is no break in the smoothed curve of figure 2 which corresponds to the hibschite composition. Thus the mineral hibschite exists only as an intermediate member of a solid-solution series. It forms, when

the water vapor pressure is above 6000 bars, in the presence of excess quartz, at $510 \pm 15^\circ\text{C}$.

The unit-cell size of grossularite, obtained from the average of all runs above 780°C , is 11.852 Å. This agrees well with the determination by Skinner (1956) of the unit-cell of pure grossularite, 11.851 Å.

Belyankin and Petrov (1941) showed that when hibschite was heated at one atmosphere, a strong endothermic reaction occurred at 650°C . The effect is apparently not reversible and they suggest that the transition is "from the original crystalline phase into an amorphous phase". Skinner (1956) pointed out that this reaction probably corresponds to a breakdown of hibschite, presumably into amorphous components, and a loss of water.

However, hibschite does not totally break down at the higher H_2O pressures of our experiments, but undergoes a reaction which may be represented as



where m_1 and m_2 are numbers between 0 and 3. Hibschite and grossularite are represented by the special cases where m equals 2 and 3, respectively.

All runs, with the exception of runs 91-94, were made in the piston-anvil device described by Griggs and Kennedy (1956). Runs 91-94 were made in a large bomb fitted with an internal furnace capable of pressures to 10 kilobars. The pressure medium was argon gas and samples were sealed in small platinum envelopes. Runs 91 and 93 were made using a mixture of oxides and water as starting material. Runs 92 and 94 were made on a starting material of finely powdered anorthite and wollastonite and water. Results of these runs (see table 1) confirmed the position of the curve and equilibrium composition of garnets as determined by the piston-anvil device. It is interesting to note that the value for a_0 of the garnet, produced from a starting mixture of anorthite and wollastonite in run 92, was the same as those produced from a starting mixture of the oxides in run 91 and thus independent of the direction of the approach to equilibrium.

Runs 43 and 44 were made with less than stoichiometric amounts of silica for grossularite. The hydrogrossularite showed a much larger water-silica ratio than hydrogrossularites made at similar temperatures and pressures where quartz was present as a free phase. Our runs indicate that hydrogrossularite will not form above 780°C if free quartz is present. Even in the presence of large amounts of excess silica, they form with expected composition at all temperatures below 780°C if water vapor pressure is sufficiently high. Run 32 was made with an anhydrous mixture of oxides with hope of preparing grossularites below 780°C . No crystallization was observed after six hours at 712°C and 9 kilobars confining pressure.

The entropy change, Δs , and heat of transition, Δh for the reaction hydrogrossularite plus quartz equals anorthite plus wollastonite plus water can be estimated from the slope of the equilibrium curve, shown in figure 1. The slope of this curve changes with temperature and pressure as the composition of hydrogrossularite changes with temperature and pressure. Thus this boundary

possesses neither the typical form of a hydration-dehydration boundary nor of a solid-solid reaction boundary (Kennedy, 1954). The slope of the boundary curve was determined graphically at intervals of approximately 50° , and Δv , Δs , and Δh were calculated for the series of temperatures. These results are shown in table 2. It was necessary to estimate the molar volumes of the various

TABLE 2
Thermochemical Data for the Reaction Hydrogrossularite + Quartz
= Anorthite + Wollastonite + Water

P kb	T °C	a_0 Å	$\frac{dP}{dt}$ bars/degree	Spec. vol. of water cc/gm.	ΔV cc/mole reaction	ΔS cal/deg. mole reaction	Δh k cal/ mole re- action
6.2	510	11.995	45.0 ± 15	1.100	87.6	94 ± 30	74 ± 23
8.0	550	11.944	42.4 ± 8	1.047	81.2	82 ± 16	67 ± 13
10.0	600	11.905	40.2 ± 8	1.018	77.4	74 ± 15	65 ± 13
12.0	650	11.880	38.1 ± 6	.993	75.4	69 ± 12	64 ± 11
13.7	700	11.864	27.4 ± 6	.978	74.4	49 ± 11	48 ± 11
14.7	750	11.855	17.1 ± 6	.971	73.9	30 ± 11	31 ± 11
15.1-15.4	780-820	11.852	$8.6 \begin{smallmatrix} +4.4 \\ -2.6 \end{smallmatrix}$	—	73.7	$15.2 \begin{smallmatrix} +8 \\ -5 \end{smallmatrix}$	$16.3 \begin{smallmatrix} +8.6 \\ -5.3 \end{smallmatrix}$ at 800°C

phases at each of the temperatures involved in the calculation. Differences in compressibility and thermal expansion of the various solid phases were assumed negligible and disregarded, since the major uncertainty in the calculations was that of the graphical determination of the instantaneous slope of the equilibrium curve at various temperatures. The specific volume of the hydrogrossularite was computed from the x-ray measurements of unit-cell size. No experimental data were available for the specific volume of water at pressures and temperatures of this reaction. However, Knopoff, Holser and Kennedy (unpublished data) have prepared tables of the specific volume of water by use of a Thomas-Fermi-Dirac type equation of state to interpolate between the specific volumes of water at lower pressures and specific volumes of water at extreme pressures, as found by shock wave methods. The measured values of Δv and dp/dt , with derived values of Δs and Δh , are listed in table 2.

It is clear that in an anhydrous environment, where the only pressure is confining pressure, hydrogrossularites cannot form. Under such circumstances the reaction would be anorthite plus wollastonite equals grossularite plus quartz. The curve for this reaction then is the prolongation of the boundary found above 780°C . This curve intersects the 0°C axis at a pressure of approximately $8.4 \begin{smallmatrix} +2.5 \\ -4.0 \end{smallmatrix}$ kilobars. Thus within these limits of error, pure grossularite is unstable in the presence of quartz with respect to anorthite and wollastonite at all pressures under 8 kilobars. It probably cannot form in the Earth's crust

at pressures of less than 9-11 kilobars, due to the geothermal gradient (Birch, 1955). This corresponds to a depth of somewhat more than 30 kilometers and suggests a much higher pressure environment for grossularite than is generally estimated.

CONCLUSIONS

Grossularite is associated either with wollastonite or with anorthite in the metamorphism of impure calcareous rocks. Anorthite and wollastonite seem to be incompatible in most instances (Harker, 1939). Thus the majority of field observations agree with the phase diagram as presented in this paper.

Some exceptions are known, however. In the Carlingford District (Osborne, 1932) and in Deeside (Harker, 1939) wollastonite and a lime-bearing feldspar are found in close association, with or without grossularite. From the evidence of our phase diagram, it may be presumed that these rocks were formed at high temperatures and low pressures. Rocks with wollastonite, grossularite and anorthite can only form close to the equilibrium curve or form where there is insufficient silica for the various reactions to run to completion.

Yoder (1950) suggests that the majority of garnets described as grossularites are in fact members of the hydrogrossularite series. Under the very rare geological circumstances where the total pressure is equal to the partial pressure of water, pure grossularite cannot form under 780°C, but under most conditions the partial pressure of water is believed less than the total confining pressure. Thus pure grossularites can form at any temperature if the confining pressure is sufficiently high, that is, above the prolongation of the grossularite boundary shown in figure 1.

Unfortunately, the phase diagram we present cannot be applied directly to many geological circumstances. Natural grossularite usually contains other ions, especially trivalent ions, and the influence of these other ions on the stability field of grossularite is unknown. Similarly the reaction we discuss is that of anorthite plus wollastonite equals grossularite plus quartz. Normally a lime-bearing feldspar is involved in the natural reaction and the equilibrium position of the boundary will be influenced by an unknown but appreciable amount by the sodium in the feldspar. The reaction with soda feldspars will be one in which jadeite is an additional high pressure product formed and a complete understanding of this equilibrium involves further experimentation. Further, if free quartz is not present and similarly the partial pressure of water is low, pure grossularites will be stable to much lower temperatures and pressures than indicated on our phase diagram.

ACKNOWLEDGMENTS

Aid of Hugh Heard in the runs made in the hydrostatic apparatus with argon gas is gratefully acknowledged. The skilled work of Irving Cordell, William Hoffman and Lester Emarine in construction and maintenance of the apparatus is acknowledged and appreciated. Dr. Hatten Yoder has critically read this manuscript and offered many useful suggestions. His aid is much appreciated.

REFERENCES

- Belyankin, D. S., and Petrov, V. P., 1941, The grossularoid group: *Am. Mineralogist*, v. 26, p. 450-453.
- Birch, F., 1955, Physics of the crust, in Poldervaart, Arie, ed., *Crust of the earth*, p. 101-117: *Geol. Soc. America Spec. Paper* 62.
- Coes, L., 1954, personal communication, quoted by Fyfe and Turner (1958).
- Flint, E. F., McMurdie, H. F., and Wells, L. S., 1941, Hydrothermal and x-ray studies of the garnet-hydrogarnet series and the relationship of the series to hydration products of Portland cement: *Natl. Bur. Standards Jour. Research*, v. 26, p. 13-33.
- Fyfe, W. S., and Turner, F. J., 1958, Correlation of metamorphic facies with experimental data, in Fyfe, W. S., Turner, F. J., and Verhoogen, J., *Metamorphic reactions and metamorphic facies*, p. 149-185: *Geol. Soc. America Mem.* 73.
- Griggs, D. T., and Kennedy, G. C., 1956, A simple apparatus for high pressures and temperatures: *AM. JOUR. SCI.*, v. 254, p. 722-735.
- Harker, A., 1939, *Metamorphism*: London, Methuen, p. 93-95.
- Kennedy, G. C., 1954, A note on the hydrothermal synthesis of single crystals of silicates and other rock-forming minerals: *Am. Mineralogist*, v. 39, p. 654-660.
- , 1959, Phase relations in the system $Al_2O_3-H_2O$ at high temperatures and pressures: *AM. JOUR. SCI.*, v. 257, p. 563-573.
- Knopoff, L., Holser, W. T., and Kennedy, G. C., unpublished data.
- Osborne, G. D., 1932, Limestones and associated contaminated igneous rocks of the Carlingford District, Co. Louth: *Geol. Mag.*, v. 69, p. 209-233.
- Pabst, A., 1942, Re-examination of hibschite: *Am. Mineralogist*, v. 27, p. 783-792.
- Skinner, B. J., 1956, Physical properties of end-members of the garnet group: *Am. Mineralogist*, v. 41, p. 428-436.
- Vegard, L., 1927, Gitterschwankungen bei Mischkristallbildung durch Fällung von Lösungen: *Videnskapsselsk. Skrifter Oslo*, no. 5, p. 1-11.
- Yoder, H. S., Jr., 1950, Stability relations of grossularite: *Jour. Geology*, v. 58, p. 221-253.
- , 1954, personal communication, quoted by Fyfe and Turner (1958).

