

phase  
transitions

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## HIGH PRESSURE STUDIES OF THE SYSTEM $Mg_2GeO_4$ - $Mg_2SiO_4$ WITH SPECIAL REFERENCE TO THE OLIVINE-SPINEL TRANSITION\*

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**ABSTRACT.** The system  $Mg_2GeO_4$ - $Mg_2SiO_4$  has been studied to the experimental limits of available hydrothermal and uniaxial high pressure apparatuses.

The inversion temperature for the  $Mg_2GeO_4$ (spinel)- $Mg_2GeO_4$ (olivine) equilibrium is  $810^\circ C$  at atmospheric pressure. The  $\Delta V$  of the inversion is 3.5 cc/mole;  $\Delta H$  is  $3690 \pm 180$  cal/mole. The inversion temperature is raised by  $0.025^\circ C$ /bar for the first 5500 bars. Infra-red absorption spectra, x-ray intensities and molar refractivities clearly show that  $Mg_2GeO_4$  is an inverse spinel.

Solid solution between  $Mg_2GeO_4$  and  $Mg_2SiO_4$  is complete in the olivine phase at temperatures above that of the inversion in  $Mg_2GeO_4$ . The maximum silicate content of the spinel solid solutions at lower temperatures increases steadily with pressure, from 10 mole percent at 700 bars to 50 mole percent at 60,000 bars at  $542^\circ C$ . Extrapolation places the spinel-olivine transition for  $Mg_2SiO_4$  at  $100,000 \pm 15,000$  bars. The change in the lattice spacings of the spinel solid solutions of  $Mg_2(Ge,Si)O_4$  shows that  $Mg_2SiO_4$ (spinel) has a cell edge of 8.22Å. Therefore the  $\Delta V$  for this transition is 2.0 cc/mole. The pressure dependence of the transition in  $Mg_2SiO_4$  is estimated by extrapolation at  $0.013^\circ C$ /bar.

Experiments show that substitution of  $Fe^{2+}$  for  $Mg^{2+}$  markedly increases the maximum silicate content of the spinel solid solution under corresponding p-t conditions.

The geophysical implication of these results is that an olivine-spinel transition in the mantle of the earth does appear to be a reasonable explanation of the seismic and density discontinuities starting at 400 km.

### INTRODUCTION

In a paper presented to the Royal Astronomical Society Dr. H. Jeffreys (1936) gave evidence of a discontinuity in the properties of the earth some hundreds of kilometers beneath the surface. He reported that at a depth of  $480 \pm 20$  kilometers a change could be measured in the velocities of seismic waves. Specifically P-waves above this depth had a velocity of 9.08 km/sec, but below this depth the velocity was 9.8 km/sec. Calculations by K. E. Bullen (1936) for the density distribution in the earth also suggested a nearly discontinuous change in density at a depth of 300-400 km. Since no known materials could fit this data Dr. J. D. Bernal, in attendance at the meeting, was asked if it was likely that an olivine-like material could be converted to a new state at great pressures. A direct quotation from Observatory (1936) will serve to present important crystal chemical concepts in the paraphrase of Dr. Bernal's discussion:

Dr. J. D. Bernal said at ordinary pressures olivine, which is magnesium orthosilicate with part of the magnesium replaced by ferrous iron, is a hexagonal lattice of oxygen atoms in which the silicon and metals occupy the cavities, somewhat unsymmetrically. It appeared possible that when the lattice was much compressed the cavities might become too small to hold the silicon atoms, and a different

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structure would have to be found. The structure of a crystal was largely a matter of the sizes of the atoms, the cavities having to be neither too large nor too small to hold them. Thus the effect of compressing the lattice as a whole would be similar to that of inserting a larger atom, such as a germanium in place of silicon. Magnesium germanate had been studied by Goldschmidt and found to exist at ordinary pressures in two forms, one isomorphous with olivine and the other cubic. The latter is about 9 percent denser, and therefore is the high pressure form. By analogy it therefore seemed probable that at high pressure olivine would adopt a cubic form. The change of density suggested by the germanate would be of the right order of magnitude.

The reference to V. M. Goldschmidt introduces a series of developments having to do with the reality of the transition noted by Goldschmidt (1931). In a footnote in this paper it was stated that magnesium orthogermanate,  $Mg_2GeO_4$ , was prepared in a spinel-like form. A year later Jander and Stamm (1932) placed the inversion temperature for the spinel-olivine polymorphs at  $1063^\circ C$ . Incidental to work on synthetic clay phases, Roy and Roy (1954) prepared reproducibly under high water pressures the  $Mg_2GeO_4$  as euhedral spinel-structure crystals. Aware of the change in density of the polymorphs as reported by Bernal and restated by B. Mason (1952), Roy and Roy determined fairly accurately the volume change as 8.3 percent of the spinel volume. They gave the inversion temperature as  $1005^\circ C$  using dry techniques. This work has in general been overlooked since it appeared with much other material on a different subject. Subsequent to this time four reports appeared with the claim that the spinel polymorph of  $Mg_2GeO_4$  *could not be made*. Thus Urey (1952) says

... the observations of Goldschmidt were very approximate and it has proven impossible to prepare the cubic modification in this laboratory. Therefore, Bernal's suggestion rests only on pure hypothesis and it seems desirable to explore the possibility that iron phase is present in the mantle.

Similarly Ringwood (1956) says

The evidence ... indicates that the olivine structure is probably thermodynamically stable above  $600^\circ C$ . Accordingly the author would agree with Romeijn that Jander and Stamm were probably wrong about the transition of  $Mg_2GeO_4$  at  $1065^\circ C$ .

It is of interest to note that although Romeijn (1953) had to conclude that the dimorphism did not exist, he did acknowledge that the absence of dimorphism in  $Mg_2GeO_4$  was a serious flaw in his analysis of spinel structures. E. F. Bertaut in his early work with germanate spinels (1954 and personal communications) was likewise unable to make the spinel form.

The location with respect to depth of the seismic discontinuity reported by Jeffreys has also been changed with subsequent investigations. The current belief is that two discontinuities exist, one at 413 km and one at 984 km. Mason (1952) summarizes the general implications of the hypothesis of solid phase changes in this manner:

... olivine would begin to change to a higher-density polymorph at a depth of 413 km, and the change would become complete at a depth of 984 km. The change would be gradual through the intervening region, the transition depending on temperature, pressure and the magnesium-iron ratio in the olivine, all of which probably vary with depth. A polymorph change of this sort within the mantle also provides a mechanism for periodic orogeny; an increase in the amount of the denser polymorph during geological time would result in contraction of the earth as a whole, thus giving a plausible explanation for crustal shortening and orogeny. All this is highly speculative, however. As Adams (1947) remarked, speculation of this kind point up the desirability of devising means for the investigation of

phase changes in silicates at pressures of the order of 10<sup>5</sup> atm and temperatures above 1,000°.

Obviously a direct experimental attack on the problem of a transition in natural olivine was not possible with known and available techniques and apparatus. However, it was decided that a fruitful and feasible approach to the problem would be a study of the system Mg<sub>2</sub>GeO<sub>4</sub>-Mg<sub>2</sub>SiO<sub>4</sub>, with emphasis on solid solubility and on the polymorphic transitions of the olivine to the spinel type with a view to obtaining reliable data on the Mg<sub>2</sub>SiO<sub>4</sub> by extrapolation. The essence of the experimental approach and some results, including the effect of the substitution of some Fe<sup>2+</sup> for Mg<sup>2+</sup> were reported to the Geological Society of America, Minneapolis meeting (1956). Additional work concerned with some modification and calibration of high pressure apparatus was reported to the same group at the Atlantic City meeting (1957), and at the St. Louis meeting (1958) the results of work on the system Mg<sub>2</sub>GeO<sub>4</sub>-Mg<sub>2</sub>SiO<sub>4</sub> at pressures up to 60 kilobars were presented.

#### EXPERIMENTAL PROCEDURES

Work was begun on the system Mg<sub>2</sub>GeO<sub>4</sub>-Mg<sub>2</sub>SiO<sub>4</sub> using the hydrothermal techniques necessary to catalyze reaction in the solid state. Details of the basic apparatus for these techniques are given by Roy and Tuttle (1956) and Roy and Osborn (1952). The hydrothermal bombs may be used to provide desired and controlled pressure and temperature conditions on prepared samples. The practical upper limits of pressure are 60,000-70,000 psi and of temperature 900-1,000°C, but these limits are not coincident. The higher pressures lower considerably the usable temperature limits.

A second major piece of apparatus necessary in the investigations is the uniaxial pressure device in which pressures can be attained an order of magnitude greater than those feasible in the test tube bomb apparatus. Generally the unit is a modification by Tuttle and Harker in our laboratory on designs of Bridgman along the lines of Griggs and Kennedy (1956).

A description of equipment and procedures is given elsewhere (Dachille and Roy, in press a). In this type of device a large thrust is developed by a hydraulic ram which is intensified and transmitted into a small sample by the use of very hard small piston faces. These pistons have been made of cemented carbides, polycrystalline alumina or mullite, or of special hardenable steels. Directed pressure, that is, total thrust divided by reduced area, may approach 900,000 to 1,000,000 psi, but the effective coincident temperature limits fall very rapidly to about 600°C at these pressures. Pressure to the "jack" is supplied and automatically controlled by means of a Foxboro controller and Aminco oil pump. Temperatures are controlled by Honeywell millivoltmeter instruments. Many techniques for experiments at these pressures were worked out during this and allied studies with a view to studying reversible equilibria rather than only preparing phases. Thus in general we have made efforts to make runs from 1 day to 2 weeks long rather than several minutes to a few hours. It is perhaps accurate to say that no similar work has been described either with respect to range or detail other than that of MacDonald (1956).

The petrographic microscope and the x-ray diffractometer were the primary analytical tools, the latter being much more useful to give not only the

phases present but their composition from the spacings. A Perkin-Elmer Double Beam Model 21 infra red spectrometer was used to obtain absorption spectra in series of compounds with systematic substitution of one cation for another to indicate the coordination of the ion in the spinel phases.

## PREPARATION OF MIXTURES

The method of preparation of most of the mixtures in this study was the direct mulling of the finely powdered oxides under absolute alcohol, then heating for 2-3 hours at 400°C. The magnesia was C. P. Reagent grade of Baker and the germania was the soluble form of GeO<sub>2</sub> prepared by the Eagle-Picher Company. Silicon dioxide was used in the form of silicic acid, the water content of which was determined by dehydration at 1350-1400°C.

A few mixtures used were prepared by the nitrate method and by the method of coprecipitation of germanium and silicon hydrous gels from solutions of their tetrachlorides (Roy, 1956). No significant advantages were found with these latter methods so that systematic work was restricted to mixtures prepared from the oxides.

TABLE 1

X-ray data on Mg<sub>2</sub>GeO<sub>4</sub> and Mg<sub>2</sub>SiO<sub>4</sub> spinel and olivine polymorphs

SPINEL				OLIVINE				
hkl	Mg <sub>2</sub> GeO <sub>4</sub>		Mg <sub>2</sub> SiO <sub>4</sub>	hkl	Mg <sub>2</sub> GeO <sub>4</sub>		Mg <sub>2</sub> SiO <sub>4</sub> **	
	d(A)	I(est.)	d(A) (extrap.)		d(A)	I(est.)	*	
111	4.77	40	4.74	020	5.15	20	5.11	26
220	2.92	30	2.907	110	4.44	40		
311	2.492	100	2.480	021	3.91	80	3.88	69
222	2.384	2	2.374	101	3.81	10	3.73	25
320	2.292	2	2.280	111,120	3.57	10	3.487	21
400	2.066	10	2.056	121	3.06	10	3.000	17
330	1.947	5	1.938	130	2.619	20	2.768	53
331	1.896	10	1.886	131	2.546	100	2.513	73
422	1.687	50	1.678	112	2.488	90	2.458	100
333	1.590	50	1.583	041	2.364	10	2.348	9
	*		***	210	2.390		2.316	9
	a = 8.255A		8.22A	122	2.295	10	2.268	59
	b = "			140	2.279	2	2.250	33
	c = "			211	2.220	20	2.161	15
	v = 562.5A <sup>3</sup>		555.4	132	2.056	2	2.034	5
	z = 8		8	042	1.956	2	1.945	4
				150	1.898	2	1.878	5
				113	1.825		1.811	2
				151	1.810		1.792	3
				222	1.783	20	1.748	60
				241	1.730	2	1.670	13
				061	1.652	5	1.636	12
				133	1.632	5	1.618	15
				152	1.603	5	1.589	2
				043	1.581	10	1.572	10
					4.915A		4.76A	
					10.295		10.20	
					6.020		5.99	
					304.6(609.2)		290.8(581.6)	
					4(8)		4(8)	

\* Roy and Roy (1954)

\*\* Swanson and Tatge NBS Circular 539, v. 1

\*\*\* Extrapolated from figure 2.

In the course of the investigation starting compounds were prepared by the hydrothermal treatment or even dry fusion of the oxide mixtures. Compounds so prepared were then used to test a criterion of reversibility in transitions or to seek clear evidence of exsolution and change in solid solubility under various conditions of pressure and temperatures.

RESULTS

*Data on the phases encountered.*—In table 1 are recorded the characteristic x-ray diffraction data for the olivine and spinel polymorphs of  $Mg_2GeO_4$ . Data for the olivine phase of  $Mg_2SiO_4$ , forsterite, are included to permit a direct comparison with the germanate isomorph. Further x-ray data are given in figures 1 and 2 to demonstrate the effect of replacing some of the ger-

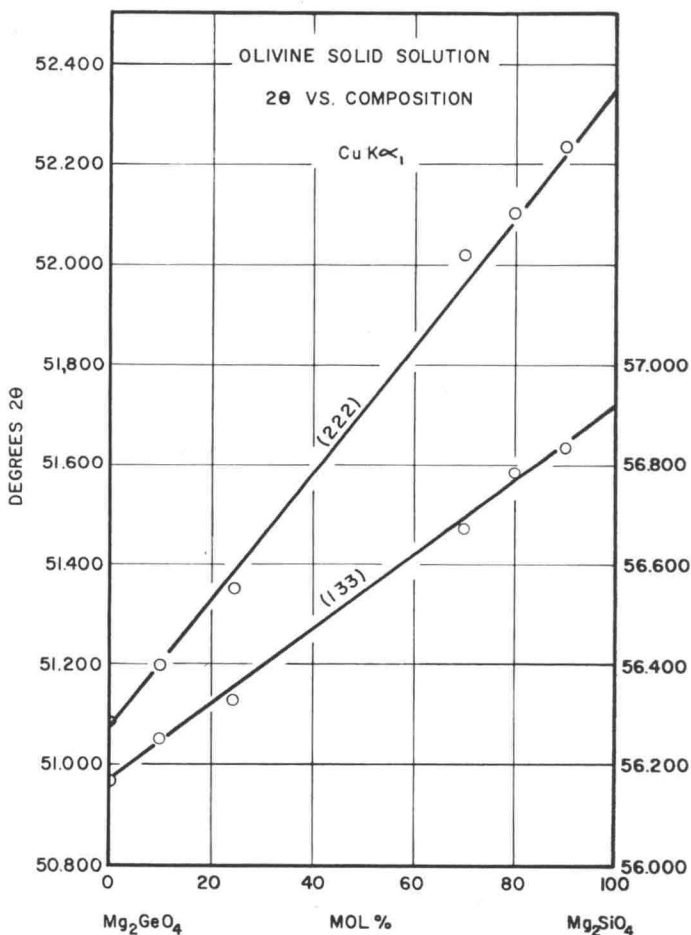


Fig. 1. System  $Mg_2GeO_4$ - $Mg_2SiO_4$ . Change of  $2\theta$  values with composition of the olivine polymorph.

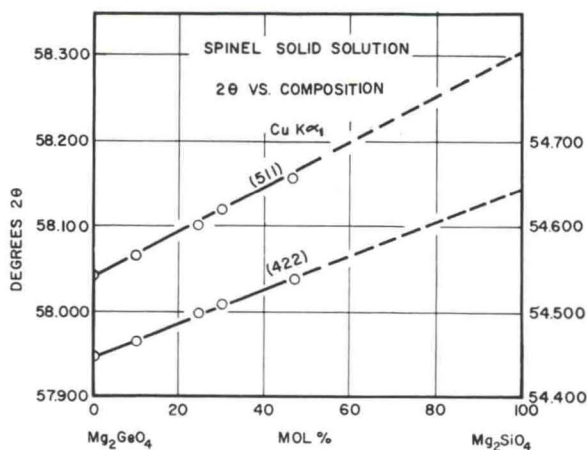


Fig. 2. System  $Mg_2GeO_4$ - $Mg_2SiO_4$ . Change of  $2\theta$  values with composition of the spinel polymorph.

manium with silicon in the olivine and spinel phases respectively. The shifts in these "d-spacings" approach the ideal Vegard relation for substitution in solid solution. They will permit a comparison of volume change between the olivine and spinel polymorphs up to almost 50 percent silicate content, the upper limit of the spinel solid solution prepared. Extrapolation of the d-spacings, figure 2, show that the spinel phase of  $Mg_2SiO_4$  will have a cell edge of 8.22 Å and a unit cell volume of 555.4 Å<sup>3</sup>. This volume is only 4.7 percent smaller than that of the olivine. Hence the volume change in the silicate end member is only 56 percent of that found in the germanate. Although such an extrapolation is considerably more reliable than various guesses in the past, the possibility of strong deviations from ideality in spinel solid solutions cannot be completely ignored.

*The transition in  $Mg_2GeO_4$ .*—The end member  $Mg_2GeO_4$  provided an example for a direct study of the pressure-temperature dependency of the olivine-spinel inversion within limits set by the hydrothermal apparatus. Clean cut and easy reversibility of the transition was achieved under hydrothermal conditions (see table 2). At 10,000 psi the transition occurs at 823°C and the use of higher pressures raises the temperature rapidly to the point at which bomb damage or failure occur frequently. Nevertheless a number of runs were made at higher temperatures and pressures in order to follow this dependence. Similarly equipment problems limited the exploration by the uniaxial devices. It was possible however to make a number of runs at pressures and temperatures approaching 1,000°C and 100,000 psi in this equipment by using pistons made of polycrystalline  $Al_2O_3$  or of mullite. Within these limits the pistons held up remarkably well with no distortion of the circular faces bearing the maximum stress. Unfortunately these surfaces were subject to pitting or flaking when they were separated to recover the sample wafer so that regrinding of the pistons was necessary after each run. Further, the pistons, which were made of rods 4 inches by 1 inch in diameter, on continued use did fail by shearing and

splitting at pressures considerably below 100,000 psi. The information from these experiments is collected in table 2 and the pressure-temperature dependency deduced therefrom is indicated in figure 3. From the slope of this line and the measured difference in volume of the two polymorphs at some selected temperature, it is possible to calculate from the Clapeyron equation a change in enthalpy for the transition. The  $\Delta H$  of transition obtained (olivine-spinel) is 19.9 cal/gm or 3,690 cal/mole with an error of  $\pm 5$  percent. These values will be reviewed later in the discussion.

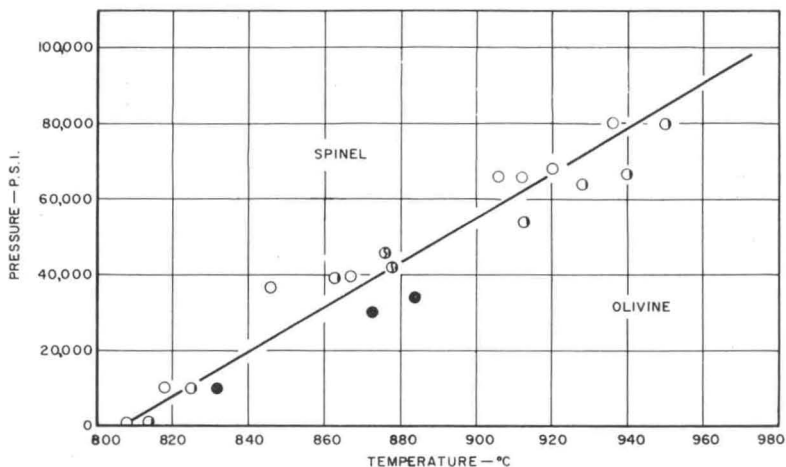


Fig. 3. Univariant p-t curve for the spinel-olivine transition in  $Mg_2GeO_4$ . (Partially filled circles indicate persistence or formation of olivine. Curly division shows runs in which pistons fractured after start of spinel phase.)

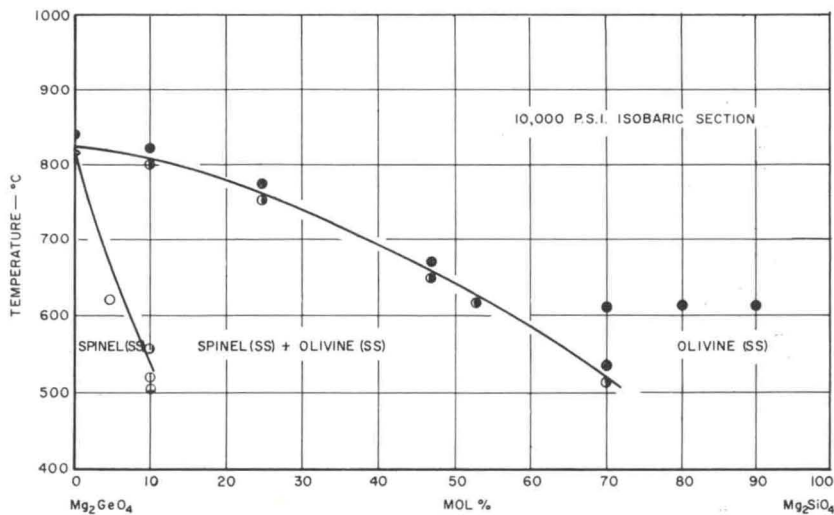


Fig. 4. System  $Mg_2GeO_4$ - $Mg_2SiO_4$ —Isobaric section at 10,000 psi water pressure.

TABLE 2

Data on the system  $Mg_2GeO_4-Mg_2SiO_4$ 

Composition	Run (No.)	(°C) Temp.	Pressure 1000 psi	Dura- tion Hrs.	Phase
$Mg_2GeO_4$ (Hydro- thermal) Oxides	7043	925	5	15	Olivine
" "	7153	833	10	70	"
" "	7076	830	10	70	Spinel & ol.
" "	7081	828	10	70	Sp. + trace ol.
" "	7088	822	10	120	Sp.
" "	7089	801	1	200	Sp.
" "	7094	808	1	44	Sp.
" "	7096	813	1	90	Sp. + trace ol.
" "	7107	830	26	70	Sp.
" "	7146	873	30	40	Ol.
" "	7148	864	39	40	Sp. + trace ol.
Spinel Form	7135	865	39	40	Sp.
Olivine Form	7136	865	39	40	Sp. + minor ol.
Spinel Form	7028	820	10	20	Sp.
" "	7029	825	10	40	Sp. + trace ol.
" "	7030	845	10	44	Sp. + minor ol.
" "	7031	875	10	40	Ol.
" "	7133	845	37	40	Sp.
Olivine Form	7134	845	37	40	Sp. + trace ol.
(Uniaxial) Oxides	7437	925	150	1	Split. Spinel, MgO, $GeO_2$ ru.
" "	7441	1088	90	½	Split. trace ol. MgO, $GeO_2$
" "	7444	906	69	6	Dry.
" "	7445	903	73	24	MgO, $GeO_2$ ru. Sp. + trace $GeO_2$ , MgO
" "	7451	913	57	24	Sp. + ol.
" "	7454	938	65	40	Trace sp. + ol. + oxides
Spinel Form	7457	958	78	40	Sp. + ol. trace
" "	7458	950	36	2	Split. + ol. tr.
" "	7460	918	72	60	Sp.
" "	7485	925	62	40	Sp. + tr. ol.
" "	7479	935	62	40	" + " "
Olivine Form	7489	930	62	40	Spinel
" "	7500	868	32	40	Olivine
" "	7501	863	32	40	"
Oxides + olivine seeds	7524	927	61	40	Sp. + tr. ol.
" " " "	7529	934	52	60	" + ol.
" " " "	7532	910	50	40	" + tr. ol.
(Hydrothermal) 5 mol% $Mg_2SiO_4$	7016	548	10	47	Sp. + tr. ol.
" "	7121	623	10	80	"
" "	7108	626	10	40	"
" "	7095	640	10	96	"
" "	7021	670	10	48	" + " "
" "	7056	745	10	200	" + minor ol.
" "	7078	812	10	96	Ol. + tr. sp.



TABLE 2 (Continued)

Composition	Run (No.)	(°C) Temp.	Pressure 1000 psi	Duration Hrs.	Phase	
10%	"	7091	521	10	80	Sp. + serp.
"	"	7583	529	10	72	" + tr. serp.
"	"	7017	548	10	47	" + " ol.
"	"	7087	595	10	70	" + minor ol.
"	"	7079	814	10	96	Ol.
"	"	7063	821	10	72	"
24.8%	"	7018	548	10	47	Sp. + ol.
"	"	7057	750	10	240	"
"	"	7064	772	10	70	Ol.
30%	"	7164	665	10	90	"
"	"	7073	712	10	48	" + minor sp.
47%	"	7053	650	10	30	" + tr. sp.
"	"	7003	651	10	48	" + " "
"	"	7023	670	10	48	" + " "
53%	"	7554	613	10	70	" + " "
70%	"	7161	503	10	120	" + " talc.
"	"	7583	529	10	72	" + " sp. & talc.
5 mol% $Mg_2SiO_4$	"	7109	626	55	48	Sp.
10	"	7105	565	55	40	"
10	"	7104	584	54	72	" + tr. ol.
24.7	"	7155	745	67	10	" + minor ol.
24.7	"	7157	796	52	29	Ol. + minor sp.
30	"	7156	745	67	10	" + " "
30	"	7158	796	52	29	"
47	"	7162	737	54	48	"
47	"	7160	770	54	9	"
70	"	7183	652	45	24	"
70	"	7184	595	53	72	"
(Uniaxial)						
Oxides						
10 mol% $Mg_2SiO_4$	"	7548	543	122	70	"
18	"	7573	540	282	21	"
18	"	7570	547	196	14	" + tr. ol.
18	"	7568	605	200	24	" + " "
24.7	"	7546	542	260	44	" + " "
24.7	"	7530	542	450	48	" + " serp.
24.7	"	7520	570	570	46	"
24.7	"	7541	546	203	25	" + minor ol.
24.7	"	7476	560	350	24	" + " "
(3/8" sample)						
30	"	7563	537	515	23	" + tr. ol.
30	"	7569	545	553	16	" + " "
30	"	7537	547	405	48	" + " "
38	"	7571	537	740	12	"
38	"	7559	538	570	22	" + minor ( $GeO_2$ ) (rut.)
47	"	7562	530	750	11	" + tr. ( $GeO_2$ rut)
47	"	7567	530	849	6	" + tr. " tr. talc.
47	"	7527	541	585	48	" + minor ol.
47	"	7468	545	670	22	" + " "
47	"	7561	622	190	22	" + " "
53	"	5797	542	780	5	" + " "
53	"	7534	562	408	32	" + 20% "
70	"	7596	536	950	3 1/2	" + ol. (3/8" s.)
80	"	7579	530	200	24	No $H_2O$ . No reaction
80	"	7555	538	100	23	Ol.
80	"	7550	540	311	20	" + minor serp.

The system  $Mg_2GeO_4$ - $Mg_2SiO_4$ .—Data from critical runs in the hydrothermal and uniaxial pressure units are collected in table 2. From these data the phase diagrams shown in figures 4, 5, 6, and 7 have been constructed. The dashed portions in these figures indicate regions not accessible to the known and available techniques. However, the two rather complete isobars at 10,000 and 55,000 psi and the isotherm at  $542^\circ$  (fig. 8) indicate a self consistency in the pressure-temperature-composition relations of the system. Figure 9 is a three dimensional p-t-x diagram of the system  $Mg_2GeO_4$ - $Mg_2SiO_4$  constructed from the data.

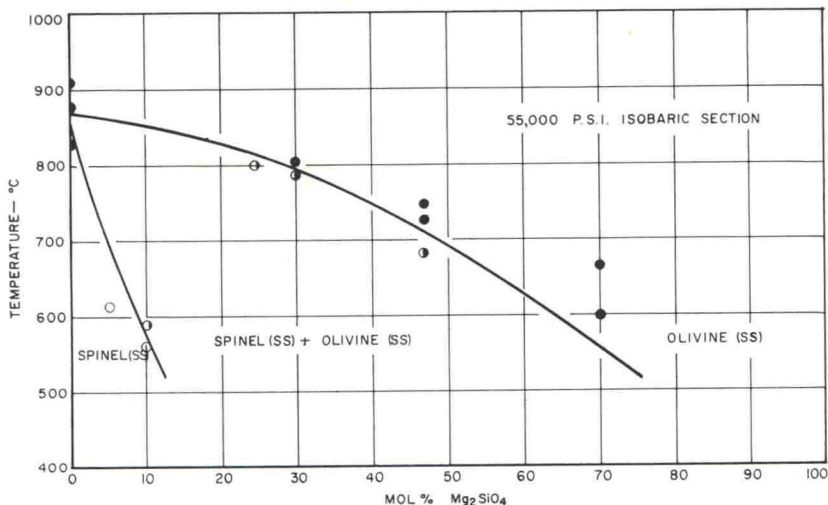


Fig. 5. System  $Mg_2GeO_4$ - $Mg_2SiO_4$ —Isobaric section at 55,000 psi water pressure.

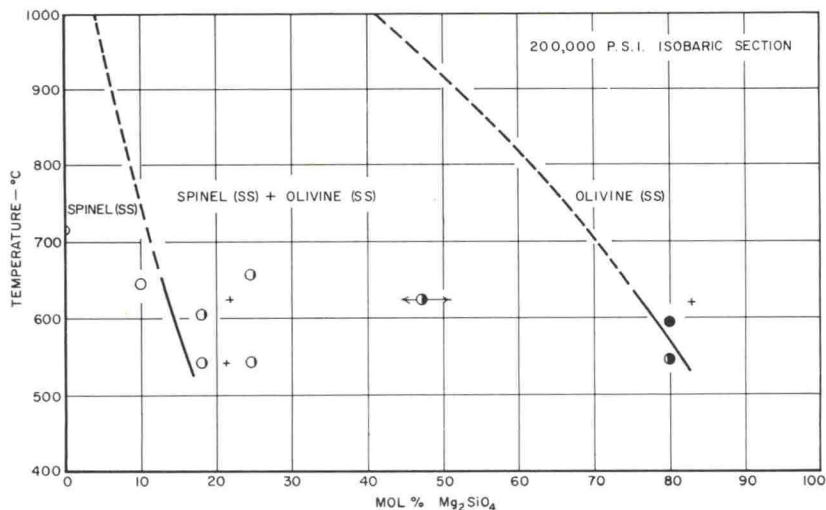


Fig. 6. System  $Mg_2GeO_4$ - $Mg_2SiO_4$ —Isobaric section at 200,000 psi (uniaxial pressure).

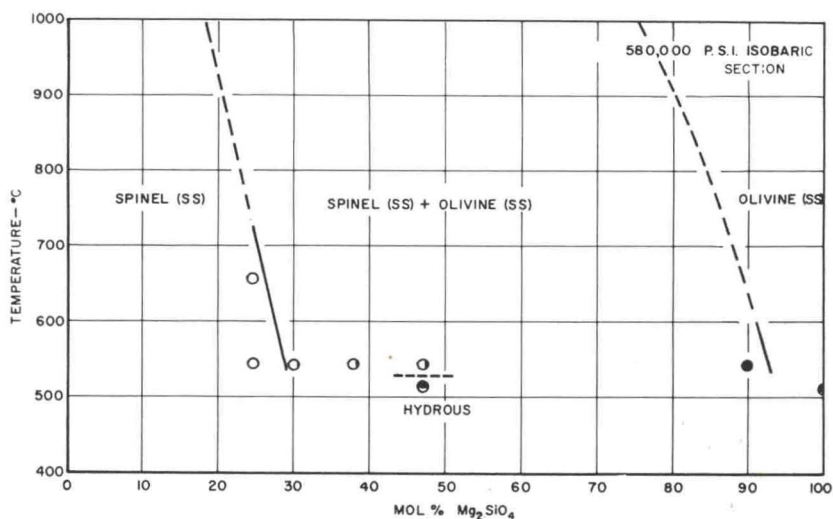


Fig. 7. System  $Mg_2GeO_4$ - $Mg_2SiO_4$ —Isobaric section at 580,000 psi (uniaxial pressure).

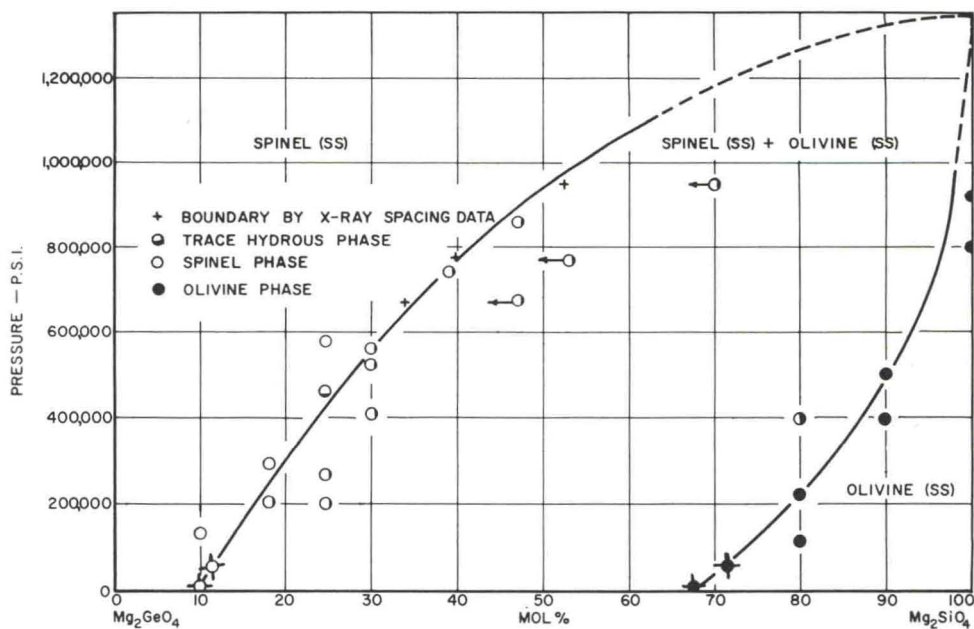


Fig. 8. System  $Mg_2GeO_4$ - $Mg_2SiO_4$ —Isothermal section at 542°C (uniaxial pressure).

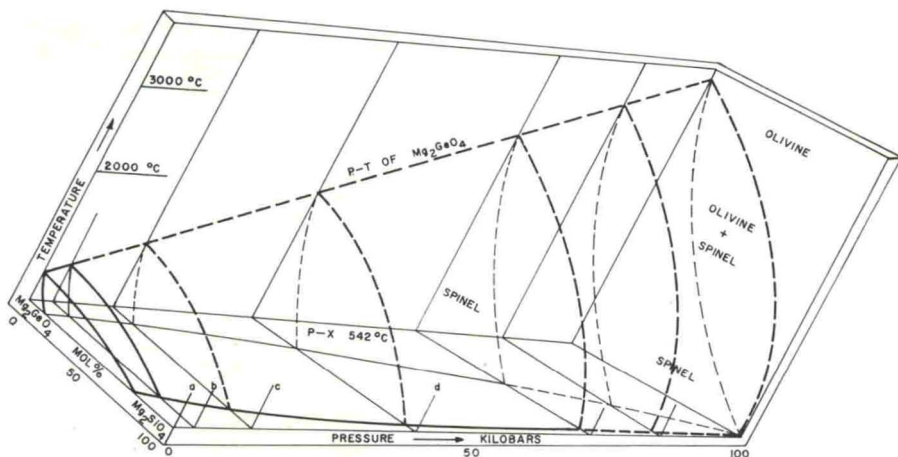


Fig. 9. Perspective of p-t-x of system  $Mg_2GeO_4$ - $Mg_2SiO_4$ . Sections a, b, c, and d are isobars of preceding figures. The isotherm of figure 8 provides base of the construction.

*Substitution of  $Fe^{2+}$  for  $Mg^{2+}$ .*—The term olivine has the very definite connotation in mineralogy of an iron bearing magnesium orthosilicate. In fact, the word is applied as a group name for the solid solution series between forsterite,  $Mg_2SiO_4$  and fayalite,  $Fe_2SiO_4$ . The importance of  $Fe^{2+}$  as an additional component in the system under study was recognized early in the experimental work. A number of runs were made with starting mixtures in which a portion of the  $Mg^{2+}$  was replaced by  $Fe^{2+}$ . Fayalite compositions also were used in seeking a direct inversion of fayalite to a spinel-like form. The problem of maintaining the oxidation state of  $Fe^{2+}$  was tackled by the use of ferrous oxalate in the starting mixture, and the addition of powdered metallic iron. In the uniaxial pressure device the samples in some runs were encased in pure iron rings and disks. Data for this phase of the investigation are in table 3. Reaction products were often rather difficult to identify unambiguously so that working out phase boundaries in detail by phase identification would be a tedious job even in a study directed specifically at this system. However, the data do show plainly that in any isobaric section the spinel solid solution area is appreciably larger than that in the completely magnesian system. Increasing the  $Fe^{2+}$  content broadens further the spinel solid solution field so that one might expect the fayalite inversion pressure to be relatively low. The poor spinel-like x-ray pattern obtained on a fayalite composition at about 500,000 psi may very well be a confirmation of this observation.<sup>1</sup> However, this could well be a solid solution between  $Fe_2SiO_4$  and  $Fe_3O_4$ . Quantitative work in this field was postponed in view of the elaborate arrangements which would be necessary to control the valence of the iron. Indeed it is not even sure whether  $Fe^{2+}$  and  $Ge^{4+}$  could exist in equilibrium (Muan, personal communication) although Bertaut claims to have made  $Fe_2GeO_4$ . Routine chemical analysis of

<sup>1</sup> A. E. Ringwood subsequently appears to have confirmed this finding in his brief note (1958a) on the formation of a spinel form of  $Fe_2SiO_4$  at 400°C and 45 kilobars. A more complete description of his results in this area appeared recently (1958b).

TABLE 3

Data for the system  $Mg_2GeO_4-Mg_2SiO_4$  with Fe substitution for Mg

Composition		Run No.	(°C)	1000 psi Pressure	Duration (hrs.)	Phases
Mg/Fe	Ge/Si		Temperature			
9:1	7:3	7169	715	10	60	Ol. + Sp. + ?
9:1	7:3	7170	737	10	60	Added Fe. Less sp.
"	10:0	7171	699	10	80	Sp. complete
"						Sp.
"	7:3	7172	813	10	40	Added Fe. Ol., sp.
"	"	7173	915	10	20	Olivine
"	"	7174	544	10	60	Olivine, Serp.
"	"	7175	880	10	40	Trace sp.
"	"	7176	880	10	40	Added Fe. Ol.
9:1	1:1	7177	704	10	40	" " sp.
9:1	1:1	7179	745	10	40	Excess Fe. Sp.
9:1	7:3	7181	650	180	190	Oxides + trace sp.
9:1	85:15	7182	720	10	20	Sp. + ol.
9:1	85:15	7185	633	10	90	All spinel
9:1	7:3	7186	628	170	160	Sp. + tr. ol.
						Hematite, serp.
8:2	7:3	7187	655	11	70	Sp. + minor ol.
8:2	7:3	7188	592	11	70	Sp. + trace ol.
8:2	7:3	7189	740	11	70	Sp. + ol.
8:2	7:3	7190	600	180	190	" hematite
8:2	7:3	7225	530	250	70	" "
8:2	7:3	7229	520	350	90	" carbonates
9:1	1:1	7230	540	350	90	No reaction
Natural Olivine		7236	515	250	250	Ol. + serp. + enstatite
2FeO, SiO <sub>2</sub>		7249	542	180	70	Oxides
"		7391	550	720	40	Cubic phase, green

these very small samples was not attempted in view of the problem of the added iron or contamination from the iron washers.

## DISCUSSION

*Effect of water.*—All through the investigation water was used, and considered, strictly as a catalytic agent. In a few runs, however, it did enter into the composition of the products with the formation of small amounts of germanium-bearing serpentines and talcs together with either the olivine or the spinel phases. Since the main interest was in the phase relations of the olivine-spinel polymorphs conditions leading to the production of hydrous phases were avoided whenever possible. Hydrous phases appeared at temperatures below 520-523° in the lower pressure studies, but also appeared at temperatures close to 542° at the higher pressures. The latter appearances are somewhat suspect because of the possibility of the hydrous phases forming while quenching the runs, but they cannot be dismissed without further systematic study. It is interesting to note that the stability of the serpentine appears to be affected so little by pressure changes from Roy and Roy's value of 520°C at 1,000 atmospheres to nearly 60,000 atmospheres in this work. Evaluation of the catalytic effect of water in this system can be only qualitative because experiments were not set up to study rate phenomena. It has been pointed out that the  $Mg_2GeO_4$  spinel-olivine reaction was found to take place only above 1,005°C in a dry

system by Roy and Roy (1954). Extrapolating the hydrothermally determined pressure-temperature dependency of the transition back to atmospheric pressure the present data would place the transition near 810°C.

An empirical observation may be made concerning a measure of the "catalytic effect" of water in this reaction. The presence of water enables it to proceed at a rate so that essentially complete conversion may be achieved at a temperature at least 200°C below the equivalent temperature in the absence of water. In this reaction the lower limit is set by the stable equilibrium temperature. In other cases such as the exsolution of  $\text{Al}_2\text{O}_3$  from spinel solid solutions this catalytic effect in terms of temperature would be 400-500°C. An evaluation of the importance of water-catalysis in terms of time is gained from the following: A reaction of the dry oxides plus water will yield the spinel and forsterite phases in a matter of a few hours in the uniaxial devices. In the total absence of water, two weeks reaction time at 500,000 psi and 450°C failed to react the oxides, although the  $\text{GeO}_2$  did go to the rutile form. Numerous observations of this type were made on many reactions in the uniaxial devices which did not go to completion because of loss of added water due to splitting of the reaction capsule or to cracking of the piston surfaces. Thus it was observed that even at 880°C and 45,000 psi reaction which apparently had started the spinel phase growth of  $\text{Mg}_2\text{GeO}_4$  was interrupted after a few minutes by the cracking of a piston face with the presumable loss of water. The pressure and the high temperature were maintained on the sample at least 10 hours without obtaining complete reaction.

#### THE NATURE OF PRESSURE IN UNIAXIAL DEVICES

Many observations in this and related studies give support to the interpretation that the pressures calculated, or at least their effects, are very close to those of hydrostatic systems. Considerable work was done expressly to evaluate the nature of the pressure (Dacheille, Shafer, Roy, in preparation) but only an outline is given here:

1. Field boundaries in the system  $\text{Mg}_2\text{GeO}_4$ - $\text{Mg}_2\text{SiO}_4$  as determined in a purely hydrostatic run, kindly made for us by Dr. H. S. Yoder, at  $550^\circ \pm 5^\circ\text{C}$  and  $10,000 \pm 50$  bars water pressure agree with those determined in the uniaxial devices.

2. The formation of the  $\text{CS}_2$  "polymer" within 10 percent of the 42,000 bars reported by Bridgman (1941).

3. Uniformity of pressure and reproducibility were studied in the  $\text{SiO}_2$  quartz-coesite reaction by varying the sample area-metal area ratios and by determining the p-t dependence of this reaction in the 350-650° interval. This dependence was found to be essentially the same as that reported by MacDonald who worked with a sample system entirely omitting a containing ring.

*The transitions in  $\text{Mg}_2\text{GeO}_4$  and  $\text{Mg}_2\text{SiO}_4$ .*—The reality and reversibility of the olivine-spinel transition (contrary to the assertion of Bertaut, 1954, 1956) has been amply demonstrated and the equilibrium temperature at atmospheric pressure set at 810°C. In figure 3 the pressure-temperature dependence

of the transition in  $Mg_2GeO_4$  is shown, obtained as a composite of runs from both the hydrothermal and uniaxial pressure systems. The slope of this line is equivalent to the reciprocal of  $24.6^\circ\text{C}$  per kilobar with an uncertainty of  $1.2^\circ\text{C}$  per kilobar. A precise calculation of the  $\Delta H$  of transition by use of the Clapeyron equation requires thermal expansion (and compressibility) data of both polymorphs at the inversion. The data are not available and therefore the  $\Delta H$  has been calculated with the assumption that the volume difference at room temperature applies for the transition at one atmosphere and  $810^\circ\text{C}$ . The error in the value caused by neglecting the  $\Delta\alpha$  term is unlikely to be more than 1 percent of the total  $\Delta V$  term since thermal expansion coefficients of similar materials are about  $100 \times 10^{-7}/^\circ\text{C}$ . By far the largest error is involved in the graphical determination of the slope.

The pressure-temperature dependence in the transition of the silicate end member is of geological interest but remains beyond direct experimental determination at present. An estimate may be made considering some aspects of the system  $Mg_2GeO_4$ - $Mg_2SiO_4$ . In various oversimplified calculations the slope may be assumed to be the same as that of the germanate end member. Therefore in the Clapeyron equation  $dt/dp = T\Delta V/\Delta H$  an identity of  $dt/dp$  for the germanate and silicate end members requires that the  $\Delta V/\Delta H$  ratios are the same for the same absolute temperature. However, the isotherm of figure 8 and the  $p$ - $t$ - $x$  of figure 9 suggest that at the pressures at which the transition in the silicate first appears possible the temperature is more than  $2,000^\circ\text{C}$  below that of the germanate member. If this difference were only  $1,000^\circ\text{C}$  the absolute temperatures of the transitions at 100 kilobars will be nearly  $800^\circ\text{K}$  and  $1800^\circ\text{K}$  for the silicate and germanate members respectively. The value of  $dt/dp$  for the silicate will be correspondingly higher unless the  $\Delta V/\Delta H$  value increases in the proportion of  $1800/800$ . The  $\Delta V$  of the silicate transition is only 56 percent of that found in the germanate. Therefore its  $\Delta H$  value would have to be only about 25 percent that of the former, illustrating the danger of making simple assumptions. This is in agreement with the work of Majumdar and Roy (1958) which shows there are no data to justify assuming equality or any simple relation between  $\Delta H$ ,  $\Delta V$ , or  $dp/dt$  even for analogous transitions between dimorphic substances, removing any justification that values from the Clapeyron equation can be extrapolated from one isotype to another. The observation by Mason (1952) that the unit cell of spinel  $Al_2MgO_4$  was about 9 percent smaller than the corresponding  $Mg_2SiO_4$  olivine unit encouraged the above assumptions, but it appears that in addition to the above objection an interesting detail of crystal structure intervenes. Later in the discussion it will be shown that the germanate spinel is of the inverse type with  $Ge^{4+}$  in octahedral sites whereas in the silicate spinel  $Si^{4+}$  is probably in tetrahedral sites. However, in both olivine structures the  $4^+$  cations are in tetrahedral sites. Therefore, it is reasonable to expect that  $Ge^{4+}$  changing from 4 to 6 coordination will produce a greater volume decrease than found in the silicate member where the coordination is unchanged.<sup>2</sup>

<sup>2</sup> The smaller unit cell of the  $Al_2MgO_4$  may mean that in this spinel the  $Al^{3+}$  is in fact in octahedral sites in agreement with neutron diffraction confirmation that  $Al_2MgO_4$  is a normal spinel.

In view of the serious limitations of extrapolation of the Clapeyron relations an evaluation of  $dt/dp$  of the silicate transition directly by graphical means may be more accurate. Isotherms at 600, 660 and 730°C for the spinel-spinel + olivine boundary from the data and construction of the four isobaric sections are plotted on figure 10 on a logarithmic scale. The isotherm at 542°

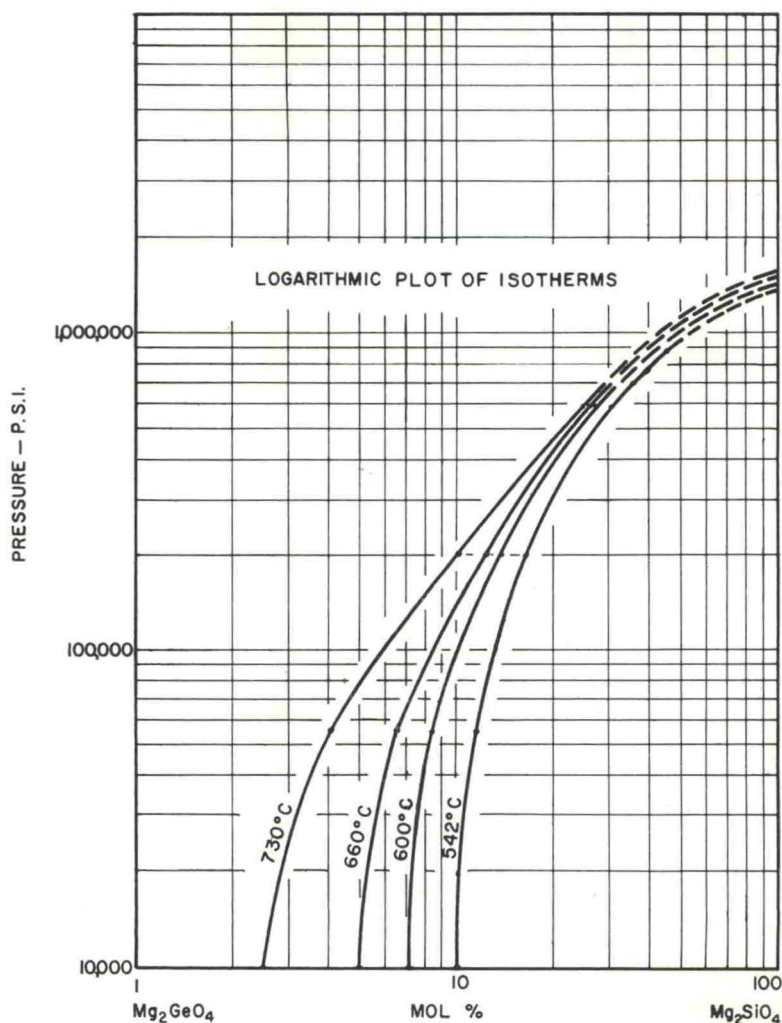


Fig. 10. System  $Mg_2GeO_4$ - $Mg_2SiO_4$ . Logarithmic plot of isotherms constructed from data of the  $t$ - $x$  and  $p$ - $x$  sections.

for the same boundary also is plotted to include the results at higher experimental pressures. From the results of graphical extrapolations to 100 percent the values of  $dt/dp$  obtained are seen to decrease from 24.6°C per kilobar for the germane member to about 13°C per kilobar for the silicate member.



The experimental work on the substitution of some  $Fe^{2+}$  in the system does no more than indicate that the spinel phase is stable to higher temperatures (or lower pressures) than in the iron free systems. The effect of fayalite solid solution on  $dt/dp$  cannot be determined from our data, but for substitutions up to 20 mol percent an assumption is made that it is the same as that of the magnesian member. From these data and the few runs on the  $Fe_2SiO_4$  composition one can only confirm that which is easily guessed that the presence of  $Fe^{2+}$  in the olivine will lower the pressure necessary for its transition to a spinel.

*Certain geophysical implications of the data.*—A consideration of the geophysical aspects of the results is summarized in figure 11. On this figure are

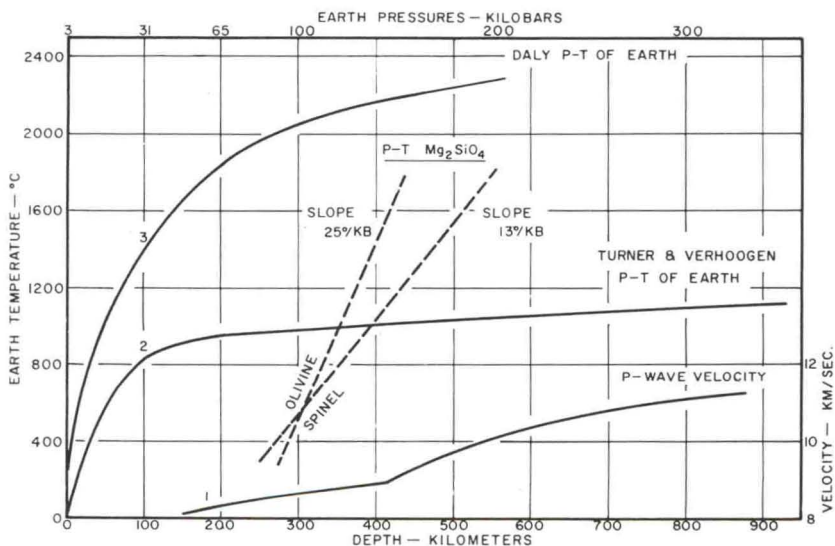


Fig. 11. Pressure, temperature and p-wave velocity relations for a portion of the mantle on which are superimposed possible p-t relations of  $Mg_2SiO_4$ .

shown for a portion of the earth 1) the variation of the P-wave velocity 2) the pressure-temperature relation of Turner and Verhoogen (1951) 3) the pressure-temperature relation of Daly (1943). The two p-t lines representing the limits of the uncertainty of the p-t dependence of the  $Mg_2SiO_4$  transition, have slopes of nearly 25 and 13°C per kilobar and are plotted passing through 542° and 100 kilobars (300 kilometers depth).

An inspection of figure 11 shows that a transition of olivine to spinel could be the determining factor in the second order discontinuity just below 400 km depth. If the seismic discontinuity is accurately placed at 413 km depth and if the composition of the mantle is essentially forsterite with up to 10-20 mol percent fayalite, the main considerations then are the  $dt/dp$  of the transition and the p-t curve of the earth.

It is clear that using either of the widely divergent earth p-t curves, one can reconcile the seismic discontinuity "reasonably" with the transition. The

general agreement is certainly in the right order of magnitude since the experiments conclusively rule out 10 or 1,000 kilobars as the transition pressure at say 1,000°C. The problem to determine directly the p-t relation of the transition for forsterite in order to narrow the uncertainty of the extrapolation made here remains urgent. These refinements will then permit a closer examination of the temperature variation in the earth.

#### CRYSTAL CHEMICAL OBSERVATIONS

In work from this laboratory (Dacheille and Roy, 1959) it has been shown that in the absence of the complete assignment of absorption frequencies in

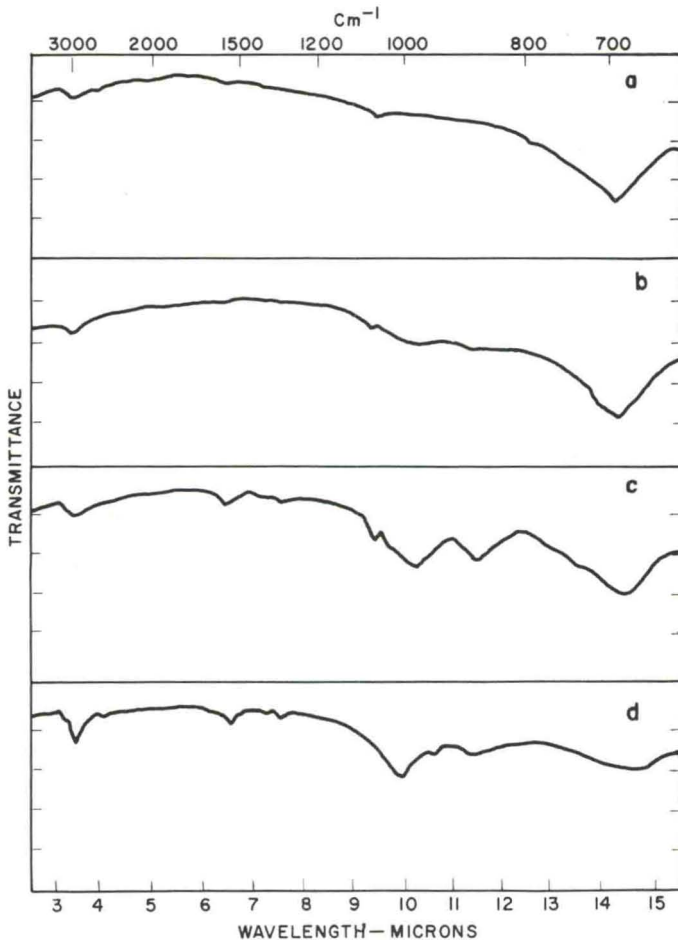


Fig. 12. Infrared absorption spectra.

- a.  $Mg_2GeO_4$  spinel form
- b.  $Mg_2(Ge,Si)O_4$  spinel form (25 mol% silicate)
- c.  $Mg_2(Ge,Si)O_4$  spinel form (38 mol% silicate)
- d.  $Mg_2(Ge,Si)O_4$  spinel form (47 mol% silicate)

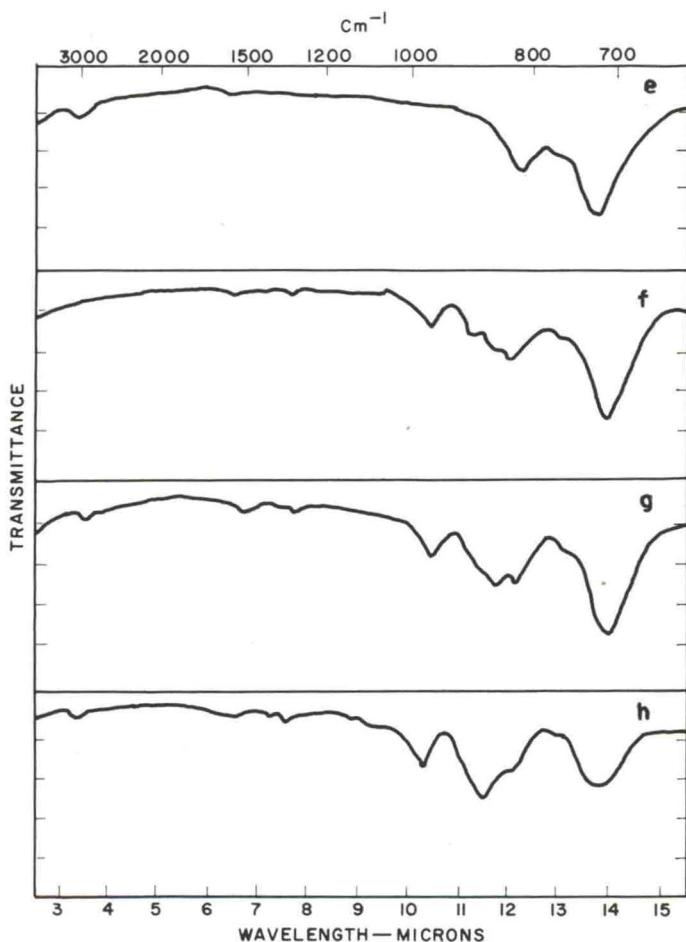


Fig. 13. Infrared absorption spectra

- e.  $Mg_2GeO_4$  olivine form  
 f.  $Mg_2(Ge,Si)O_4$  olivine form (10 mol% silicate)  
 g.  $Mg_2(Ge,Si)O_4$  olivine form (25 mol% silicate)  
 h.  $Mg_2(Ge,Si)O_4$  olivine form (47 mol% silicate)

complex solids one can use the main absorption frequencies in the infra-red region to indicate primary coordination changes of the cations. Naturally the present substances presented excellent examples for checking such ideas. Figures 12, 13, and 14 present the infra-red absorption patterns for some of the spinel and olivine structure solid solutions. The following deductions are pertinent:

1. In  $Mg_2GeO_4$  spinel all the  $Ge^{4+}$  is in 6 c.n. (cf. Ge-O absorption in  $GeO_2$  <sub>qtz</sub> at 11.5 and in  $GeO_2$  <sub>rutile</sub> at 14.0).
2. In both the olivine forms the Si and Ge ions appear to be of two types with

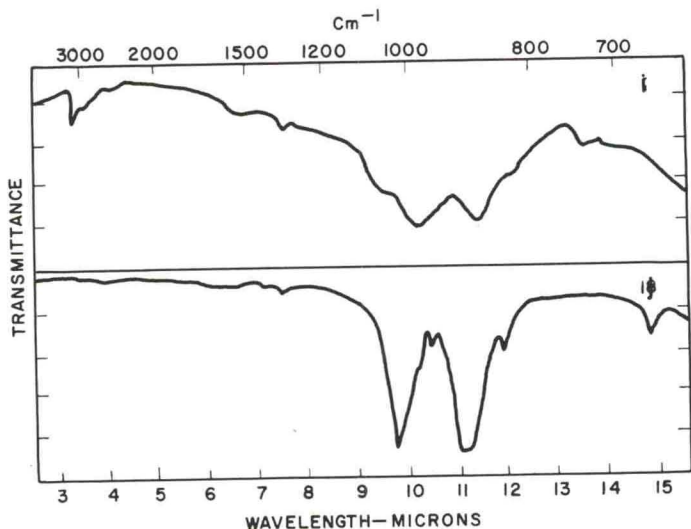


Fig. 14. Infrared absorption spectra  
 i.  $Mg_2(Ge,Si)O_4$  olivine form (90 mol% silicate)  
 j.  $Mg_2SiO_4$  olivine form

appreciably different Si-O (Ge-O) distances. Indeed the patterns themselves suggest the highly unlikely possibility of an inverse olivine structure.

3. Although this is not clearcut, the spinel solution towards the silicate member appears to be changing from an inverse to a normal spinel.

Unequivocal confirmation of the first deduction that  $Mg_2GeO_4$  is an inverse spinel has been obtained from the x-ray intensities. In 1956 Durif-Varambon, Bertaut and Pauthenet came to precisely the opposite conclusion on the basis of intensities measured from a very poorly crystallized sample. They calculated that a distinctive criterion to judge between the various spinel arrangements is the ratios of the intensities of the 422 and 400 reflections. The following values were calculated:

$$\frac{I_{422}}{I_{400}} = \text{For Normal, 1.67; For Inverse, 6.6; For Random, 3.3}$$

Their conclusion was based on their measurement of the intensity ratio as 1.7. On examination of the ratio in random x-ray diffractometer mounts it was immediately noticed that the ratio was consistently very much higher than 1.7; indeed it never fell below 3.8 for the germanate end member, and values as high as 6.5 were found. Obviously it had not been possible to avoid all orientation in the slide preparations although the crystal size was extremely small. Since the more likely cubic habit or cleavage would tend to increase the 400

intensity in relation to 422 the true ratio  $\frac{I_{422}}{I_{400}}$  is seen to approach if not equal the 6.6 figure for the inverse spinel.

With increasing  $Si^{4+}$  content there is a shift to lower values of the intensity ratios which suggests that as the  $Si^{4+}$  takes more tetrahedral positions the structure approaches the normal spinel.

Molar refractivity (Rm in cc/mole), table 4, affords another line of evidence on cation coordination. (Safford and Silverman, 1947; Roy, 1950; Dacheille and Roy, in press b). The "measured" Rm of the olivine forms of  $Mg_2SiO_4$  and  $Mg_2GeO_4$  are 15.87 and 18.33 respectively, and each value is 0.4 less than the value calculated from the "ideal" values for component oxides. Similar small differences have been noted for binary and ternary compounds. In the olivines the Mg ions are in VI, and the Si,Ge ions are in IV coordination. The measured Rm for  $Mg_2GeO_4$  spinel ( $n = 1.768$ ) is 17.62, a value which is 1.09 less than that calculated for the normal spinel and 0.59 less than for the inverse. This latter value is comparable with the usual differences between observed and calculated values and suggests an inverse spinel  $Mg_2GeO_4$ . It can then be shown that the relative refractivity contribution of  $GeO_2$  in the inverse spinel is about 14 percent less than that in a normal spinel, which difference is close to that found between the rutile and quartz forms of  $GeO_2$ .

TABLE 4  
Molar Refractivities, Rm

Substance		Measured	Calculated	Difference
$Mg_2SiO_4$	olivine	15.87	16.27	.40
$Mg_2GeO_4$	olivine	18.33	18.71	.38
$Mg_2GeO_4$	inverse spinel	17.62	18.21	.59
$Mg_2GeO_4$	normal spinel	17.62	18.71	1.09

Values used for oxides (see Refs. cited for cation coordination)

	Coordination	VI	IV
MgO		4.54	5.18
$SiO_2$		—	7.19
$GeO_2$		8.49	9.63

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REFERENCES

Bertaut, E. F., Durif-Varambon, A. and Pauthenet, R., 1954, Proprietes cristallographiques et magnetique de quelques nouvelles series de spinelles mixtes: 3rd Internat. Congr. of Crystallography, Paris.  
 ———, 1956, Etude des germanates spinelles: Ann. de Chimie, v. 13, tome 1, p. 525-553.  
 Bullen, K. E., 1936, The variation of density and the ellipticities of the strata of equal density within the earth: Royal Astron. Soc., London, Monthly Notices, Geophys. Supp., v. 3, p. 395, 1932-1936.  
 Dacheille, F. and Roy, R., 1956, System  $Mg_2SiO_4$ - $Mg_2GeO_4$  at 10,000, 60,000 and about 300,000 psi.: Geol. Soc. America Bull., v. 67, p. 1682-1683.  
 ———, 1957, Silica structure studies. The high pressure region of model and half-breed derivatives: Geol. Soc. America Bull., v. 68, p. 1713.  
 ———, 1958, Experimental study of the olivine-spinel inversion in  $Mg_2SiO_4$ : Geol. Soc. America Bull., v. 69, p. 1550.  
 ———, 1959, A new high pressure form of  $B_2O_3$  and inferences on cation coordination from infra red spectroscopy: Am. Ceram. Soc. Jour., v. 41, p. 78-80.

- , in press a, The high pressure region of the silica isotypes: *Zeitschr. Kristallographie*.
- , in press b, Use of infra-red absorption and water refractivities to check coordination: *Zeitschr. Kristallographie*.
- Dachille, F., Shafer, E. C., and Roy, R., in preparation, High pressure studies in the system  $\text{GeO}_2\text{-SiO}_2$ .
- Daly, R. A., 1943, Meteorites and an earth model: *Geol. Soc. of America Bull.*, v. 54, p. 401-455.
- Goldschmidt, V. M., 1931, Zur kristallchemie des germaniums: *Nachr. gesell. wiss. Göttingen, math. phys. Kl. fachgr. IV*, v. 1, no. 184, p. 190.
- Griggs, D. T. and Kennedy, G. C., 1956, A simple apparatus for high pressures and temperatures: *AM. JOUR. SCI.*, v. 254, p. 722-735.
- Jander, W. and Stamm, W., 1932, The internal structure of solid inorganic compounds at higher temperatures. V. electrical conductivity, diffusion, and reactivity of magnesium orthosilicate and magnesium on the germanate in the solid state: *Zeitschr. anorg. Allg. Chem.*, v. 207, p. 289-307.
- Jeffreys, H., 1936, The structure of the earth down to the 20° discontinuity: *Royal Astron. Soc., London, Monthly Notices, Geophys. Supp.*, v. 3, p. 401, 1932-1936.
- MacDonald, G. J. F., 1956, Quartz-coesite stability relations at high temperatures and pressures: *AM. JOUR. SCI.*, v. 254, p. 713-721.
- Majumdar, A. J. and Roy, R., 1957, Experimental phase rule studies involving transitions of various kinds: *Geol. Soc. America Bull.*, v. 68, p. 1762-1763.
- Mason, B., 1952, Principles of geochemistry: New York, John Wiley and Sons, Inc., p. 33. (In personal communication with Professor Roy, Dr. Mason explained that his estimate of volume change of about 9% was based on an assumption that the  $\text{Mg}_2\text{SiO}_4$  spinel would have the cell dimensions of  $\text{Al}_2\text{MgO}_4$ .)
- Observatory, 1936, On J. D. Bernal: London, no. 748, p. 267-268.
- Ringwood, A. E., 1956, The system  $\text{Mg}_2\text{SiO}_4\text{-Mg}_2\text{GeO}_4$ : *AM. JOUR. SCI.*, v. 254, no. 11, p. 707-711.
- , 1958a, The system  $\text{Mg}_2\text{SiO}_4\text{-Mg}_2\text{GeO}_4$ : *Geol. Soc. America Bull.*, v. 69, p. 129.
- , 1958b, The system  $\text{Mg}_2\text{SiO}_4\text{-Mg}_2\text{GeO}_4$ : *Geochim. et Cosmochim. Acta*, v. 15, p. 18-29.
- Romeijn, F. C., 1953, Physical and crystallographic properties of some spinels. pt. 3: *Phillips Research Reports*, v. 8, p. 321-341.
- Roy, Rustum, 1950, Magnesium in fourfold coordination in glass: *Am. Chem. Soc. Jour.*, v. 72, p. 3307.
- , 1956, Aids in Hydrothermal experimentation. II. Methods of making mixtures for both "dry" and "wet" phase equilibrium studies: *Am. Ceram. Soc. Jour.*, v. 39, no. 4, p. 145-146.
- Roy, D. M. and Roy, R., 1954, An experimental study of the formation and properties of synthetic serpentines and related layer silicates minerals: *Am. Mineralogist*, v. 39, p. 957-975.
- Roy, R. and Osborn, E. F., 1952, Some simple aids in the hydrothermal investigation of mineral systems: *Econ. Geol.*, v. 47, p. 717.
- Roy, R. and Tuttle, O. F., 1956, Investigations under hydrothermal conditions in Physics and chemistry of the earth: London, Pergamon Press, v. 1, p. 138-180.
- Safford, H. W., and Silverman, A., 1947, Alumina-silica relationship in glass: *Am. Ceram. Soc. Jour.*, v. 30, p. 203-211.
- Turner, F. J. and Verhoogen, J., 1951, Igneous and metamorphic petrology: New York, McGraw-Hill Book Co., Inc., p. 357-358.
- Urey, H. C., 1952, The planets: New Haven, Yale University Press, p. 69.