

H. J. Hall

## The constitution of the mantle—II

### Further data on the olivine–spinel transition\*

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**Abstract**—Subsolidus phase equilibria were studied in the system  $Mg_2SiO_4$ – $Mg_2GeO_4$  at 660°C and 30,000 bars in a squeezer apparatus. From the compositions of co-existing phases, the free energy of transition of forsterite from the olivine to the spinel structure is calculated. This enables the total pressure needed to cause this transition in forsterite to be determined. It is found to be about 90,000 bars at 660°C. This result, combined with analogous data obtained in Part I makes it possible to construct a  $P$ – $T$  curve defining the olivine–spinel transition in forsterite.

A similar study was made in the system  $Fe_2GeO_4$ – $Fe_2SiO_4$  at 700°C and 25,000 bars and it was predicted that a spinel polymorph of fayalite should become stable around 50,000 bars at 700°C. The predicted polymorph was subsequently synthesized and its transition pressure determined as 38,000 bars at 600°C. The spinel has a lattice constant of 8.235 Å and is 12 per cent denser than fayalite.

A thermodynamic study of the stability of  $MgSiO_3$  pyroxene in the mantle is made. It is concluded that it will break down into  $Mg_2SiO_4$  spinel and coesite at a maximum pressure not much greater than that required to produce the olivine–spinel transition in forsterite.

The pressures and temperatures required to cause the olivine–spinel transition indicate that the transition will occur in the upper 1000 km of the mantle. Because of solid solution effects, the transition will occur over an appreciable depth range.

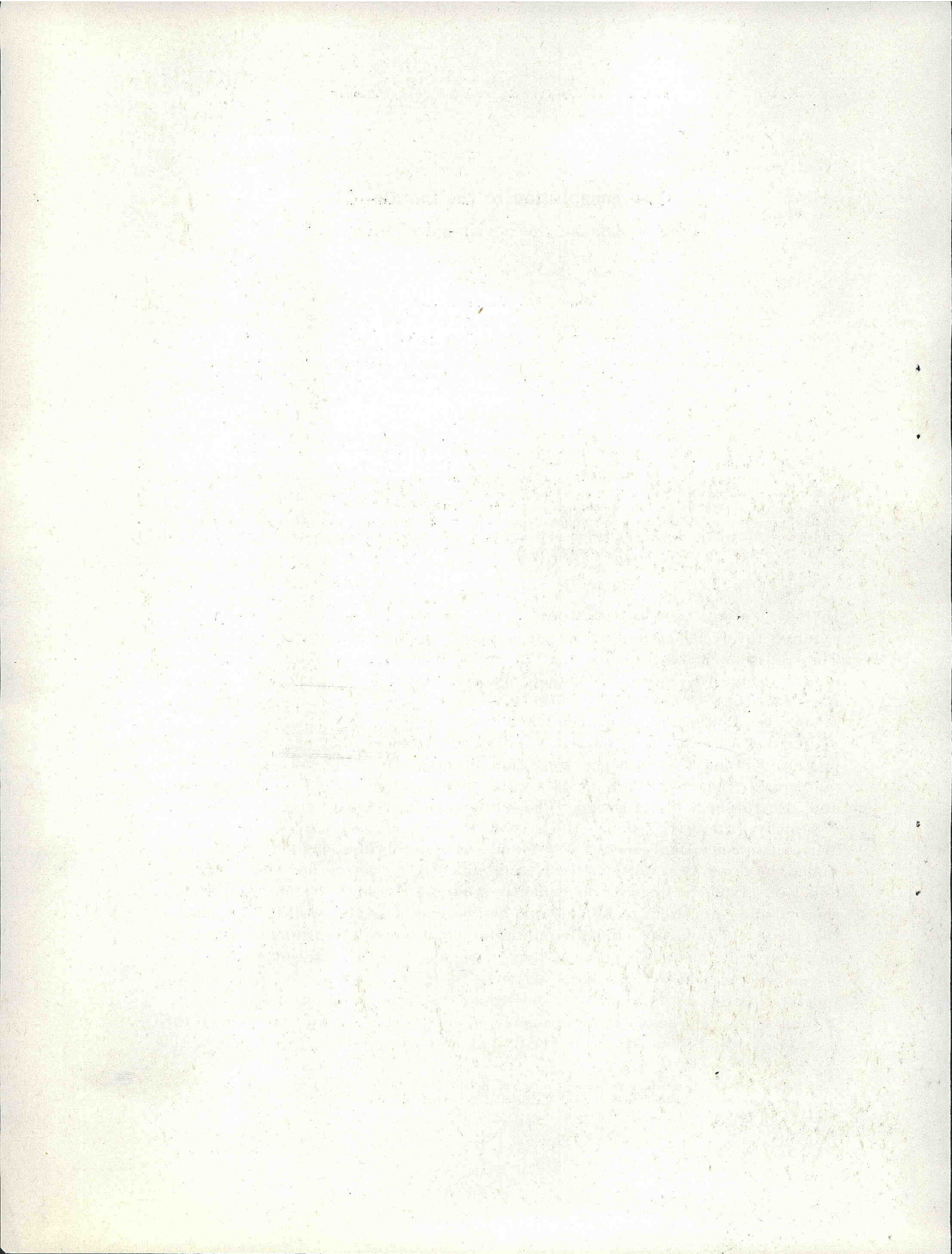
#### 1. INTRODUCTION

In Part I of this series (RINGWOOD, 1957) a method of estimating the pressure required to invert forsterite from an olivine to a spinel structure was described. The transition pressure found was  $175,000 \pm 55,000$  bars at 1500°C. This result indicated that the transition should occur in the upper mantle and might be related to the 20° discontinuity (JEFFREYS, 1952) and the inhomogeneous region inferred by BIRCH (1952) between 300 and 900 km.

Further study of these questions indicated the desirability of determining the pressure needed to cause the transition in forsterite at a substantially lower temperature than 1500°C. Such data would give the slope ( $dP/dT$ ) of the transition and also the heat of transition. The author had previously tried to obtain this datum by an investigation of the system  $Mg_2SiO_4$ – $Mg_2GeO_4$  (RINGWOOD, 1956). This was unsuccessful since it was found that equilibrium could not be reached under the dry-way conditions used. Subsequently it was learned that DACHILLE and ROY (1956) had been independently studying the same system using hydrothermal and “squeezer” techniques and had been successful in working out some of the phase relationships under equilibrium conditions. Accordingly, when the necessary equipment became available, it was decided to make some runs across the subsolidus field of the system  $Mg_2SiO_4$ – $Mg_2GeO_4$  at a fixed temperature and pressure in order to determine the desired solid solution relationships.

$Mg_2GeO_4$  has a spinel structure below about 800°C. Above that temperature it inverts to an olivine structure (DACHILLE and ROY, 1956). The object of this

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study was to determine the amount of  $\text{Mg}_2\text{SiO}_4$  which would enter into solid solution in the spinel form of  $\text{Mg}_2\text{GeO}_4$  under appropriate  $P$ - $T$  conditions, and also to determine the composition of the olivine solid solution in equilibrium with the spinel. Using these data it is possible to calculate the free energy of transition of  $\text{Mg}_2\text{SiO}_4$  from the olivine to the spinel structure, and the pressure needed to cause this transition (Part I).

## 2. THE SYSTEM $\text{Mg}_2\text{GeO}_4$ - $\text{Mg}_2\text{SiO}_4$

The object of studying this system was not to furnish complete phase equilibria. This project has been undertaken by DACHILLE and ROY (1956) with valuable results. The data required by the author were obtained by studying various compositions in the system at  $660^\circ\text{C}$  in a squeezer-type apparatus (GRIGGS and KENNEDY, 1956) under a pressure of 30,000 bars.

### EXPERIMENTAL

A series of intimate mixtures of  $\text{GeO}_2$  and  $\text{SiO}_2$  was made up using a method suggested by ROY (personal communication);  $\text{SiCl}_4$  and  $\text{GeCl}_4$  were thoroughly mixed in the required amounts and hydrolysed with ammonium hydroxide. A hydrated, intimately mixed precipitate of  $\text{SiO}_2$  and  $\text{GeO}_2$  separates. This is quickly filtered, washed and ignited. Samples were made up across the composition range  $(\text{SiO}_2)_{100}$ - $(\text{GeO}_2)_{100}$  at intervals of 10 mole per cent. These were thoroughly mixed by grinding under acetone with calcined magnesium oxide in the appropriate ratios to form compounds of  $\text{Mg}_2(\text{Ge}_x\text{Si}_{1-x})\text{O}_4$  composition.

Charges thus prepared were placed between the pistons of a squeezer apparatus and a small drop of water added to facilitate reaction. A pressure of 30,000 bars was then applied and kept constant whilst the temperature was raised to  $660^\circ\text{C}$  for 1 hr. Temperature and pressure were then swiftly lowered and the charge was removed. The olivine-spinel inversion in this system is known to be extremely sluggish (RINGWOOD, 1956) and this procedure furnishes a satisfactory quench. Descriptions of the squeezer apparatus and its operation have not been supplied since these have already been published in detail by other workers (GRIGGS and KENNEDY, 1956; MACDONALD, 1956), and standard procedure was followed. Charges thus treated were examined by X-ray and optical methods.

Results of this investigation are set out in Table 1.

For the purposes of calculation it is necessary to know the compositions of co-existing olivine and spinel solid solutions in equilibrium under the stated conditions. From Table 1 the composition of olivine  $\text{Mg}_2\text{SiO}_4$  saturated with  $\text{Mg}_2\text{GeO}_4$  is seen to be  $\text{MS}_{85}\text{MG}_{15}$  with an uncertainty of 5 mole per cent (higher accuracy is not required since the calculation is not sensitive to this value). The composition of the saturated spinel solid solution cannot be found from Table 1 since only a small amount of  $\text{Mg}_2\text{SiO}_4$  has been dissolved. However, it may be obtained in an indirect manner.

The increase in density when  $\text{Mg}_2\text{SiO}_4$  inverts from the olivine to the spinel structure is approximately 11 per cent (Part I). The volume of the unit cell of forsterite (containing four molecules) is  $291 \text{ \AA}^3$  (SWANSON and TATGE, 1953) or  $582 \text{ \AA}^3$  for eight molecules. The volume of the unit cell of  $\text{Mg}_2\text{SiO}_4$  spinel (eight

molecules) would therefore be  $524 \text{ \AA}^3$ , giving it a lattice constant of  $8.06 \text{ \AA}$ . The average lattice constant of the saturated spinel solid solutions is  $8.240 \text{ \AA}$ . According to Vegard's law, the spinel having this value must lie on a straight line joining the

Table 1. Phases present in system  $\text{Mg}_2\text{SiO}_4$ - $\text{Mg}_2\text{GeO}_4$  at  $660^\circ\text{C}$  and 30,000 bars

Composition (mole %) MS = $\text{Mg}_2\text{SiO}_4$ MG = $\text{Mg}_2\text{GeO}_4$	Optical examination	X-ray	Lattice constant of spinel phase ( $\text{\AA}$ )
MG <sub>100</sub>	Homogeneous spinel	Spinel	8.248
MG <sub>90</sub> MS <sub>10</sub>	2-phase	Spinel + olivine	8.242
MG <sub>80</sub> MS <sub>20</sub>	2-phase	Spinel + olivine	8.241
MG <sub>70</sub> MS <sub>30</sub>	2-phase	Spinel + olivine	8.239
MG <sub>60</sub> MS <sub>40</sub>	2-phase	Spinel + olivine	8.238
MG <sub>50</sub> MS <sub>50</sub>	2-phase	Spinel + olivine	8.240
MG <sub>40</sub> MS <sub>60</sub>	2-phase	Spinel + olivine	
MG <sub>30</sub> MS <sub>70</sub>	2-phase	Spinel + olivine	
MG <sub>20</sub> MS <sub>80</sub>	2-phase	Spinel + olivine	
MG <sub>10</sub> MS <sub>90</sub>	Olivine	Olivine	
MS <sub>100</sub>	Olivine	Olivine	

lattice constant of  $\text{Mg}_2\text{GeO}_4$  ( $8.248 \text{ \AA}$ ) to that of  $\text{Mg}_2\text{SiO}_4$  spinel (determined above). This allows determination of the composition of the spinel solid solution. It is found to be  $\text{MG}_{96} \text{MS}_{4}$ .

## DISCUSSION

In Part I of this series the free energy of transition of forsterite from the olivine to the spinel structure was derived from the compositions of coexisting olivine and spinel solid solutions in which  $\text{Mg}_2\text{SiO}_4$  was a component. It was found that

$$\Delta F = RT \ln \frac{a_2}{a_1}$$

where  $\Delta F$  is the molar free energy difference between the olivine and spinel forms of  $\text{Mg}_2\text{SiO}_4$ ,  $T$  is the absolute temperature,  $R$  is the gas constant,  $a_1$  is the activity of  $\text{Mg}_2\text{SiO}_4$  in the spinel solid solution and  $a_2$  is the activity of  $\text{Mg}_2\text{SiO}_4$  in the olivine solid solution with which it is in equilibrium at a temperature  $T$ . For further details of this derivation, the reader is referred to the previous paper.

In Part I, the system studied was  $\text{Ni}_2\text{GeO}_4$ - $\text{Mg}_2\text{SiO}_4$  but similar principles hold in this case. The solid solutions are assumed to be ideal and consequently the activity of an ion becomes equal to its ionic fraction defined as the ratio of the number of specified ions ( $n$ ) to the total number of lattice sites available to it. Since the ions which display mutual replacement in this case are  $\text{Si}^{4+}$  and  $\text{Ge}^{4+}$ , the activity of the component  $\text{Mg}_2\text{SiO}_4$  is given by  $(n_{\text{Si}})/(n_{\text{Si}} + n_{\text{Ge}})$ , or  $[\text{Si}]$ , which is equal to the mole fraction of the component  $\text{Mg}_2\text{SiO}_4$ . In the general case, as exemplified in Part I, where there is more than one independently replacing pair

of ions (Ni-Mg and Ge-Si) this simple expression does not hold, and the activity of  $\text{Mg}_2\text{SiO}_4$  is given by the TEMPKIN (1945) expression  $[\text{Mg}]^2 [\text{Si}]$ .

In the case under consideration,  $a_1$  is equal to  $(0.04 \pm 0.01)$  and  $a_2$  to  $(0.85 \pm 0.05)$ . From these values  $\Delta F$  is calculated according to the above expression:

$$\Delta F_p = 23,600 \text{ J/mole}$$

It should be remembered that  $\Delta F_p$  is the difference in free energy under the experimental conditions employed,  $p = 30,000$  bars and  $T = 660^\circ\text{C}$ .

The total pressure  $P$  required to produce equilibrium between the polymorphs at the given temperature is:

$$P\Delta v_1 = \Delta F_p + p\Delta v_2$$

where  $\Delta v_1$  is the difference in molar volume of the two phases at a pressure  $P$  and  $\Delta v_2$  is the difference in molar volume at a pressure ( $p$ ) of 30,000 bars. Because of the relative incompressibility of olivine and spinel,  $\Delta v_1$  may be put equal to  $\Delta v_2$  with negligible sacrifice of accuracy. Therefore

$$(P - p)\Delta v = 23,600$$

where  $p = 30,000$  bars.  $\Delta v$  for the transition in forsterite was determined in Part I as  $4.4 \pm 1.0 \text{ cm}^3/\text{mole}$ . When an allowance for the effect of compression at the approximate transition pressure is made,  $\Delta v$  becomes equal to  $4.1 \pm 1.0 \text{ cm}^3/\text{mole}$ .

Consequently for equilibrium at  $660^\circ\text{C}$  between the olivine and spinel modifications of forsterite:

$$4.1(P - p) \text{ (bars)} = 23,600 \text{ (J)}$$

thus

$$P = 88,000 \text{ bars}$$

When allowance for uncertainty of data is taken into account, a maximum pressure of 116,000 bars and a minimum of 72,000 bars are found. The range of possible error is asymmetrically distributed around the most probable value of 88,000 bars because of the form of the equation for equilibrium.

In Part I, the transition pressure was calculated to be 175,000 bars at  $1500^\circ\text{C}$ . These two determinations allow an approximate  $P$ - $T$  curve to be constructed for the transition (Fig. 1). The transition curve is found to have a slope of about  $100 \text{ bars}/^\circ\text{C}$ . The range of uncertainty is considerable, and is controlled principally by uncertainty in the value of  $\Delta v$ . Since this affects both calculations in the same direction, a change in  $\Delta v$  tends to cause a parallel displacement of the transition curve without a large change of slope. However, other sources of error are capable of affecting the slope and this must be regarded as tentative. Data on other polymorphic transitions suggest it is more likely to be decreased than increased.

Once again it should be emphasized that all calculations are based upon the assumption of ideal behaviour of the solid solutions. For further discussion of this point, the reader is referred to Part I, where it is concluded that ideality is probably realized.

From the slope of the transition curve and the volume change, it is possible to calculate the entropy change for the transition ( $\Delta S$ ) using the Clapeyron–Clausius equation. The entropy change,  $\Delta S$ , is found to be approximately 10 cal/°C per mole.

It is believed that the above data on the olivine–spinel transition in forsterite are of considerable significance in understanding the constitution of the mantle. Detailed discussion of this aspect will be taken up in Part III.

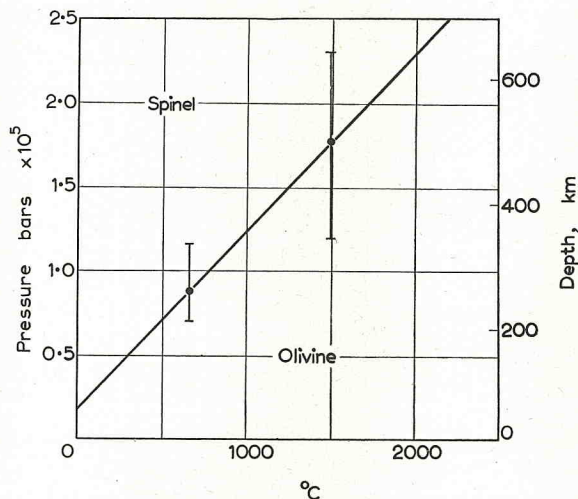


Fig. 1. Calculated equilibrium curve for the olivine–spinel transition in  $\text{Mg}_2\text{SiO}_4$ . Vertical lines indicate ranges of possible error due to experimental uncertainty.

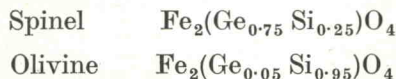
### 3. THE OLIVINE–SPINEL TRANSITION IN FAYALITE

Common olivine contains about 10 per cent of fayalite in solid solution. Consequently it is desirable to obtain data on the olivine–spinel transition in fayalite as well as forsterite. The first method used was analogous to that employed in the case of forsterite. Subsidiary phase equilibria in the system  $\text{Fe}_2\text{GeO}_4$ – $\text{Fe}_2\text{SiO}_4$  were used to obtain the free energy of transition, which was then equated to a  $P\Delta V$  term.

Charges were prepared by weighing out  $\text{Fe}_2\text{O}_3$ , metallic iron powder, and the required mixed  $\text{GeO}_2$ – $\text{SiO}_2$  oxide in the proportions required to make an  $\text{Fe}_2(\text{Ge}_x\text{Si}_{1-x})\text{O}_4$  solid solution of the desired composition. A slight excess of metallic iron was included. The components were then intimately mixed under acetone. The charges thus prepared covered the composition range at intervals of 10 mol per cent. They were placed in the squeezer and subjected to a temperature of 700°C and a pressure of 25,000 bars for 3 hr. After completion of the run, charges were removed, ground, and examined by X-ray methods.

Phases present were spinel, olivine, and usually residual metallic iron. The  $\text{Fe}_2\text{GeO}_4$  spinel end member had a lattice constant of 8.401 Å. In bulk the crystals were opaque but when observed singly under magnification were found to be transparent with a greenish brown colour. Compositions of coexisting spinel and

olivine solid solutions in equilibrium under the conditions specified were found by determining limits of phase homogeneity from powder photographs.



The uncertainty was estimated as  $\pm 5$  per cent  $\text{Fe}_2\text{SiO}_4$ .

Using this data, and assuming the difference in density between the olivine and spinel polymorphs as 11 per cent, the pressure required to invert fayalite from the olivine to the spinel structure at 700°C may be calculated. The procedure is completely analogous to that used in the previous section for  $\text{Mg}_2\text{SiO}_4$ - $\text{Mg}_2\text{GeO}_4$  solid solutions. The inversion pressure thus found is approximately 50,000 bars.

Subsequently the author has realized that the experimental data above are capable of more than one interpretation due to the possibility of various oxidation-reduction equilibria involving  $\text{Fe}^2$ ,  $\text{Fe}^3$  and  $\text{Ge}^2$ ,  $\text{Ge}^4$ . It was assumed that the spinel produced was  $\text{Fe}_2^2\text{Ge}^4\text{O}_4$ . It is conceivable however, that some  $\text{Ge}^2$  was formed by the reaction  $2\text{Fe}^2 + \text{Ge}^4 = 2\text{Fe}^3 + \text{Ge}^2$  and that the spinel actually observed was  $(\text{GeFe})^2\text{Fe}_2^3\text{O}_4$ . There is some reasonably strong evidence that the original assumption was justified, but the situation is by no means clear, and further data are required.

Accordingly it must be emphasized that the previous calculations are based upon the assumption that the system is binary and that the spinel was  $\text{Fe}_2^2\text{Ge}^4\text{O}_4$ . If this assumption is incorrect, the calculation becomes meaningless.

The previous estimate, that a pressure around 50,000 bars at 700°C should suffice to invert fayalite from the olivine to the spinel structure, suggested that the transition might be within the range of capabilities of the squeezer. It was decided to explore for the transition around 400°C. MACDONALD (1956) had previously squeezed fayalite at 56,000 bars and 480°C without effect. It appears that reaction rates in crystallized silicates may be too low at these temperatures to allow equilibrium to be reached. It seemed that a more promising approach would be to synthesize fayalite from its components in the squeezer under high pressure.

Ferric oxide, metallic iron powder and Mallinckrodt silicic acid were thoroughly mixed in the proportions required to give fayalite plus a 10 per cent excess of metallic iron. The purpose of the excess iron was to maintain the oxidized iron in the divalent state. The samples were held in the squeezer at 400°C at pressures of 20, 30, 38, 50 and 60 kilobars for periods varying between 4 and 16 hr. The resultant products were then examined by X-ray and optical methods.

The runs at 20, 30 and 38 kilobars consisted substantially of fayalite, together with indeterminate fine grained material and metallic iron. The runs at 50 and 60 kilobars produced considerable amounts of green, transparent, isotropic crystals. Because of their small size and the presence of metallic iron and fine unidentified material, the refractive index was difficult to determine accurately. A value of  $1.955 \pm 0.020$  was found.

Additional runs showed that the degree of crystallization was improved by using higher temperatures and leaving a longer time for reaction. A run of 450°C and 55,000 bars resulted in about 80 per cent conversion to the new phase. X-ray

powder patterns showed that the crystals possessed a spinel structure with a lattice constant of 8.235 Å  $d$  spacings and approximate visual intensities are listed in Table 2.

Table 2. Approximate visual intensities and interplanar spacings of fayalite spinel

$I$	$d$ (Å)	Plane
4	4.7542	111
2	2.9057	220
10	2.4804	311
<1	2.3711	222
5	2.0542	400
2	1.8877	331
4	1.5832	333)
		511)
7	1.4540	440
2	1.2548	533
1	1.2414	622
1	1.1896	444
<1	1.1001	642
4	1.0721	553)
		731)
1	1.0292	800

$a = 8.235 \text{ \AA}$

The calculated density is 4.85 g/cm<sup>3</sup>, 12 per cent higher than that of fayalite. This is in agreement with the increase in density derived by applying the Gladstone-Dale law, relating density and elasticity of the two polymorphs.

Further runs have been carried out at 600°C and the position of the transition located around 38,000 bars. It appears that the formation of fayalite at 38,000 bars and 400°C in the first set of runs was due to metastability, since later work has shown that spinel is stable under these conditions. A run at 70,000 bars and 600°C using moistened Rockport fayalite as starting material resulted in complete conversion to the spinel. It seems clear that the new phase is the predicted spinel polymorph of fayalite.

#### 4. $P$ - $T$ CONDITIONS GOVERNING THE STABILITY OF PYROXENES

Since pyroxenes may be important constituents of the mantle it seems desirable to investigate their stability at elevated temperatures and pressures. It is known that protoenstatite melts incongruently to forsterite plus liquid at 1557°C, whilst the pyroxene FeSiO<sub>3</sub> does not even occur at liquidus temperatures in the system FeO-SiO<sub>2</sub>. Fayalite crystallizes instead. This suggests that Mg-Fe pyroxenes may not be very stable relative to olivines, and that under the high temperatures and



pressures occurring in the mantle, the reaction  $2(\text{MgFe})\text{SiO}_3 \rightarrow (\text{MgFe})_2\text{SiO}_4 + \text{SiO}_2$  a possibility. The olivine might crystallize as such, or if the breakdown occurs under sufficient pressure, it might crystallize as the spinel modification. Fortunately, sufficient thermochemical data exist to study this reaction.

The change in free energy with temperature for the reaction:



has been computed (Table 4). The data used were from the collection by MACDONALD (1954). For convenience, the form of silica occurring in the reaction has

Table 3. Free energies for the reaction  $\text{Mg}_2\text{SiO}_4 + \text{SiO}_2 \rightarrow 2\text{MgSiO}_3$

$T$ (°K)	$\Delta G$ (cal)
298	-2208
1000	-1523
1500	-183
2000	2046
2500	5277

Table 4. Effect of pressure on solubility of  $\text{Mg}_2\text{SiO}_4$  in  $\text{Ni}_2\text{GeO}_4$  around 600°C

No.	Composition of charge (mol. %)	Temp. (°C)	Pressure (bars)	Phases present*	Lattice constant of spinel solid solution (Å)	Estimated mol. per cent of $\text{Mg}_2\text{SiO}_4$ in spinel
1	NG <sub>100</sub>				8.221	0
2	NG <sub>90</sub> MS <sub>10</sub>	600	10,000	spinel	8.220	<1
3	NG <sub>90</sub> MS <sub>10</sub>	800	10,000	spinel	8.217	3
4	NG <sub>45</sub> MS <sub>55</sub>	650	20,000	spinel, olivine	8.202	13
5	NG <sub>45</sub> MS <sub>55</sub>	650	30,000	spinel, olivine	8.197	16
6	NG <sub>45</sub> MS <sub>55</sub>	660	40,000	spinel, olivine	8.167	36
7	NG <sub>45</sub> MS <sub>55</sub>	650	50,000	spinel, olivine	8.172	32
8	NG <sub>45</sub> MS <sub>55</sub>	560	55,000	spinel	8.157	42
9	NG <sub>45</sub> MS <sub>55</sub>	580	70,000	spinel	8.137	55
10	NG <sub>25</sub> MS <sub>75</sub>	580	70,000	spinel, hydrous phase	8.137	55
11	NG <sub>25</sub> MS <sub>75</sub>	580	90,000	spinel, hydrous phase	8.117	68

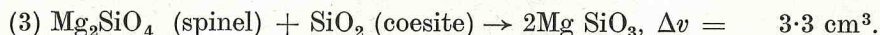
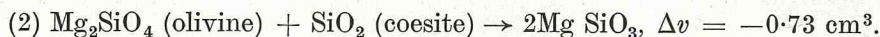
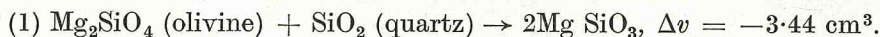
\* Identified from powder photograph. In runs 1, 2 and 8 a small amount of olivine was observed in product by microscopic examination.

been taken to be  $\alpha$  quartz. This introduces some uncertainty into the results, but this is unlikely to affect the general conclusions.

Table 3 shows that clinoenstatite (as indicated by the small free energies of formation) is only slightly more stable than a mixture of forsterite and quartz at

temperatures less than 1500°K. At temperatures much above 1500°K, clinoenstatite becomes unstable and breaks down to forsterite and quartz. This is in agreement with the phase equilibrium data.

Because of the low thermal stability of  $\text{MgSiO}_3$  at atmospheric pressure, it seems that the direction of the reaction considered will be largely controlled by pressure. The following reactions may possibly be of geologic significance:



Reaction (1) shows that pressure will increase the stability of clinoenstatite substantially (by about  $-80$  cal/kbar). Therefore clinoenstatite is stable under conditions existing in the crust and upper mantle.

At shallow depths in the mantle, it is probable that the quartz form of  $\text{SiO}_2$  would be replaced by a denser polymorph such as coesite. MACDONALD'S (1956) results show that at 1500°C, coesite would be stable at a pressure equivalent to that at a depth of approximately 120 km in the mantle. With smaller temperatures, coesite would be stable at lesser depths. Under these conditions reaction (2) becomes applicable. However the  $\Delta v$  for this reaction is small and negative showing that pressure will tend to favour the stability of pyroxene (at temperatures below about 2000°K).

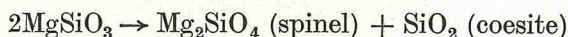
Reaction (3) is of greatest significance. The combination  $\text{Mg}_2\text{SiO}_4$  (spinel) + coesite has a total molar volume which is  $3.3 \text{ cm}^3$  smaller than that of the equivalent  $\text{MgSiO}_3$ . It is therefore apparent that high pressures will favour the formation of  $\text{Mg}_2\text{SiO}_4$  spinel and coesite at the expense of pyroxene. Since increasing temperature also has this effect, it is apparent that (MgFe) pyroxene can possess only a very limited stability range in the mantle.

The total change of free energy when pyroxene breaks down to spinel plus coesite is  $\Delta G_{P \rightarrow S+C}$ , where

$$\Delta G_{P \rightarrow S+C} = \Delta G_{P \rightarrow F+Q} + \Delta G_{F \rightarrow S} + \Delta G_{Q \rightarrow C} \quad \left\{ \begin{array}{l} P = \text{pyroxene} \\ S = \text{spinel} \\ F = \text{forsterite} \\ Q = \text{quartz} \\ C = \text{coesite} \end{array} \right.$$

The  $\Delta G$  terms apply to the reactions indicated by the subscripts,  $\Delta G_{P \rightarrow F+Q}$  as tabulated in Table 3.  $\Delta G_{F \rightarrow S}$  has been determined earlier, whilst  $\Delta G_{Q \rightarrow C}$  may be estimated from MACDONALD'S (1956) paper.

By far the largest term is  $\Delta G_{F \rightarrow S}$ . Previous data in this paper show that this is about 12,000 cal/mole at 1000°C and 30,000 cal/mole at 3000°C.  $\Delta G_{Q \rightarrow C}$  is only about one-sixth of  $\Delta G_{F \rightarrow S}$  at the same temperature.  $\Delta G_{P \rightarrow Q+F}$  was found (Table 4) to be insignificant at 1500°C and becoming strongly positive (i.e. favouring pyroxene breakdown) at temperatures greater than this. Thus for the transition:



the total free energy at zero pressure will be only slightly greater than that for the

fundamental olivine-spinel transition (by about one-sixth) and the  $\Delta v$  change is about three-quarters as great. It is clear then that pyroxene will decompose as indicated in the spinel field in the mantle. The pressure required for this decomposition will be about one-third greater than that required for the olivine-spinel transition at 1500°C. This is a maximum difference, however, since increasing the temperature above 1500°C decreases pyroxene stability and decreases the amount of excess pressure (above that for the olivine-spinel transition) required to cause decomposition. It is clear that the breakdown of pyroxene to spinel plus coesite is dominated by the conditions causing the olivine-spinel transition. The stability of natural pyroxenes will probably be further decreased according to the amount of  $\text{Fe}^{2+}$  occurring in solid solution.

##### 5. TRANSITION PHENOMENA IN THE MANTLE

For an olivine-spinel transition in natural olivine, the transition line for forsterite (Fig. 1) will become broadened into a band, characterized by coexistence of olivine and spinel. This is caused by the presence of fayalite in solid solution. The data in this paper show that at similar temperatures, fayalite requires a much smaller pressure to invert to spinel than forsterite. Accordingly the low-pressure spinels will be rich in fayalite, which is in equilibrium with magnesian olivine. As pressure rises transition occurs continuously over a defined range. It was shown also that MgFe pyroxenes may invert to  $\text{Mg}_2\text{SiO}_4$  spinel, liberating coesite. The maximum pressures required for this inversion may be somewhat greater than those required for the olivine-spinel transition. The effect of  $\text{FeSiO}_3$  in solid solution is analogous to the olivine. A transition band is formed which will probably overlap the olivine-spinel transition band.

From an inspection of Fig. 1 it is apparent that these transitions will probably occur in the mantle at depths less than 1000 km if the temperature at this depth is less than 3000°C. Most estimates of temperatures in the mantle (VERHOOGEN, 1956) imply that the temperature at 1000 km is less than 3000°C. If this is correct, then the phase transition phenomena studied in this paper should occur at depths shallower than 1000 km, covering an appreciable zone. The implications of this conclusion will be considered in detail in Part III.

##### APPENDIX—THE EFFECT OF PRESSURE ON THE SOLUBILITY OF $\text{Mg}_2\text{SiO}_4$ IN $\text{Ni}_2\text{GeO}_4$

A supplementary series of experiments has recently given strong support to previous conclusions regarding the stability of  $\text{Mg}_2\text{SiO}_4$  spinel. The experiments are of a reconnaissance nature and a considerable amount of further work will be necessary before the behaviour of the system under high pressures is accurately determined. Nevertheless the general outline seems clear.

It was shown in Part I that  $\text{Ni}_2\text{GeO}_4$ , which has a spinel structure, will dissolve about 9 per cent of  $\text{Mg}_2\text{SiO}_4$  at 1500°C. At 600°C the solubility appears to be small, probably less than 3 per cent. However at that temperature, solubility is found to increase very substantially with increasing pressure. An analogous effect has been observed in the system  $\text{Mg}_2\text{GeO}_4$ - $\text{Mg}_2\text{SiO}_4$  (DACHILLE and ROY, 1956).

Reactive charges were prepared by mixing co-precipitated magnesium and nickel hydroxides dried at 110°C with co-precipitated hydrous silica and germania, in the ratios required to form  $(\text{NiMg})_2(\text{GeSi})\text{O}_4$  compounds of desired composition. Chemical analyses of the silica-germania co-precipitates were kindly carried out by Mr. JUN ITO of the Department of Geology, Harvard University. The charges used had compositions  $\text{NG}_{90}\text{MS}_{10}$ ,  $\text{NG}_{45}\text{MS}_{55}$  and  $\text{NG}_{25}\text{MS}_{75}$  (molecular ratios). Numerous other charges were prepared in different ways, but did not prove sufficiently reactive in the squeezer.

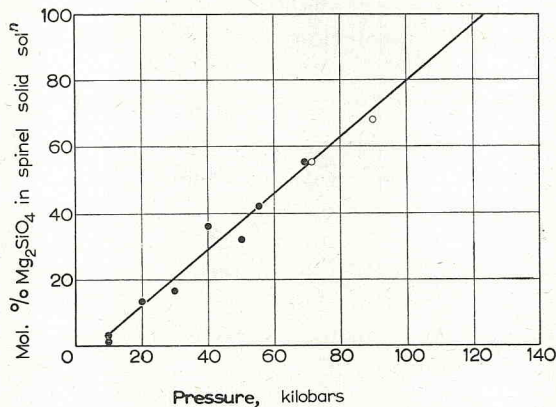


Fig. 2. Effect of pressure on solubility of  $\text{Mg}_2\text{SiO}_4$  in  $\text{Ni}_2\text{GeO}_4$  around 600°C.

● Spinel in equilibrium with olivine  
 ○ Spinel in equilibrium with hydrous phase  
 Pressure at which pure  $\text{Mg}_2\text{SiO}_4$  spinel should become stable around 600°C (extrapolated)—  
 125,000 bars

Samples were placed in the squeezer and subjected to different pressures at temperatures between 560 and 660°C. Variation of temperature between these limits was aimed at establishing optimum conditions for reaction of charges and obtaining maximum pressure from the squeezer. Runs up to 55,000 bars were made using pistons with faces  $\frac{1}{4}$  in. in diameter. For higher pressures pistons with  $\frac{3}{16}$  in. faces were used. Results are set out in Table 4.

In run No. 9 a sample of  $\text{NG}_{45}\text{MS}_{55}$  was found by X-ray and optical examination to form a homogeneous spinel at 70,000 bars and 580°C. The lattice constant was 8.137 Å. The lattice constant of pure  $\text{Ni}_2\text{GeO}_4$  is 8.221 Å. Extrapolation, using Vegard's Law allows determination of the lattice constant of  $\text{Mg}_2\text{SiO}_4$  spinel, which is found to be 8.07 Å, giving a theoretical density of 3.55 g/cm<sup>3</sup>. This is 11 per cent higher than that of forsterite, and thus confirms the value derived in Part I.

Knowledge of the relationship between lattice parameter and composition allows estimation of the composition of the other spinels formed. (Table 4.) Apart from the normal experimental uncertainties, the estimates are subject to the assumption that the behaviour of the system is binary. This subject was fully discussed in Part I where a reasonably close approach was demonstrated. Checks of refractive indices have shown that this is maintained in the system under the present  $P$ - $T$  conditions. Equality of spinel compositions in runs 9 and 10 support

this. Since in most cases there is only a relatively small amount of olivine present in equilibrium with the spinel, it would need a large deviation from binary behaviour to affect the result significantly.

With the composition  $\text{NG}_{25}\text{MS}_{75}$ , at pressures of 70,000 and 90,000 bars, the spinel is no longer in equilibrium with olivine, but with a phase having a 9.9 Å spacing. This is probably a hydrous phase which has become stable relative to olivine at the extreme pressure.

Spinel compositions have been plotted against pressure in Fig. 2. The results are not strictly comparable because of variation of temperature between 560 and 660°C. It does not appear however that this variation is sufficient to significantly change the equilibria. A linear extrapolation indicates that  $\text{Mg}_2\text{SiO}_4$  spinel should be stable around 600°C at 125,000 bars. This is probably a maximum since the higher experimental pressures may have been somewhat overestimated in the squeezer due to piston distortion. This result thus confirms in essentials, the previous calculations.

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