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## MINERALOGY OF PERIDOTITIC COMPOSITIONS UNDER UPPER MANTLE CONDITIONS

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An experimental study of the stability fields at high pressure of plagioclase peridotite, aluminous pyroxene ( $\pm$ spinel) peridotite and garnet peridotite, has been carried out in compositions matching estimates of the average undifferentiated upper mantle (pyrolite). The appearance of garnet at high pressures results from either of two complex reactions:

- a. spinel + pyroxene  $\rightleftharpoons$  olivine + garnet,  
(solid solutions)
- b. aluminous pyroxene  $\rightleftharpoons$  garnet + pyroxene (lower  $\text{Al}_2\text{O}_3$ ).  
(solid solution)

In the model pyrolite composition, garnet appears at 21 kb (1100 °C) to 24 kb (1300 °C) by reaction (a) but at temperatures above 1300 °C spinel is absent from the low pressure assemblage and garnet develops by reaction (b) at pressures of 24 kb (1300 °C) to 31 kb (1500 °C). Reactions (a) and (b) have very different  $P, T$  gradients. In the garnet peridotite field, the amount of garnet is inversely proportional to the alumina content of the pyroxenes. This is confirmed by microprobe analyses of ortho-

pyroxene (ranging from 6.0 to 2.2%  $\text{Al}_2\text{O}_3$ , 0.7-0.9%  $\text{Cr}_2\text{O}_3$ ) coexisting with garnet, olivine and clinopyroxene. Coexisting clinopyroxenes have higher  $\text{R}_2\text{O}_3$  content and exhibit a variable, temperature dependent enstatite solid solution.

The experimental data are applied to estimate mineralogical, density and seismic velocity variations along oceanic and continental geothermal gradients in a pyrolite upper mantle. Although the mineralogical variation may produce a low velocity zone, the alternate explanation of incipient or minor partial melting is preferred. Experimental data on the maximum stability limit of amphibole in pyrolite (with 0.1-0.2% water) are presented showing that amphibole breaks down to olivine + pyroxenes + garnet + fluid phase at approximately 29 kb, 1000 °C. The instability of amphibole at depths  $>80-90$  km is considered to result in a zone of incipient or minor melting in a pyrolite upper mantle with 0.1-0.2% water. The nature of the liquid in this zone is considered to be highly undersaturated olivine basanite or olivine nephelinite.

### 1. Introduction

The uppermost region of the Earth's mantle acts as the immediate source region for basaltic magmas and is the one part of the mantle "sampled" by magmatic or tectonic processes and, in certain circumstances, exposed for direct petrological and geochemical investigation. The properties of the upper mantle can also be rather closely defined by geophysical methods, particularly by seismological and gravity studies. The weight of geological and geophysical evidence on upper mantle composition favours an overall peridotitic composition and arguments against an alternative of eclogitic composition have previously been presented (RINGWOOD and GREEN, 1966; RINGWOOD, 1966a). In seeking to define an upper mantle composition more closely the petrologist must interpret the variety of basaltic magmas, of peridotitic xenoliths in magmas and vent breccias, high-temperature peridotites, and other peridotite

occurrences in terms of parental mantle compositions, partial melting products, crystal residues and crystal accumulates. No unique synthesis of these data is possible at this stage but in previous papers we have used the term "pyrolite" for parental mantle capable of yielding basaltic magmas by partial melting and advanced arguments for specific pyrolite compositions (GREEN and RINGWOOD, 1963; RINGWOOD, 1966a). Other authors (ITO and KENNEDY, 1967; KUSHIRO and KUNO, 1963; KUSHIRO *et al.*, 1968; HESS, 1964; HARRIS *et al.*, 1967) have derived possible upper mantle compositions on other grounds or have selected specific samples of peridotite xenoliths. These compositions also have essential  $\text{Al}_2\text{O}_3$ , CaO and  $\text{Na}_2\text{O}$  and, like the pyrolite compositions, may crystallize in four different mineral assemblages within the  $P, T$  conditions of the upper mantle (minor accessory minerals such as ilmenite, apatite, phlogopite are omitted):

- a. Olivine + amphibole  $\pm$  enstatite ("ampholite"),



- b. Olivine + pyroxenes + plagioclase + chromite,  
("plagioclase pyrolite")  
c. Olivine + aluminous pyroxenes ± spinel,  
("pyroxene pyrolite")  
d. Olivine + pyroxenes + garnet ("garnet pyrolite").

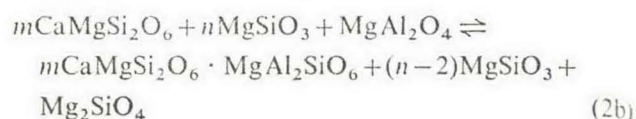
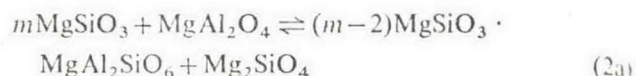
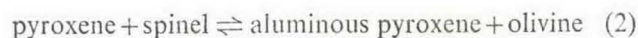
## 2. Previous investigations

Experimental investigations of the stability relationships of these assemblages have been undertaken by several authors using either complex systems or simple, end member systems. Reactions between olivine and plagioclase to yield aluminous pyroxenes + spinel have been studied for the system Fo-An (KUSHIRO and YODER, 1966) and for the systems Fo-An, olivine (Fo<sub>92</sub>)-labradorite (Ab<sub>41</sub>An<sub>59</sub>), and for pyrolite composition (GREEN and HIBBERSON, 1969). These investigations show that plagioclase pyrolite will not occur as the stable mantle assemblage along typical geothermal gradients in either continental or oceanic regions but may be present in areas of particularly high heat flow and thin crust, e.g. if near-solidus temperatures are reached at depths of 25–35 km beneath mid-oceanic ridges. More interest centres on the conditions for the incoming of garnet and the role of garnet pyrolite and pyroxene pyrolite assemblages in upper mantle mineralogy.

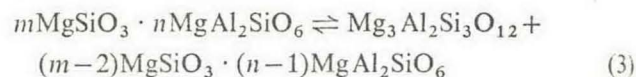
MACGREGOR (1964, 1965) studied the reaction



in the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and in the system MgO-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. In the latter system MACGREGOR (1965) used pyroxene proportions (enstatite/diopside) of 75/25, 25/75 and 0/100. KUSHIRO and YODER (1965) studied the analogous reaction for enstatite: diopside = 50:50 and established a boundary for the incoming of garnet close to that found by Macgregor for the enstatite + diopside bearing mixtures. MACGREGOR (1964) did not report olivine on the low pressure side of the reaction (1) in the system MgAl<sub>2</sub>O<sub>4</sub> + 4MgSiO<sub>3</sub> but did observe olivine in the low pressure assemblages (Ol + Al-pyroxene(s) + spinel) in the systems 2MgAl<sub>2</sub>O<sub>4</sub> + CaMgSi<sub>2</sub>O<sub>6</sub> + 6MgSiO<sub>3</sub> and 2MgAl<sub>2</sub>O<sub>4</sub> + 3CaMgSi<sub>2</sub>O<sub>6</sub> + 2MgSiO<sub>3</sub>. The appearance of olivine results from a reaction



The apparent absence of reaction (2a) (MACGREGOR, 1964) contrasts with other data showing high solubility of Al<sub>2</sub>O<sub>3</sub> in enstatite and with the presence of reaction (2b) (or an analogous reaction involving (CaAl<sub>2</sub>SiO<sub>6</sub>) solid solution) in the Ca-bearing system. The study of reaction (1) in the system MgO-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> by MACGREGOR (1965) utilized mixes containing both high and low pressure assemblages and the position of the reaction boundary was determined by changes in intensity of garnet and pyroxene reflections. However metastable growth of garnet from aluminous pyroxene (e.g. reaction (3))



may have proceeded more rapidly than reaction of the aluminous pyroxene with olivine to yield less aluminous pyroxene and spinel. A difficulty involving metastable growth of garnet may account for some results of KUSHIRO and YODER (1966, fig. 2) in which, using a mix of An + Fo seeded with Ga + Fo + Cpx, they obtained some runs in which garnet and plagioclase disappeared in favour of Cpx + Opx + Fo + Sp but others at lower pressure in which the seed phases, Ga + Fo + Cpx, increased at the expense of An + Fo. Although there are no true reversals, it would seem that the boundary for reaction (1) should lie at higher pressures at 1100°–1300 °C, than shown by KUSHIRO and YODER (1966).

Other apparent discrepancies exist in the experimental data attempting to define the conditions for reaction (3), i.e. the breakdown of aluminous enstatite to garnet and less aluminous pyroxene. BOYD and ENGLAND (1964) and MACGREGOR and RINGWOOD (1964) carried out experiments homogenizing different garnet + pyroxene mixtures to a single pyroxene phase using pure pyrope and enstatite and natural pyrope-rich garnet and enstatite respectively. The natural enstatite in equilibrium with garnet contained 1.5–2 mol% more (Al, Cr, Fe)<sub>2</sub>O<sub>3</sub> in solid solution than the enstatite in

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(2a) the MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system. RINGWOOD *et al.* (1964) and RINGWOOD (1966) integrated the data from the enstatite + pyrope studies with the pyrolite (RINGWOOD 1966a) composition\* to infer stability fields for the assemblages olivine + pyroxenes + spinel, olivine + aluminous pyroxenes, and olivine + pyroxenes + garnet. Direct experimental study (GREEN and RINGWOOD, 1967a) of the pyrolite III revealed a much lower solubility of Al<sub>2</sub>O<sub>3</sub> in orthopyroxene than that predicted from the study of the simple systems—this resulted in persistence of spinel to higher temperature ( $\approx 1200$  °C, 11 kb to  $\approx 1300$  °C, 23 kb) than the 900 °C predicted by RINGWOOD *et al.* (1964) and in appearance of garnet from breakdown of aluminous pyroxene at lower pressures ( $\approx 26.5$  kb at 1400 °C) than previously predicted ( $\approx 39$  kb at 1400 °C). These surprisingly large differences imply that the presence of coexisting olivine or clinopyroxene considerably alters the solubility of Al<sub>2</sub>O<sub>3</sub> in orthopyroxene—this can readily occur if the coexisting phases can enter solid solution in either garnet or orthopyroxene. The addition of clinopyroxene to the assemblage obviously establishes new partition relations involving grossular solid solution in garnet and diopside solid solution in enstatite. However MACGREGOR and RINGWOOD (1964) found higher solubilities of garnet in orthopyroxene for the natural enstatite (0.82% CaO) + garnet (5.21% CaO) mixes than for the pure enstatite + pyrope system. MACGREGOR and RINGWOOD (1964) homogenized mixtures of 50% garnet, 50% enstatite to a pyroxene phase at 30 kb, 1500 °C implying that the pyroxene contained 3.0% CaO (by weight)—this either exceeds or is very close to saturation in diopside solid solution for these *P-T* conditions (DAVIS and BOYD, 1966; GREEN and RINGWOOD, 1967b). Thus it does not appear that diopside solid solution greatly inhibits Al<sub>2</sub>O<sub>3</sub> solubility in enstatite. If the addition of olivine to garnet-enstatite assemblages is the factor inhibiting Al<sub>2</sub>O<sub>3</sub> solubility then it is implied that olivine has a significant solid solubility in enstatite. This possibility requires further investigation but it may be noted that KUSHIRO (1964) reported olivine solid solution in diopside and BOYD and ENGLAND (1960) noted that natural enstatites from peridotites had values of the molecular ratio  $M^{2+}/Si > 1$ . The observation of spinel exsolution lamellae within ensta-

\* This composition is denoted as pyrolite III in the rest of this paper (see table 1).

tite of lherzolite nodules and some intrusive peridotites also implies non-stoichiometric composition of the orthopyroxene (cf. reaction (2)).

MACGREGOR (1967) briefly reported data on mixtures of natural orthopyroxene + clinopyroxene + spinel using separated minerals from lherzolite inclusions. Two assemblages differing mainly in Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> ratio were used and the preliminary data indicate that high Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> ratios of spinel will have a marked effect on stabilizing the olivine + orthopyroxene + clinopyroxene + spinel assemblages to higher pressures. ITO and KENNEDY (1967) presented data on the solidus and melting relations in a garnet lherzolite nodule from kimberlite. They obtained solidus temperatures approximately 100 °C lower than those of GREEN and RINGWOOD (1967a) but the pressure obtained for the incoming of garnet ( $\approx 23$  kb, 1320 °C) agrees with that obtained by GREEN and RINGWOOD (1967a) on pyrolites I and II\*. ITO and KENNEDY (1967) did not obtain a field of olivine + aluminous pyroxenes (without spinel) although this would be anticipated from a comparison of their composition with that of GREEN and RINGWOOD (1967a) for pyrolites I, II and III. Ito and Kennedy used a natural garnet lherzolite as starting material—this presents difficulties in representative sampling of the initial coarse-grained rock and in the avoidance of sample composition change during the extremely fine-grinding needed to ensure some chance of reactions proceeding to equilibrium.

From the preceding summary of published data, it is apparent that there is as yet no general agreement on the *P, T* coordinates of reactions (1), (2) and (3), either in simple systems or in complex natural peridotitic compositions. More detailed work is required, attempting to eliminate the possibility of metastable reactions or other experimental uncertainties. From the data already obtained, it is clear that the reaction (1) is one in which the pyroxene will vary in composition along the reaction boundary. This boundary is actually the locus of intersections of reactions (2) and (3) which define the curves of constant Al<sub>2</sub>O<sub>3</sub> content of pyroxene in peridotitic compositions. The position of reaction (1) will also depend sensitively on the spinel composition

\* This agreement may be fortuitous as GREEN and RINGWOOD (1967a) applied a (-10%) pressure correction while ITO and KENNEDY (1967) applied no pressure correction. It should also be noted that MACGREGOR (1964, 1965, 1967) did not apply a pressure correction.



(Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> ratio) in complex compositions and this will vary due to coupled reaction (2) with pyroxene.

With the complexity of the reactions in mind, there is much to be said for the direct experimental testing of model pyrolite compositions. In the following sections the data obtained on the model pyrolite compositions of GREEN and RINGWOOD (1963) and RINGWOOD (1966a) are summarized and emphasis is placed on the attempts to establish reaction boundaries by unequivocal reversals.

### 3. Experimental data on the incoming of garnet in pyrolite

#### 3.1. Experimental methods

The experimental compositions (table 1) were prepared from AR grade chemicals, carefully ground and reacted together under high temperature reducing conditions and then analyzed for FeO and Fe<sub>2</sub>O<sub>3</sub> contents. The initial mixes were extremely finegrained ( $\leq 1 \mu$ ) and consisted of olivine, clinopyroxene, orthopyroxene, plagioclase and minor chromite and ilmenite. To facilitate identification of minor phases and of the presence or absence of small degrees of partial melting, compositions were prepared which are equivalent to the pyrolite compositions of table 1 after extraction of 50% olivine (Mg<sub>91.5</sub>Fe<sub>8.0</sub>Ni<sub>0.4</sub>Mn<sub>0.1</sub>) from pyrolites I and II and after extraction of 40% olivine (Mg<sub>91.6</sub>Fe<sub>8.1</sub>Ni<sub>0.2</sub>Mn<sub>0.1</sub>) from pyrolite III. In all experiments conducted with these modified pyrolite compositions, excess olivine was present. Hence the above procedure did not affect in any way the equilibrium relationships which are discussed below.

Crystallization of the experimental compositions was carried out using a single-stage, piston-cylinder apparatus and a pressure correction of -10% was applied to the nominal pressure for all runs. Samples were run in both platinum capsules and in graphite capsules. The run conditions using platinum capsules were such that iron loss to the Pt capsule was less than 25% of the amount present. Analyses of samples after experimental runs are listed in table 1a, the average iron content is 5.7% FeO, 0.7% Fe<sub>2</sub>O<sub>3</sub> yielding a normative composition with approx. 33% Ol and 30% enstatite. The worst examples (in table 1a) give normative olivine of approximately 31% and 33% enstatite.

Microprobe analyses across a polished sample (36 kb,

TABLE I

Chemical compositions and CIPW norms of model pyrolite compositions used in experimental runs. Pyrolite I and pyrolite III refer to the model compositions calculated by GREEN and RINGWOOD (1963) and RINGWOOD (1966a) respectively. They differ principally in their MgO/SiO<sub>2</sub> ratios and thus in pyroxene (Al, Cr)<sub>2</sub>O<sub>3</sub> and pyroxene/olivine ratios. Pyrolite II is a composition intermediate between the two in which the enstatite/olivine ratio of pyrolite I was increased without appreciable change in the R<sub>2</sub>O<sub>3</sub> content

	Pyrolite I	Pyrolite II	Pyrolite III	Pyrolite III less 40% olivine
SiO <sub>2</sub>	43.20	43.95	45.20	47.84
TiO <sub>2</sub>	0.58	0.57	0.71	1.18
Al <sub>2</sub> O <sub>3</sub>	4.01	3.88	3.54	5.90
Cr <sub>2</sub> O <sub>3</sub>	0.42	0.41	0.43	0.72
Fe <sub>2</sub> O <sub>3</sub>	0.35	0.75	0.48	0.80
FeO	7.88	7.50	8.04	8.21
MnO	0.13	0.13	0.14	0.13
NiO	0.39	0.39	0.20	0.18
MgO	39.54	39.00	37.48	28.73
CaO	2.67	2.60	3.08	5.14
Na <sub>2</sub> O	0.61	0.60	0.57	0.95
K <sub>2</sub> O	0.22	0.22	0.13	0.22
100 Mg/(Mg+Fe <sup>2+</sup> ) atomic ratio	89.9	90.3	89.2	86.5
CIPW Norm				
Or	1.1	1.1	0.8	1.3
Ab	5.2	5.2	5.0	8.3
An	7.5	7.3	6.6	11.0
Di	4.6	4.3	6.8	11.3
Hy	3.8	9.4	15.8	26.4
Ol	75.6	69.8	62.5	37.5
Ilm	1.1	1.1	1.3	2.2
Mt	0.5	1.2	0.7	1.1
Chr.	0.6	0.6	0.6	1.0

TABLE 1a

Effect on FeO, Fe<sub>2</sub>O<sub>3</sub> contents of pyrolite III less 40% olivine of loss of iron to platinum capsules during experimental runs (E. Kiss, analyst)

P (kb)	T (°C)	Time (hrs)	% FeO	% Fe <sub>2</sub> O <sub>3</sub>	% total Fe as FeO
27	1500	0.33	5.62	0.38	5.96
29.3	1500	0.33	5.18	0.78	5.88
30.4	1500	0.33	5.11	1.03	6.04
29.3	1400	1.0	5.10	0.54	5.59
30.4	1400	1.0	5.56	0.75	6.24
24.8	1300	2.0	5.21	0.56	5.71
20.3	1200	2.0	6.89	1.01	7.80
22.5	1100	4.0	7.17	0.75	7.70



1500 °C, 20 mins, pyrolite III less 40% olivine) showed average Fe as FeO content of 6.1% (i.e. sample 100 Mg/(Mg+Fe) = 89.5) at the edge against platinum and Fe as FeO content of 7.0% (i.e. sample 100 Mg/(Mg+Fe) = 88) in the centre of the sample. Microprobe analyses of olivines and orthopyroxenes from runs in Pt capsules yield values of 100 Mg/(Mg+Fe) = 90–91.5, whereas from subsolidus runs in graphite capsules the olivine and orthopyroxene had 100 Mg/(Mg+Fe) = 87–88. Runs across the pyroxene pyrolite/garnet pyrolite boundary at 1350 °C and a reversal on the boundary at 1400 °C were carried out in graphite capsules. The use of graphite capsules in longer runs allowed access of water producing depression of the solidus and the presence of amphibole in runs at 1100 °C, 22.5 kb and 20.5 kb. These effects were eliminated by repeating these runs in sealed Pt capsules. To summarize, the use of sealed Pt capsules appears necessary for reliable determination of the solidus and prevention of growth of amphibole at low temperatures. The use of platinum causes slight iron loss changing the overall sample 100 Mg/(Mg+Fe) ratio by 2–3% but this does not perceptibly affect the position of the phase boundary marking the appearance of garnet as subsolidus runs in graphite and platinum are mutually consistent. The iron loss also causes a small increase in normative Hy/Ol ratio and thus in pyroxene/R<sub>2</sub>O<sub>3</sub> ratio. It may be noted that the effect of Fe increase due to experiments in Fe capsules by ITO and KENNEDY (1967) appears to be similar in magnitude (modal olivine ≈ Fo<sub>95</sub> but experimental olivines in subsolidus assemblages range from Fo<sub>88</sub>–Fe<sub>91</sub>) but has the opposite effect in decreasing normative Hy/Ol and pyroxene/R<sub>2</sub>O<sub>3</sub> ratios.

Samples were examined optically and by X-ray powder diffraction. Orthopyroxene forms quite large tabular porphyroblasts; garnet is commonly subhedral but contains many inclusions at lower temperatures and olivine and clinopyroxene form small anhedral grains. Spinel occurs as small, equant, green, isotropic grains and differs from ilmenite (ilmenite + geikielite solid solution) in that the latter is commonly elongate, brown, translucent and with high birefringence. The orthopyroxene crystals are readily analyzed by electron microprobe techniques and some data have been obtained on olivine, clinopyroxene and garnet compositions. The presence of small amounts of amphibole

required detection by X-ray powder diffraction photographs.

In the experiments on the stability of amphibole, the methods used should outline the *maximum* stability of amphibole at 1000 °C and were designed to specifically test the model that pyrolite contains 0.1–0.2% H<sub>2</sub>O at shallow mantle depths. The use of a very small water content also avoids the problems of large degrees of melting and depression of the solidus, and of the possibility of solubility of components in a vapour phase. The starting material for these runs was prepared by adding 0.3% H<sub>2</sub>O to the "pyrolite III less 40% olivine" mix. This mix was run at 10.8 kb, 900 °C for 4½ hrs yielding a fine-grained assemblage of olivine, pyroxenes and amphibole (≈ 15%). This was then rerun at 1000 °C and at pressures of 18 kb to 29 kb and examined carefully by optical and X-ray methods for the disappearance of amphibole and the appearance of garnet.

### 3.2. Experimental results

The results of the determination of the synthesis fields for garnet pyrolite and pyroxene pyrolite are presented in fig. 1. The data points denote the phase assemblages present in pyrolite III composition. Plagioclase pyrolite is stable under dry conditions on the low pressure side of AB. Between AB and ELF, both garnet and plagioclase are absent and the mineral assemblage is dominated by aluminous pyroxenes. Within this field, spinel is present as a minor phase at temperatures below the line marked K but only olivine, aluminous pyroxenes and accessory ilmenite are present at higher temperatures. Garnet first appears in trace amounts along the line ELF and, at a given temperature, steadily increases in abundance as pressure increases.

The data points for pyrolites I and II are not shown in fig. 1 but in these compositions the first appearance of garnet is along EJ and spinel remains up to solidus temperatures on the low pressure side of EJ. Garnet and spinel co-exist together over a very small pressure interval on the high pressure side of EJ. The triangular P, T field FLJ is one in which the olivine + aluminous pyroxenes assemblage occurs in pyrolite III but olivine + aluminous pyroxenes + garnet occurs in pyrolites I and II.

The boundary for the appearance of garnet was apparently defined by different reactions at low and high temperatures and it was desirable to obtain reversals



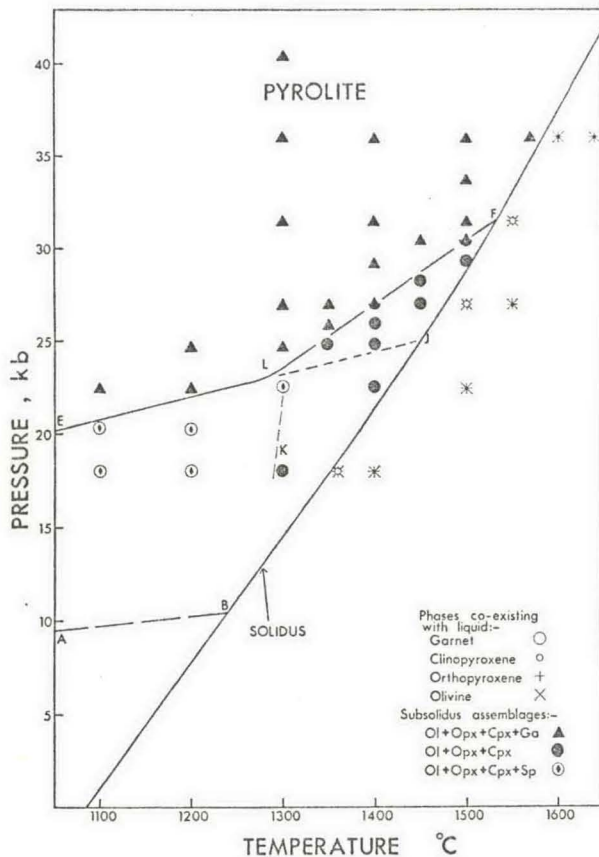


Fig. 1. Experimental runs on pyrolite III composition. Garnet is absent on the low pressure and present on the high pressure side of ELF. Spinel is absent on the high temperature side of the line K. In pyrolites I and II garnet is present on the high pressure side of ELJ. (From GREEN and RINGWOOD, 1967a).

across these boundaries as previous data (BOYD, 1960) had demonstrated difficulty in nucleation of magnesian garnet near its low pressure stability limit. Reversals

involving complete disappearance of garnet on the low pressure side of the boundary, were achieved at 1400 °C and 1200 °C (table 2). The starting mix for the 1400 °C reversals was a large capacity run at 36 kb, 1000 °C, 3 hrs yielding fine grained olivine and pyroxene and very poikilitic garnet. For the 1200 °C reversal, the starting material was a 50:50 mix of runs carried out at 1200 °C, 18 kb, 2 hrs and 1200 °C, 27 kb, 2 hrs. The reversals at 1400 °C and 1200 °C confirm the positions of the boundaries established from the olivine + pyroxenes + plagioclase + chromite starting mixtures. The analysis of the roles of spinel and aluminous pyroxenes gives a theoretical explanation for the change in slope of the boundary marking the appearance of garnet in pyrolite III and the absence of such a change in slope of the boundary in pyrolites I and II. Microprobe analyses of orthopyroxene (table 4) show regular variations in  $Al_2O_3$  and  $CaSiO_3$  solid solution which are in themselves very good evidence that the experimental assemblages closely approach equilibrium.

In the runs (table 3) on the olivine + amphibole + pyroxenes mix, amphibole breaks down finally between 27 kb and 28.8 kb at 1000 °C. There is a transitional assemblage of olivine + pyroxenes + garnet + amphibole from 23.5 kb to 28 kb. In this assemblage the amount of garnet is less than in lower pressure runs. Experiments on the stability of amphibole in basaltic compositions (ESSENE *et al.*, 1970) have demonstrated that amphibole may form readily from (glass +  $H_2O$ ) mixtures and persist metastably at high pressures and at 700–800 °C beyond its stability field as defined by growth in garnet + pyroxene + amphibole + water mixtures. This possibility has not been fully tested in the

TABLE 2

Results of experimental runs aimed at reversal of the boundary for appearance of garnet from olivine + aluminous pyroxenes and from olivine + spinel + pyroxenes assemblages

Run no.	Capsule	Pressure (kb)	Temperature (°C)	Time (hrs)	Starting material	Products
1096	Graphite	27.0	1450	1	Ol + Opx + Cpx + Ga	Ol + Opx + ?Cpx + Melt
1098	Graphite	28.1	1450	1	Ol + Opx + Cpx + Ga	Ol + Opx + Cpx + Melt
1099	Graphite	25.9	1400	1	Ol + Opx + Cpx + Ga	Ol + Opx + Cpx
1055	Pt	25.9	1400	1	Ol + Opx + Cpx + Plag + Chromite	Ol + Opx + Cpx
1100	Graphite	27.0	1400	2	Ol + Opx + Cpx + Ga	Ol + Opx + Cpx + rare Ga
1016	Pt	27.0	1400	1	Ol + Opx + Cpx + Plag + Chromite	Ol + Opx + Cpx + rare Ga
2289	Pt	20.7	1200	4	50% (Ol + Opx + Cpx + Ga) 50% (Ol + Opx + Cpx + Sp)	Ol + Opx + Cpx + rare Spinel
2290	Pt	22.5	1200	4	50% Ol + Opx + Cpx + Ga 50% Ol + Opx + Cpx + Sp	Ol + Opx + Cpx + Ga (minor garnet but with euhedral form)

Experiment

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TABLE 3

Experiments on the stability of amphibole in pyrolite with low water content. All runs used "pyrolite III less 40% olivine" mix containing 0.3% H<sub>2</sub>O and all were carried out in sealed Pt capsules

Run no.	Pressure (kb)	Temperature (°C)	Time (hrs)	Starting material	Products
2170	18	1100	7	Ol+Amph+Px	Ol+Amph+Px
2173	19.8	1000	15	Ol+Amph+Px	Ol+Amph+Px
2168	22.5	1000	17	Ol+Amph+Px	Ol+Amph+Px
2189	24.8	1000	12	Ol+Amph+Px	Ol+Amph+Px+rare Ga
2338	25.2	1000	26	Ol+Amph+Px	Ol+Amph+Px+rare Ga
2339	27.0	1000	24	Ol+Amph+Px	Ol+Amph+Px+minor Ga
2344	28.8	1000	24	Ol+Amph+Px	Ol+Px+common Ga+ trace amphibole
2347	25.2	1000	48	90% Ol+Amph+Px 10% Ol+Px+Ga	Ol+Px+minor Ga+minor amphibole

present experiments although the higher temperature of the runs and the persistence of amphibole in a 48 hr run seeded with garnet + pyroxene + olivine at 25.2 kb, 1000 °C suggest that the effect may be small. Another difference from the experiments on basaltic amphibolites is that the experiments on pyrolite are devised with a specific model i.e. mantle composition with 0.1–0.2% water (RINGWOOD, 1969), in mind and the problem of partial melting at low temperatures for  $P_{\text{H}_2\text{O}} = P_{\text{total}}$  has been avoided. KUSHIRO *et al.* (1968) reported data on melting of a lherzolite nodule under anhydrous and hydrous conditions and found the solidus to be  $\approx 1000$  °C for  $P_{\text{H}_2\text{O}} = P_{\text{total}}$  at 20–30 kb. They did not report amphibole at 26 kb, 980 °C but apparently used optical methods only in identification of phases and minor amphibole may have been missed.

Partial analyses by electron probe micro-analyser are listed in table 4. The orthopyroxenes, because of their porphyroblastic habit, could be analysed with similar accuracy to those in partial melting runs (GREEN and RINGWOOD 1967b) but the finer grain size of olivine and clinopyroxene and the poikilitic nature of the garnet made analysis more difficult. The figures given in table 4 include only those grains where two or more consecutive analyses (2–3  $\mu$  steps) gave consistent analytical data. The data show a very clear pattern of decreasing Al<sub>2</sub>O<sub>3</sub> solubility in orthopyroxene with increasing pressure within the garnet pyrolite field. The Al<sub>2</sub>O<sub>3</sub> content of orthopyroxene from pyrolite III at the incoming of garnet (boundary LF, fig. 1) is  $6.0 \pm 0.2\%$ . Coexisting clinopyroxene contains ap-

proximately 7.7% Al<sub>2</sub>O<sub>3</sub> and the Cr<sub>2</sub>O<sub>3</sub> contents are 0.9% Cr<sub>2</sub>O<sub>3</sub> (orthopyroxene) and  $\geq 1.0\%$  Cr<sub>2</sub>O<sub>3</sub> (clinopyroxene). The higher Al<sub>2</sub>O<sub>3</sub>+Cr<sub>2</sub>O<sub>3</sub> content of the clinopyroxene is due to NaR<sup>3+</sup>Si<sub>2</sub>O<sub>6</sub> solid solution. The minimum Al<sub>2</sub>O<sub>3</sub> content of analyzed orthopyroxene is 2.2% at 40.5 kb, 1300 °C. Clinopyroxene contains 4.6% at 36 kb, 1300 °C in equilibrium with orthopyroxene with 2.6% Al<sub>2</sub>O<sub>3</sub>. The degree of mutual solid solution between pyroxenes shows a consistent pattern although the difficulty of analysing the small clinopyroxenes prevents any confident statement on limits of pyroxene solid solution in the complex composition. Orthopyroxene ( $\approx \text{En}_{90}$ ) coexisting with clinopyroxene contains approximately 2.4% CaO at 1500 °C, 2.2% CaO at 1400 °C, 2.0% CaO at 1350 °C and 1–5% CaO at 1300 °C. Coexisting clinopyroxene contains  $\geq 11.4\%$  CaO at 1400 °C and  $\geq 14.5\%$  CaO at 1350 °C – this is a higher CaO content than in clinopyroxene obtained at similar temperatures at 9–18 kb from more iron-rich basaltic compositions (GREEN and RINGWOOD, 1967b, p. 136–8). The garnets are more Fe-rich than coexisting clinopyroxene and olivine and contain 4.5–5.0% CaO and  $\approx 1.7\%$  Cr<sub>2</sub>O<sub>3</sub>. Higher values of CaO (6.9% and 5.6%) are probably due to small clinopyroxene inclusions.

The experimental data on pyrolite III composition are summarized in fig. 2 in which we have plotted curves showing maximum solubility of Al<sub>2</sub>O<sub>3</sub> (with  $\approx 0.8\%$  Cr<sub>2</sub>O<sub>3</sub> in addition) in orthopyroxene coexisting with garnet, olivine and clinopyroxene. Data are inadequate to draw similar curves in the olivine + py-

TABLE 4  
 Partial analyses, using electron probe microanalyser, of crystalline phases from pyrolite

Temperature (°C)	Pressure (kb)	Time (hrs)	Sample capsule	Phase analysed	Analysed constituents				Garnet content of assemblage	Remarks
					Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	FeO	CaO		
Pyrolite III less 40% olivine										
1500	22.5	0.33	Pt	Opx	3.5	—	4.0	2.2	Nil	≈ 50% melting, Ol+Opx+Quench, Opx > Ol
1500	27.0	0.33	Pt	Opx	5.4	—	5.2	2.4	Nil	Minor melting, Ol+Opx+Cpx+Quench
1500	29.3	0.33	Pt	Opx	5.7	0.9	5.2	2.4	Nil	No identifiable melting, Ol+Opx+Cpx
1500	30.4	0.33	Pt	Opx	5.9	0.8	5.3	2.4	Trace	No identifiable melting, Ol+Opx+Cpx+Ga
				Ol	≤ 0.5	—	8.5	≤ 0.5	Trace	
1500	31.5	0.33	Pt	Opx	5.6	0.7	5.7	2.4	Minor	Ol+Opx+Cpx+Ga
				Ga	23.0	1.7	—	4.9	—	
1500	33.8	0.33	Pt	Opx	4.8	—	5.2	2.3	Minor	Ol+Opx+Cpx+Ga
1500	36.0	0.33	Pt	Opx	3.9	—	5.5	2.3	Common	Ol+Opx+Cpx+Ga
				Ga	> 16	—	≈ 8.0	≈ 4.3	—	
				Whole sample-centre	6.1	—	7.0	5.2	—	
1450	27.0	1.0	Pt	Opx	5.4	—	4.2	2.3	Nil	No identifiable melting, Ol+Opx+Cpx
				Ol	0.1	—	8.6	0.3	—	
1400	22.5	0.66	Pt	Opx	3.9-5.1	—	4.8-5.7	2.4	Nil	Local patchy melting, Ol+Opx+Cpx
1400	24.8	1.0	Pt	Opx	4.3	—	5.1	2.4	Nil	Minor melting ?water access, Ol+Opx+Cpx
1400	25.9	1.0	Pt	Opx	5.0	0.8	5.6	2.2	Nil	No identifiable melting, Ol+Opx+Cpx
				Cpx	≥ 5.1	> 1.0	—	≥ 10.0	—	No identifiable melting, Ol+Opx+Cpx+Ga
1400	27.0	1.0	Pt	Opx	5.5	—	5.8	2.1	Trace	
				Cpx	6.6	—	4.8	11.4	—	
				Ga	22.0	1.7	6.8	5.3	—	
1350	24.8	2.0	Graphite	Opx	6.1	—	7.0	2.1	Nil	No garnet, no melting, Ol+Opx+Cpx
				Cpx	7.7	—	5.8	14.5	—	
				Ol	≤ 0.2	—	11.6	≤ 0.2	—	
1350	25.9	2.0	Graphite	Opx	5.5	—	7.1	2.1	Minor	No melting, Ol+Opx+Cpx+Ga
				Cpx	7.3	—	5.6	14.5	—	
				Ol	≤ 0.6	—	12.0	≤ 0.4	—	
				Ga	≥ 20.2	—	7.9	6.9	—	
1350	27.0	2.0	Graphite	Opx	4.9	—	7.1	1.9	Minor	No melting, Ol+Opx+Cpx+Ga
				Cpx	6.7	—	5.4	≥ 14.1	—	
1300	36.0	4	Graphite	Opx	2.6	—	7.2	1.5	Common	Ol+Opx+Cpx+Ga
				Cpx	4.6	—	4.7	≥ 13.9	—	
				Ol	≤ 0.3	—	12.5	≤ 0.2	—	
				Ga	23.5	—	8.2	4.3	—	
1300	40.5	4	Graphite	Opx	2.2	—	7.2	1.5	Common	Ol+Opx+Cpx+Ga
				Ga	≥ 20.9	—	8.7	5.6	—	
Pyrolite I less 50% olivine										
1400	22.5	1	Pt	Opx	3.0	—	4.2	2.2	Nil, uncommon spinel	Minor melting, Ol+Opx+Cpx+spinel
1400	24.8	1	Pt	Opx	5.9	—	5.0	2.1	Trace garnet, uncommon spinel	No melting, Ol+Opx+Cpx+Ga+spinel

Fig. 2.  $2\% \text{Al}_2\text{O}_3$  and 1  
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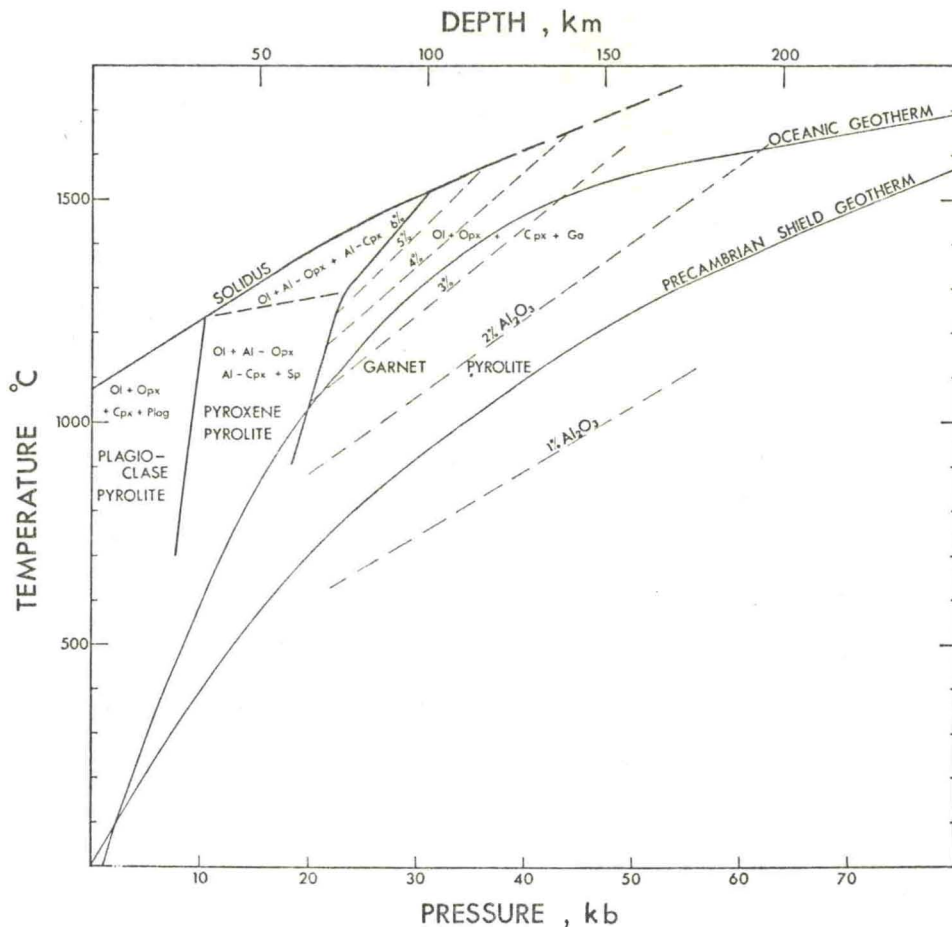


Fig. 2. Diagram illustrating the  $P, T$  fields of different mineral assemblages in pyrolite III composition. The figures 1% $\text{Al}_2\text{O}_3$ , 2% $\text{Al}_2\text{O}_3$  etc. refer to the  $\text{Al}_2\text{O}_3$  content of orthopyroxene in equilibrium with garnet in the garnet pyrolite field. The oceanic and Precambrian shield geotherms are those illustrated by RINGWOOD *et al.* (1964). (From GREEN and RINGWOOD, 1967a.)

roxenes + spinel field but such curves, combined with data on the pyroxene miscibility gap, will ultimately provide a very useful means of estimating the  $P, T$  conditions of equilibration of natural spinel and garnet pyrolite (O'HARA, 1967). With variation in bulk composition, the conditions for appearance of garnet will vary; compositions with higher  $\text{Al}_2\text{O}_3$ /pyroxene ratio will yield spinel up to solidus temperatures and garnet will appear at 23–24 kb at the solidus. For a bulk composition such that, with all  $\text{Al}_2\text{O}_3$  in pyroxenes, the orthopyroxene would contain only 3.0%  $\text{Al}_2\text{O}_3$ , then spinel would be expected to disappear above 1000 °C, 10–18 kb and there would be a greatly expanded field of olivine and aluminous pyroxenes. Garnet would not appear on the solidus of such a composition until pressures of approximately 60 kb.

#### 4. Mineralogy in a pyrolite upper mantle

In the following discussion, it is assumed that the average composition of the upper mantle beneath oceanic and geologically "young" regions is that of pyrolite III. In continental regions and particularly in Precambrian shield regions, there is probably a much greater proportion of refractory residual peridotite at shallower levels and the upper mantle may be chemically zoned. Mineralogical variation in the upper oceanic mantle is thus determined by the intersection of geothermal gradients with the stability fields of fig. 1. The variation of temperature in the continental and oceanic crusts and upper mantle has been discussed by CLARK (1962) and CLARK and RINGWOOD (1964). It is clear from these papers that there is a large difference

Minor melting, Ol + Opx + Cpx + spinel  
 No melting, Ol + Opx + Cpx + Ga + Spinel  
 Nil, uncommon spinel  
 Trace garnet, uncommon spinel  
 2.2  
 2.1  
 4.2  
 5.0  
 —  
 —  
 3.0  
 5.9  
 Opx  
 Opx  
 Pt  
 Pt  
 1  
 1  
 22.5  
 24.8  
 1400  
 1400



between oceanic and stable shield geotherms and that this difference takes the form illustrated in fig. 2. Nevertheless, the specific form of the curves, particularly their "convexity" and closeness of approach to the pyrolite solidus, depend sensitively on knowledge of the magnitude of radiative heat transfer in the upper mantle. No unique solution for geothermal gradients is currently possible but a general evaluation of the rôle of mineralogical zoning in the upper mantle can best be obtained by consideration of the two examples in fig. 2.

Along the Precambrian shield geotherm, the probability of chemical zoning would limit the possible phase assemblages. If rocks of composition approaching pyrolite occur locally, then there may be an extremely limited zone near the base of the crust where these would crystallize to olivine + orthopyroxene (1%  $\text{Al}_2\text{O}_3$ ) + clinopyroxene + spinel assemblages. Similar compositions below about 35–40 km would yield olivine + orthopyroxene (1–2%  $\text{Al}_2\text{O}_3$ ) + clinopyroxene + garnet assemblages and it may be noted that the garnet content would be relatively high (e.g. 12% garnet in pyrolite III composition). No regular change in mineralogy would occur for rocks of pyrolite composition along the Precambrian shield geotherm.

The picture is very different along the oceanic geotherm. The olivine + orthopyroxene + clinopyroxene + spinel assemblage is stable in pyrolite composition to depths of 60–70 km. Within this interval the amount of spinel would decrease and the  $\text{Al}_2\text{O}_3$  content of pyroxenes would increase with increasing depth (reaction (2)). Prior to the incoming of garnet at 60–70 km and about 1000 °C, aluminous spinel would coexist with orthopyroxene containing about 3%  $\text{Al}_2\text{O}_3$ . An intersection of the geotherm with the phase boundary at a higher temperature than that illustrated in fig. 2 would yield assemblages with less spinel and with orthopyroxene of higher  $\text{Al}_2\text{O}_3$  content (4–5%  $\text{Al}_2\text{O}_3$ ).

An extremely steep geothermal gradient, possibly realized only in regions actively producing basaltic magmas, would be required to enter the olivine + aluminous enstatite (6%  $\text{Al}_2\text{O}_3$ ) + aluminous clinopyroxene field. In regions of partial melting and magma generation, such gradients must be attained and it may be noted that garnet does not appear on the pyrolite III (anhydrous) solidus until depths > 100 kms are reached.

At depths of 60–70 km on the oceanic geotherm,

garnet appears from reaction (1) and is in equilibrium with orthopyroxene containing about 3%  $\text{Al}_2\text{O}_3$ . It is estimated that about 6% garnet would appear in pyrolite III composition at 60–70 km on the geothermal gradient illustrated. If the geothermal gradient intersected the boundary at a higher temperature, the amount of garnet appearing would be correspondingly less, e.g. about 3–4% garnet coexisting with orthopyroxene containing about 4.5%  $\text{Al}_2\text{O}_3$ .

The incoming of garnet due to reaction (1) at about 60–70 km in the oceanic mantle probably occurs over a relatively small depth interval (5–15 km). With further penetration along the geotherm into the garnet pyrolite field the amount of garnet may actually *decrease* – this will occur for temperature gradients steeper than the lines of constant  $\text{Al}_2\text{O}_3$  content of orthopyroxene shown in fig. 2. For the gradient shown, pyrolite III will contain about 5% garnet at depths between 90 and 120 km and the mineralogy will remain constant over this interval. At depths greater than 120 km the geothermal gradient becomes increasingly transgressive to the lines of constant  $\text{Al}_2\text{O}_3$  content for orthopyroxene. Thus, along this part of the geothermal gradient, the aluminous pyroxenes will gradually break down to yield an increasing garnet content and low-alumina pyroxenes. At depths of 200–250 km the assemblage of pyrolite III will probably contain 11–12% of garnet.

The transition from aluminous pyroxenes + spinel pyrolite to garnet pyrolite at depths of 60–70 km in the oceanic mantle is in agreement with MACGREGOR'S (1964) data and with the conclusions of ITO and KENNEDY (1967) on the stability of spinel and garnet-bearing peridotite. Although the present work does not support earlier conclusions (RINGWOOD *et al.*, 1964; MACGREGOR and BOYD, 1964) that garnet pyrolite would not in general be stable until depths of 120–150 km, it provides excellent confirmation of the importance at this depth interval of the breakdown of aluminous pyroxenes to garnet + low alumina pyroxenes, the reactions on which these earlier conclusions were based. It should be pointed out that for pyrolite-like compositions with higher pyroxene/(Al, Cr) $_2\text{O}_3$  ratios than pyrolites I, II and III, the field of garnet pyrolite may not be entered until depths in excess of 120 km are reached – this is particularly relevant for mantle regions from which basaltic fractions have been removed (cf. MACGREGOR, 1967). Geothermal gradients steeper than that

Fig. 3. Diagram along the oceanic geotherm.

illustrated amount of reaction (1) produced at depth.

This brief description of our model of mantle chemical zoning along the oceanic geotherm is illustrated by the variations of mineralogy discussed by GREEN and RINGWOOD (1967) reproduced in fig. 3.

The present model of mantle chemical zoning along the oceanic geotherm is illustrated by the variations of mineralogy discussed by GREEN and RINGWOOD (1967) reproduced in fig. 3. The present model of mantle chemical zoning along the oceanic geotherm is illustrated by the variations of mineralogy discussed by GREEN and RINGWOOD (1967) reproduced in fig. 3.



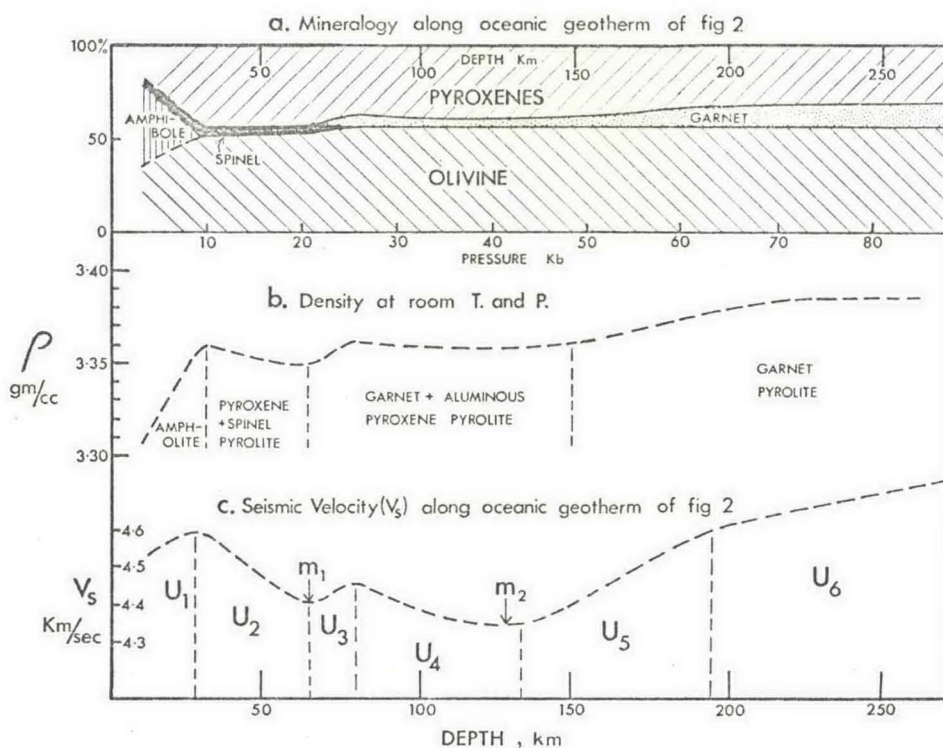


Fig. 3. Diagram illustrating the changes in mineralogy, density (room *T* and *P*) and the relative changes in seismic velocity ( $V_s$ ) along the oceanic geotherm. The mantle is assumed to be of pyrolite III composition and the critical gradient  $(\partial T/\partial P)_{V_s} = 4.5^\circ\text{C}/\text{km}$ . (From GREEN and RINGWOOD, 1967a.)

illustrated will have a similar effect in diminishing the amount of garnet produced at 60–70 km depth by reaction (1) and increasing the amount of garnet produced at deeper levels from reaction (3).

This brief discussion serves to illustrate the application of our experimental data to a more flexible range of mantle compositions and geothermal gradients than implied in fig. 2. The effects of the mineralogical variation along the oceanic geothermal gradient in causing variations of seismic velocity have been previously discussed by GREEN and RINGWOOD (1967a) and fig. 3 is reproduced from this paper.

The previous discussion and the data presented in fig. 3 illustrate the principle that both mineralogical changes and *P, T* effects on  $V_s$  are of primary importance in determining seismic velocity distributions in the upper mantle and may in themselves produce velocity minima in the upper 200 km of the mantle. Variations from the seismic velocity distributions illustrated in fig. 3 may be set up from fig. 2 by assuming various geothermal gradients and including the complexity of

chemical variation from pyrolite to refractory peridotite and dunite.

### 5. Amphibole stability, partial melting and the low velocity zone

The mineralogical variations illustrated in fig. 3 may produce  $V_s$  variations of approximately 2% but these are inadequate to account for a low velocity zone with a  $V_s$  minimum of 4.1 km/sec below the uppermost mantle "lid" with  $V_s \approx 4.6$  km/sec (ANDERSON, 1967; BERRY and KNOPOFF, 1967). Other analyses of seismic data have inferred high values of seismic attenuation in the low velocity zone (ANDERSON, 1962, 1967), or have inferred very low values of shear modulus for the low velocity zone (HALES and DOYLE, 1967). These considerations have led a number of authors to suggest that the low velocity zone of the mantle owes its existence to partial or incipient melting (ANDERSON, 1962, 1967; OXBURGH and TURCOTTE, 1968; AKI, 1967). LAMBERT and WYLLIE (1968) carried out experiments aimed at establishing the high pressure stability limit



of amphibole for  $P_{\text{H}_2\text{O}} = P_{\text{total}}$  and suggested that the existence of interstitial amounts of water-rich fluid phase or water-rich silicate melts at depths below the stability limit of amphibole would lead to low seismic velocities. At greater depths, incorporation of water into high pressure hydrous magnesian silicates and hydroxylated pyroxenes (RINGWOOD and MAJOR, 1967; SCLAR *et al.*, 1967) would produce a lower depth limit to this feature. The temperature of formation of magmas in the zone of amphibole instability and free water would be considerably below the anhydrous pyrolite solidus.

The data on maximum amphibole stability in pyrolite presented here in support this hypothesis and suggest that amphibole would be stable along the shield geotherm of fig. 2 to depths of approximately 100–120 km and along the oceanic geotherm to depths of 80–90 km. The latter estimates derive from the data of table 3 and appearance of amphibole in pyrolite runs at 1200 °C, 18 kb and 22.5 kb, unless stringent precautions against drying of furnace components are observed.

RINGWOOD (1969) inferred a water content for the upper mantle of around 0.1% and  $\text{CO}_2$  contents may also be significant. The presence of a fluid phase, even if  $P_{\text{H}_2\text{O}} < P_{\text{total}}$ , will depress the beginning of melting of pyrolite, probably by as much as 200 °C. RINGWOOD (1969) has presented arguments that a limited water content of around 0.1% will have the effect of buffering a condition of incipient melting ( $\approx 1\%$  melting) so that comparatively large changes in temperature will have little effect on the amount or nature of the melt formed – this condition would not apply for melting of anhydrous pyrolite (GREEN and RINGWOOD, 1967a). The nature of hydrous magmas in equilibrium with olivine, orthopyroxene, clinopyroxene and garnet has been shown to be highly undersaturated olivine-rich basanite (GREEN, 1969, 1970) or possibly olivine-rich nephelinite and olivine melilite nephelinite (BULTITUDE and GREEN, 1968). Thus it is inferred that regions with a relatively shallow (80–120 kms) low velocity zone with proportionately large velocity decrease owe these characteristics to the presence of very small amounts of partial melting. The liquids formed by degrees of melting up to about 5% are highly undersaturated basanites and nephelinites and extraction of such liquids will leave regions of the low velocity zone selectively depleted in elements strongly partitioned into the initial liquid.

Movement of magma batches through overlying mantle may lead to breakdown of hydrous phases and selective element depletion by “wall rock reaction” processes (GREEN and RINGWOOD, 1967b; GREEN, 1970). Models of mantle evolution such as those of OXBURGH and TURCOTTE (1968) and RINGWOOD (1969) would also lead to regions of the mantle overlying the low velocity zone which were partially or completely depleted in basaltic components.

## 6. Conclusions

Reactions producing garnet or garnet + olivine from assemblages with aluminous pyroxenes or pyroxenes + spinel are complex, involving sensitively  $P$ ,  $T$  dependent solid solution of  $\text{R}_2\text{O}_3$  components in pyroxene. There is a need for further experiments to confirm data presented for several simple systems and natural assemblages and to evaluate the role of  $\text{Cr}_2\text{O}_3$  and other components on the phase boundaries. The experimental study of the relations between pyroxene pyrolite and garnet pyrolite for the model mantle composition of RINGWOOD (1966a) has established reversals for this boundary at key temperatures and enables application of these studies to evaluation of upper mantle mineralogy.

Pyroxene + spinel pyrolite is stable to depths of 60–70 km along an estimated sub-oceanic geothermal gradient. At this depth spinel and pyroxene react to form garnet and olivine. The amount of garnet formed from this reaction depends sensitively upon the temperature at which the geotherm intersects the spinel + pyroxene  $\rightleftharpoons$  garnet + olivine boundary. At temperatures in excess of 1000 °C, less than half the potential garnet in the pyrolite compositions forms by this reaction, the rest remaining in solid solution in aluminous orthopyroxene ( $> 3\% \text{Al}_2\text{O}_3$ ) and aluminous clinopyroxene. It has been demonstrated that mineralogical variation along geothermal gradients, particularly in oceanic regions, may be expected to strongly influence the seismic velocity distribution in the upper mantle. No unique model of mineralogical or seismic velocity distribution in the upper mantle is presented, rather it is argued that regional variations in chemical composition (from pyrolite to refractory peridotite), and in geothermal gradients will produce significant, regional differences in seismic velocity distributions.

Although mineralogical variation in anhydrous py-

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rolite may cause the existence of a low velocity zone, the alternate explanation of a zone of incipient or minor partial melting is preferred. The presence of this zone is inferred to result from the presence of small ( $\approx 0.1\%$ ) quantities of water in the mantle, and from the instability of the hydrous phase amphibole at depths greater than about 80 km. The presence of a fluid, water-rich phase in limited quantity produces incipient melting well below the anhydrous pyrolite solidus. Liquids produced in this way are highly undersaturated basanites and nephelinites.

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