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D. H. GREEN and A. E. RINGWOOD

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THE STABILITY FIELDS OF ALUMINOUS PYROXENE PERIDOTITE AND GARNET PERIDOTITE AND THEIR RELEVANCE IN UPPER MANTLE STRUCTURE

D. H. GREEN and A. E. RINGWOOD

Department of Geophysics and Geochemistry, Australian National University

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An experimental study of the stability fields at high pressure of garnet peridotite and aluminous pyroxene peridotite has been carried out in compositions matching estimates of the average, undifferentiated upper mantle (pyrolite). The appearance of garnet at higher pressures in the pyrolite compositions results from either of two reactions: (1) spinel + orthopyroxene \leq olivine + garnet

(2) aluminous pyroxene ≒ garnet + pyroxene (lower alumina).

The role of spinel in the lower pressure assemblages is sensitively dependent on temperature and bulk composition. For the pyrolite composition preferred for the upper mantle, spinel is absent above 1300°C and the first appearance of garnet at pressures of 24 kb (1300°C) to 31 kb (1500°C) is due to reaction (2). In this composition garnet does not appear on the pyrolite solidus nor in its melting interval at pressures below 31.5 kb.

At temperatures less than 1300°C, garnet appears at 21 kb (1100° C) to 24 kb (1300° C) and develops by reaction (1) at the expense of spinel. The amount of garnet formed by this reaction is dependent on the alumina content of the pyroxenes and throughout the temperature range $1100-1500^{\circ}$ C the amount of garnet present increases markedly with increasing pressure within the garnet peridotite field. Microprobe analyses of orthopyroxenes demonstrate that this is matched by decreasing A1₂O₃ content of the pyroxenes and allow preliminary estimation of *P*, *T*-dependent curves of constant A1₂O₃ content for orthopyroxene in garnet peridotite assemblages.

The experimental data are applied to estimate density and seismic velocity variations along oceanic and continental geothermal gradients in a pyrolite upper mantle. It is emphasized that seismic velocity distributions are sensitively affected by variations in geothermal gradient and by mantle chemical composition, e.g. by variation from pyrolite to residual, refractory, dunite-peridotite. It is suggested that seismic velocity (V_s) variation in an oceanic upper mantle of pyrolite composition may be characterized by two low-velocity channels:

- a narrow, but sharply defined low-velocity zone at 60-70 km depth caused by mineralogical zoning in the upper mantle;
- (2) a broader low velocity zone at 120-150 km depth defined primarily by the critical gradient for V_8 in the upper mantle but accentuated by mineralogical variations in pyrolite.

1. INTRODUCTION

In previous papers we have advanced arguments for specific model compositions for the peridotite upper mantle [1-4] and have used the term "pyrolite" for these deduced mantle compositions. On theoretical grounds and on the evidence of natural rocks approaching the pyrolite composition, it has been demonstrated that pyrolite may crystallize in four different mineral assemblages within the P,T conditions of the upper mantle. These mineral assemblages are as follows [2-4]:

a. Olivine + amphibole ± enstatite ("ampholite")

b. Olivine + pyroxenes + plagioclase ("plagioclase pyrolite")

 c. Olivine + aluminous pyroxenes ± spinel ("pyroxene pyrolite")

 d. Olivine + pyroxenes + garnet ("garnet pyrolite"). The stability relationships of these assemblages in model pyrolite composition have been experimentally investigated in our laboratory and the present letter explores the implications of this study on mineralogical and seismic velocity variations in the upper mantle.

2. EXPERIMENTAL METHOD

The ultramafic compositions used in the investigation are listed in table 1.

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$\begin{array}{c c c c c c c c c c c c c c c c c c c $		0.58 4.01	0.57	0.71
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		4.01	2.00	
$\begin{array}{c cccccc} Cr_2O_3 & 0.42 & 0.41 & 0.43 \\ Fe_2O_3 & 0.35 & 0.75 & 0.48 \\ FeO & 7.88 & 7.50 & 8.04 \\ MnO & 0.13 & 0.13 & 0.14 \\ NiO & 0.39 & 0.39 & 0.20 \\ MgO & 39.54 & 39.00 & 37.48 \\ CaO & 2.67 & 2.60 & 3.08 \\ CaO & 0.61 & 0.60 & 0.57 \\ Na_2O & 0.22 & 0.22 & 0.13 \\ \hline 100 \ Mg \ atomic ratio & 89.9 & 90.3 & 89.2 \\ \hline \end{array}$			3.88	3.54
$\begin{array}{c ccccc} & 0.35 & 0.75 & 0.48 \\ FeO & 7.88 & 7.50 & 8.04 \\ MnO & 0.13 & 0.13 & 0.14 \\ NiO & 0.39 & 0.39 & 0.20 \\ MgO & 39.54 & 39.00 & 37.48 \\ CaO & 2.67 & 2.60 & 3.08 \\ CaO & 0.61 & 0.60 & 0.57 \\ Na_2O & 0.61 & 0.60 & 0.57 \\ K_2O & 0.22 & 0.13 \\ \hline \hline 100 \ Mg \ atomic ratio & 89.9 & 90.3 & 89.2 \\ \hline \end{array}$		0.42	0.41	0.43
10203 FeO7.887.508.04MnO0.130.130.14MnO0.390.390.20NiO39.5439.0037.48CaO2.672.603.08Na2O0.610.600.57K2O0.220.220.13		0.35	0.75	0.48
MnO 0.13 0.13 0.14 MnO 0.39 0.39 0.20 NiO 39.54 39.00 37.48 CaO 2.67 2.60 3.08 Na ₂ O 0.61 0.60 0.57 K ₂ O 0.22 0.22 0.13		7.88	7.50	8.04
NiO 0.39 0.39 0.20 MgO 39.54 39.00 37.48 CaO 2.67 2.60 3.08 Na ₂ O 0.61 0.60 0.57 K ₂ O 0.22 0.22 0.13	1.1	0.13	0.13	0.14
MgO 39.54 39.00 37.48 MgO 2.67 2.60 3.08 CaO 0.61 0.60 0.57 Na2O 0.22 0.22 0.13 100 Mgatomic ratio 89.9 90.3 89.2		0.39	0.39	0.20
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CaO 0.61 0.60 0.57 Na ₂ O 0.22 0.22 0.13 100 Mg atomic ratio 89.9 90.3 89.2		2.67	2.60	3.08
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$\frac{100 \text{ Mg}}{M_{\odot} + E_{\odot}^{+\pm}} \text{ atomic ratio} \qquad 89.9 \qquad 90.3 \qquad 89.2$	at a range further with	0.22	0.22	0.13
Mg + Fe.	atomic ratio	89.9	90.3	89.2
CIPW Norm	m	wite mercu at higher daments	The side of the state of the	in har the pyreshing
Or 1.1 0.8	AR Distancement of the	1.1	1.1	0.8
Ab 5.2 5.2 5.0		5.2	5.2	5.0
An 7.5 7.3 6.6	and we have the first of	7.5	7.3	6.6
Di 4.6 4.3 6.8	an an internet and a part of the	4.6	4.3	6.8
Hy 3.8 9.4 15.8	sampled trees of the range	3.8	9.4	15.8
OI 75.6 69.8 62.5	which is a strain product	75.6	69.8	62.5
IIm 1.1 1.1 1.3	AN REAL DRIVEN AND ALL	1.1	1.1	1.3
Mt 0.5 1.2 0.7		0.5	1.2	0.7
Chr. 0.6 0.6 0.6	president o grads hears	0.6	0.6	0.6

Chemical compositions and CIPW norms of model pyrolite compositions used in experimental runs.

Table 1

Pyrolite I and pyrolite III refer to the model compositions calculated by Green and Ringwood [2] and Ringwood [3], respectively. They differ principally in their MgO/SiO2 ratios and thus in pyroxene/ (A1,Cr)₂O₃ 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 R₂O₃ content. The experimental compositions were prepared from AR grade chemicals, carefully ground and reacted together under high temperature reducing conditions and then analyzed for FeO and Fe₂O₃ contents. The initial mixes were extremely finegrained $(\leq 1 \text{ micron})$ and consisted of olivine, clinopyroxene, orthopyroxene and plagioclase. 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 [Mg91.5Fe8.0Ni0.4Mn0.1] from pyrolites I

and II and after extraction of 40% olivine [Mg91.6Fe8.1Ni0.2Mn0.1] from pyrolite III. In all experiments conducted with these modified pyrolite compositions, excess olivine was present as a stable phase. 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 [5,6] and a pressure correction of -10% was applied to the nominal pressure for all runs [7]. Samples were run in both platinum capsules and in graphite capsules. In seeking to determine the solidus for the pyrolite composition it was found that the graphite capsules, while preventing Fe-loss from the sample to capsule walls, gave poorly reproducible results and indicated anomalously low temperatures for the beginning of melting. Using the dry furnace assemblies with talc + boron nitride pressure media [6,8] welded platinum capsules gave satisfactory results for the solidus determinations. The magnitude of Fe-loss from the sample in these runs, was quantitatively determined and found to be of minor importance. In subsolidus experiments the results of runs in graphite and in platinum capsules were mutually consistent.

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



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.

obtained on olivine, clinopyroxene and garnet compositions. Microprobe analyses for Fe, Ca, A1 and Cr were carried out by the methods previously reported [9] using glasses of orthopyroxene composition, analyzed olivines and anlyzed garnets as standards.

3. EXPERIMENTAL RESULTS

The results of the determination of the stability field for garnet 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 a stable phase 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 is stable in pyrolite III but olivine + aluminous pyroxenes + garnet is stable in pyrolites I and II.

The microprobe analyses so far carried out clearly demonstrate the important role that $(Ca,Mg)Al_2SiO_6$ solid solution in the pyroxenes plays in determining the phase assemblages. The Al₂O₃ contents of orthopyroxene in some of the runs are listed in table 2. The orthopyroxene at 1500°C also contains 0.7 - 0.9% Cr_2O_3 in solid solution. Co-existing clinopyroxene contains higher Al₂O₃ and Cr_2O_3 content but this is largely due to NaR⁺⁺⁺Si₂O₆ solid solution in the clinopyroxene. Neglecting the sodic pyroxene have very similar degrees of (Ca,Mg)Al₂SiO₆ solid solution. The orthopyroxenes crystallizing above 1300°C and lying on the boundary LF contain $6.0 \pm 0.2\%$ Al₂O₃.

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Table 2

Pressure	Temperature (°C)	A120 orth (weig	O3* content of opyroxene ght percent)	Garnet content of assemblage	Spinel				
Pyrolite III									
24.8	1350	×	6.1	nil	nil				
25.9	1350		5.5	minor	nil				
27.0	1350		4.9	minor	nil				
36.0	1300	a frankriger	2.6	common	nil				
40.5	1300	align a sale	2.2	common	nil				
30.4	1500		5.9	trace	nil				
31.5	1500	a line inte	5.6	minor	nil				
33.8	1500		4.8	minor	nil				
36.0	1500		4.2	common	nil				
Pyrolite I	Strach - May I Besser Re	and the party							
24.8	1400		5.9	trace	minor				

Alumina content of orthopyroxene in equilibrium with garnet in high pressure experimental runs

* Estimated accuracy, ±5% of amount present.

Preliminary curves denoting the maximum Al_2O_3 content of orthopyroxene in equilibrium with garnet in pyrolite compositions may be derived from the data of table 2 and have been shown in fig. 2.

The cause of the break in slope of the boundary ELF lies in the different equilibria involved in the formation of garnet along the curve. At temperatures below L, aluminous spinel is present in the assemblage and is in equilibrium with orthopyroxene containing $A1_2O_3 < 6.0\%$. The first appearance of garnet from this assemblage involves reaction between spinel and pyroxenes [10] and the idealized reaction is as follows:

(1) $MgA1_2O_4 + 4 MgSiO_3 \Rightarrow Mg_3Al_2Si_3O_{12}$ spinel enstatite pyrope

> + Mg₂SiO₄ forsterite

In contrast, spinel is absent above 1300° C in pyrolite III composition and the $A1_2O_3$ content of the mix is entirely in solid solution in the pyroxenes. In this assemblage the orthopyroxene contains 6% $A1_2O_3$ (weight percent) and the clinopyroxene contains > 6% $A1_2O_3$. Garnet appears from this assemblage when the load pressure is sufficient to cause the aluminous pyroxenes to break down in favour of garnet + less-aluminous pyroxene [11, 12]. Thus the simplified reaction for the appearance of garnet in pyrolite III composition along LF is as follows:

(2) m MgSiO₃ • n MgA1₂SiO₆ ≈ Mg₃A1₂Si₃O₁₂ aluminous enstatite solid pyrope solution

> + (m-2)MgSiO₃ • (n-1)MgA1₂SiO₆ enstatite solid solution

The different roles of reactions involving spinel and those involving aluminous pyroxenes are in harmony with previous work on simple systems [10-14]. The boundary EJ (fig. 1) is almost identical to that established by MacGregor [10] for reaction (1) in the pure spinel + 4 enstatite system, provided that a -10% pressure correction is applied to MacGregor's data. The boundary LF representing assemblages containing garnet in equilibrium with orthopyroxene $(6.0\% A1_2O_3)$ is similar in slope to analogous boundaries in the pure magnesian system, enstatite + pyrope [12] and the natural, simple system enstatite + chromiferous pyrope garnet [11]. However, at a given pressure and temperature, the A12O2-content of orthopyroxene in equilibrium with garnet in the complex pyrolite composition is substantially less than that obtained in the

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Fig. 2. Diagram illustrating the P, T fields of different mineral assemblages in pyrolite III composition. The figures 1%A1₂O₃, 2%A1₂O₃ etc. refer to the A1₂O₃ 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. [13].

simple 2-component systems. This effect is attributed to differences in garnet and pyroxene composition, possibly relating particularly to Ca and Cr contents and the presence of clinopyroxene, between the two component and complex systems. The persistence of spinel to around 1300°C in the pyrolite composition contrasts with its anticipated absence above 1000°C predicted by Ringwood et al. [13] and is also attributed to chemical or coupled reaction effects in the complex composition.

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. 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 [3,4]. Mineralogical variation in the upper mantle is 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 [15] and Clark and Ringwood [16]. It is clear from these papers that there is a large difference 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 their closeness of approach to the pyrolite solidus, depend sensitively on knowledge of

the magnitude of radiative heat transfer in the upper mantle. Clark and Ringwood [16] assumed an opacity of about 5 cm⁻¹ and obtained geotherms about 200°C lower at 150-200 km and 100°C lower at 100 km than those in fig. 2. Ringwood, MacGregor and Boyd [13] and Ringwood [4] assumed a higher opacity for the upper mantle and qualitatively obtained the geotherms which we illustrate in fig. 2. No unique solution for geothermal gradients is currently possible but a general evaluation of the role 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 [1,3] would limit the possible phase assemblages. If rocks of composition approaching pyrolite composition occur locally, then there may be an extremely limited zone near the base of the crust where these would crystallize to olivine + orthopyroxene $(1\%A1_2O_3)$ + clinopyroxene + spinel assemblages. Similar compositions below about 35-40 km would yield olivine + orthopyroxene (1-2% $A1_2O_3)$ + 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 (c.f. refs. [13,14]).

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 [14]. Within this interval the amount of spinel would decrease and the $A1_2O_3$ content of pyroxenes would increase with increasing depth (reaction 3):

(3) MgA1₂O₄ + m MgSiO₃ spinel enstatite

> \Rightarrow (*m*-2)MgSiO₃ · MgA1₂SiO₆ + Mg₂SiO₄ aluminous enstatite olivine

Prior to the incoming of garnet at 60-70 km and about 1000°C, aluminous spinel would co-exist with orthopyroxene containing about 3% Al₂O₃. 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 Al₂O₃ content (4-5% Al₂O₃). An extremely steep geothermal gradient, possibly realized only in regions actively producing basaltic magmas, would be required to enter the olivine + aluminous enstatite $(6\% A1_2O_3)$ + aluminous clinopyroxene field. This is a principal point of difference between the present results and earlier conclusions [13,14,4] and stems from the persistence of spinel to higher temperatures in the complex composition than that predicted by study of the two component systems.

At depths of 60-70 km on the oceanic geotherm, garnet appears from reaction (1) and is in equilibrium with orthopyroxene containing about 3% A1₂O₃. 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 co-existing with orthopyroxene containing about 4.5% A1₂O₃.

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 A12O3 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 A1₂O₃ 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 data [10] and with the conclusions of Ito and Kennedy [17] on the stability of spinel and garnetbearing peridotite. Although the present work does not support earlier conclusions [13, 14] 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/ $(A1,Cr)_2O_3$ 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. Geothermal gradients steeper than that 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 (2).

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.

5. VARIATION OF SEISMIC VELOCITY WITH DEPTH IN THE UPPER MANTLE

Seismic velocity distributions in the upper mantle will be principally determined by

- 1. The effects of pressure and temperature changes along the geothermal gradient. Previous authors [18-21] have discussed the opposing effects of temperature increase (causing seismic velocity to decrease) and pressure increase (causing seismic velocity to increase) along a geothermal gradient and concluded that, in homogeneous upper mantle material, seismic velocities V_s and V_p should initially decrease to a minimum and then increase with increasing depth in the upper mantle.
- 2. The effects of mineralogical variation in the upper mantle. Although later data on the solidus curves for basalts and peridotite have removed some of the reasons for Ringwood's [1] postulate of mineralogical zoning in the upper mantle, experimental evidence on mineral reactions in peridotitic compositions has confirmed the high probability of such effects in the upper mantle.
- 3. The effects of vertical chemical fractionation of the upper mantle such that some regions may be mainly residual, refractory dunite and peridotite, depleted of low melting components now residing in overlying crustal levels. These effects have been discussed elsewhere [1,3,16] and are probably of

greatest significance in mantle regions beneath stable continental shields.

From the data presented in previous sections it is possible to examine qualitatively the effects of the first and second factors in determining seismic velocity along the oceanic geotherm illustrated in fig. 2. It is emphasized that this exercise is of an illustrative nature and no special significance is claimed for the geotherm assumed for fig. 2 or the absolute values of seismic velocities (V_s) estimated in fig. 3.

Fig. 3a is a quantitative expression of the change in mineralogy along the oceanic geotherm, as discussed in the previous section. At depths less than 30 km it is assumed that amphibole may be an important phase in the oceanic upper mantle [2,4]. The effects of these assemblages on density (room T and P) and seismic velocity (V_s) are qualitatively estimated in figs. 3b and 3c. A principal reason for suggesting an amphibolite zone (U_1) at the top of the oceanic mantle is the seismological evidence for an initial *increase* in seismic velocity with depth just below M [18, 22].

In estimating seismic velocity variation with depth it is necessary to know the critical temperature gradient $(\partial T/\partial P)V_s$ for which the seismic velocity V_s remains constant, the opposing pressure and temperature effects just cancelling each other. In the past, critical gradients for V_s of around 6-10°C/km have been predicted on theoretical grounds but Schreiber and Anderson [23] have recently measured critical gradients for V_s in MgO of 2.7°C/km and in A1₂O₃ of 2.1°C/km, values which are considerably lower than those previously assumed for the silicate minerals of the upper mantle. It is possible that the critical gradient for olivine may be somewhat higher than these values. In fig. 3c, a critical gradient for V_s of 4.5°C/ km has been assumed, this being the value which would produce a velocity minimum in homogeneous material at a depth of about 130 km along the oceanic geothermal gradient of fig. 2. The assumption of a smaller critical gradient would have the effect of increasing the depth of the velocity minimum. The superimposition of the mineralogical zoning effects and the P,T effects on $V_{\rm S}$ suggest a "fine structure" in the oceanic upper mantle seismic velocity distribution as follows:

a) Zone U₁. A zone in which the mineralogical variation due to decreasing amphibole content produces

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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 ($\partial T/\partial P$)_{V₀} = 4.5°C/km.

an increase in seismic velocity. This is sufficiently large to overcome the temperature effect tending to produce a decrease in seismic velocity.

- b) Zone U_2 . The mineralogical effect of decreasing spinel content produces a density decrease which *augments* the temperature effect, leading to relatively rapid decrease in V_8 with depth.
- c) Zone U_3 . A velocity increase is caused by the relatively large density change over a small depth interval caused by the reaction of spinel and pyroxene to yield garnet and olivine. This is sufficient to cancel the temperature effect in decreasing V_s and leads to the narrow but rather sharply defined velocity minimum (M_1) between zones U_2 and U_3 .
- d) Zone U_4 . The temperature effect on V_s is dominant but is augmented by slight decrease in garnet content and increase in aluminous pyroxene content (a density decrease). V_s thus decreases to a minimum value with the location of this determined by the critical temperature gradient $(\partial P/\partial T)V_s$ for the

upper mantle. If this is 4.5° C/km or thereabouts then the minimum lies above the zone of increasing garnet content (U₅).

- e) Zone U_5 . This is below the critical depth for the geotherm illustrated and increasing depth leads to increase in seismic velocity, even in a homogeneous medium. This is augmented by the mineralogical change in U_5 giving increased garnet content. Thus the rate of increase in seismic velocity with depth is more rapid, leading to a more sharply defined "floor" to the low velocity minimum between U_4 and U_5 .
- f) Zone U_6 . This is homogeneous in mineralogy and the seismic velocity increase is that determined by the P,T effect on V_s alone. Zone U_6 extends to about 350 km where a more rapid increase in seismic velocity marks the beginning of the Transition Zone of the mantle and may be attributed to increase of garnet at the expense of pyroxene by solid solution of pyroxene in garnet [24].

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The above discussion illustrates the principle that both mineralogical changes and P,T effects on $V_{\rm s}$ are of prime importance in determining the seismic velocity distribution within the upper mantle. Even without any effects of chemical zoning within the upper mantle it is apparent that variations in geothermal gradients will considerably affect the velocity distributions, particularly the depth of velocity minima, the magnitude of velocity differences and the presence of one or two low velocity channels in the upper mantle. Assuming a critical gradient of 4.5° C/km for V_s a broad low velocity channel at about 150-170 km depth might be expected along the shield geotherm of fig. 2. Similar models may be set up from fig. 2 by assuming various geothermal gradients and also including the additional complexity of chemical variation from pyrolite to refractory peridotite and dunite.

6. CONCLUSIONS

An experimental study of the equilibrium relations between pyroxene pyrolite and garnet pyrolite demonstrates that pyroxene + spinel pyrolite is stable in the sub-oceanic mantle to depths of 60-70 km. 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 ⇒ garnet + olivine boundary. At temperatures in excess of 1000°C, less than half the potential garnet in the pyrolite composition forms by this reaction, the rest remaining in solid solution in aluminous orthopyroxene (> 3% Al₂O₃) and aluminous clinopyroxene. At depths between 60-70 km and about 120 km, the garnet content of the pyrolite remains roughly constant or may decrease slightly as more Al₂O₃ goes into solid solution in the pyroxenes. At depths greater than 120-130 km the geothermal gradient enters a region in which, with increasing depth, the amount of garnet gradually increases as (Ca, Mg)Al₂SiO₆ solid solution in the pyroxenes decreases.

It is 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. In particular, mineralogical zoning of the upper mantle may yield two low velocity channels (for V_s) at depths of about 65 km and between 100 and 150 km respectively. 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.

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