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## Mineral Assemblages in a Model Mantle Composition

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Abstract. The primary chemical composition of the undifferentiated upper mantle is believed to be equivalent to that of a mixture of three parts of dunite to one part of basalt. Rocks approaching this model composition are herein called 'pyrolites.' A study is made of the mineralogy and geological environment of naturally occurring pyrolites. Such rocks occur as xenoliths in kimberlites and basalts and also in some intrusive peridotites. They are observed to crystallize in one of four distinct mineral assemblages: (1) olivine + amphibole, (2) olivine + plagioclase + pyroxenes, (3) olivine + aluminous pyroxenes + spinel, or (4) olivine +pyrope garnet + pyroxenes. Evidence regarding the geological occurrence and experimental stability of these assemblages is reviewed, and the relative P-T stability fields of the different assemblages are inferred. The ability of the pyrolite model composition to crystallize in a number of very distinct mineral assemblages controlled by pressure and temperature would lead to large-scale mineralogical zoning in the upper mantle. Such zoning will have an important effect on many properties of this region, particularly including the seismic velocities.

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1. Introduction. In a model for the upper mantle proposed by Ringwood [1962a, b], observed variations in seismic velocity were attributed to different mineral assemblages exhibited by a hypothetical primitive rock type which he named 'pyrolite.' It was suggested that pyrolite possessed the mean chemical composition of the upper mantle-crust system, being approximately equivalent to a mixture of four parts of dunite or peridotite to one part of basalt. Fractional melting of this parental material could therefore yield a basaltic magma, leaving residual dunite or peridotite.

The suggested 4:1 ratio was derived from a consideration of the chemical compositions of chondritic meteorites and their bearing on the chemical composition of the earth's mantle and core. This ratio is somewhat flexible, however, since it depends sensitively upon the amounts of Ca and Al which are assumed to remain in the residual durite or peridotite after fractionation. If the residual ultramafic component should be of duritic composition, and therefore very low in Ca and Al, then a 3:1 ratio would be more applicable. On the other hand, if the residual ultramafic component should be of peridotitic composition, somewhat higher in Ca, Al, and Si, than a ratio of 4:1 or 5:1 would be appropriate.

The suggested composition of pyrolite and its complementary components are set out in Table 1 We have chosen dunite,<sup>1</sup> rather than peridotite, as the refractory ultramafic component. The basalt composition used is the mean composition between the averaged normal tholeiite (column 2a) and normal alkali basalt (column 2b) [Nockolds, 1954]. These compositions of dunite and basalt have been combined in a 4:1 and a 3:1 ratio (columns 3 and 4, Table 1). For comparison, a mantle composition derived from a consideration of chondritic meteorites [Ringwood, 1959] is also tabulated (column 5). It is seen that the 3:1 ratio gives a closer match to the chondritic composition. In the following

<sup>1</sup>Hess [1938, 1955] has defined a peridotite type characteristically occurring in orogenic belts and possessing a very high Mg/Fe ratio. It is possible that peridotites of this type are tectonic slices or structurally exposed portions from the upper mantle [Hess, 1960b]. Unfortunately, because analyses of these peridotites show a water content of 10 per cent or more [Hess, 1938], the composition before serpentinization is uncertain. The analyses used to arrive at the average of Table 1 are of ultramafic rocks with this mode of occurrence but having water contents of 2 per cent or less. These analyses are from Dun Mountain, New Zealand [Reed, 1959]; Junsterklumpen, Sweden, [Du Rietz, 1935]; Amklovdalen, Norway [Stenvik, 1952]; and Musa Valley, Papua [Green, 1961]. With their absence of CaO, Na2O, and K2O and their low Al<sub>2</sub>O<sub>8</sub> contents, these dunites define a distinctive type that is consistent with a refractory

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		· Aver	age Basalt	Pyr	olite	
	(1)	(2a) Normal	(2b)	(3)	(4)	(5) Mantle Composition
	Average	Tholeiite	Normal Alkali	1:4 ratio	1:3 ratio	from Chondritic
	Anhydrous	[Nockolds,	Basalt [Nockolds,	of Basalt	of Basalt	Model [Ringwood,
	Dunite*	1954]	1954]	to Dunite	to Dunite	1959]
	%	%	%	%	%	%
SiO,	41.32	50.83	45.78	42.71	43.06	44.69
MgO	49.81	6.34	9.39	41.41	39.32	39.08
FeO	5.91	9.06	8.73	6.51	6.66	7.81
Fe <sub>2</sub> O <sub>3</sub>	1.21	2.88	3.16	1.57	1.66	
Al <sub>2</sub> O <sub>3</sub>	0.54	14.07	14.64	3.30	3.99	4.09
CaO	Trace	10.42	10.74	2.11	2.65	3.19
Na <sub>2</sub> O	Trace	2.23	2.63	0.49	0.61	1.14
K <sub>2</sub> O	Trace	0.82	0.95	0.18	0.22	
Cr <sub>2</sub> O <sub>3</sub>	0.56	Not given	Not given	0.45	0.42	
NiO	0.52	Not given	Not given	0.42	0.39	
CoO	0.02	Not given	Not given	0.02	0.02	
MnO	0.11	0.18	0.20	0.13	0.13	
P2O5	Trace	0.23	0.39	0.06	0.08	
$H_2O^+$	Nil	0.91	0.76	0.17	0.21	
$TiO_2$	Trace	2.03	2.63	0.47 .	0.58	
	100.00	100.00	100.00	100.00	100.00	100.00

TABLE 1. Derivation of the Hypothetical Mantle Composition

\* Normative composition: 91.6% olivine; 5.3% enstatite; 3.1% spinel.

discussion we shall adopt the 3:1 mixture in column 4 as the composition of pyrolite.

In the model previously referred to, it was pointed out that material of pyrolite composition could occur in a number of distinct mineral assemblages under the P-T conditions existing in the upper mantle. The intersection of geotherms with the stability fields for these mineral assemblages would have an important effect upon the seismic velocity distributions and particularly upon the formation of a low-velocity zone.

In the previous paper the different mineral assemblages were inferred from rather limited experimental and petrographic data. In the present paper we draw attention to naturally occurring peridotitic rocks which possess chemical compositions very similar to the postulated pyrolite composition. These rocks exhibit several distinct mineral assemblages, despite their similarity in chemical composition, and these assemblages correspond closely to those suggested in the previous model. A consideration of the geologic occurrence of these assemblages, combined with experimental data, permits their induitive stability to be established as a function of temperature and pressure, thereby leading toward a concept of mineral zoning in the upper mantle.

2. Natural mineral assemblages in rocks of pyrolitic composition. We have assembled in Table 2 a series of analyses taken from the literature. These analyses are extremely similar to one another and compare closely with the postulated pyrolite composition. Their main divergences lie in having lower Na<sub>2</sub>O, K<sub>2</sub>O, and TiO<sub>2</sub> than the pyrolite. These analyses have been grouped according to the mineralogy displayed by the rock, available mineralogical information also being summarized in Table 2.

Table 2 demonstrates that from essentially the same bulk composition, four distinct mineral assemblages may form as follows:

- 1. Olivine + amphibole (edenite, pargasite) + accessory chromian spinel.
- Olivine + plagioclase + enstatite + clinopyroxene + accessory chromite.
- Olivine + aluminous enstatite + aluminous diopside + spinel.
- 4. Olivine + pyrope garnet + pyroxene(s).

These different assemblages, which give every indication of representing equilibrium, must be

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		Olivino + Amphibole		Olivine + Pyroxenes + Plagioclase			Olivine + Aluminous Pyroxenes $\pm$ Spinel					Olivine + Pyroxenes + Garnet				
	'Pyrolite' Compo- sition	Lizard	Cali- fornia (Johann- sen)	Lizard	Lizard	Cyprus In- trusive (Gass)	Rhum (Brown)	St. Paul's Rocks (Tilley)	Lizard	Nodule (Hess)	Nodule (Stan- ley)	Nodule (Wil- shire, Binns)	Nodule (Wil- shire, Binns)	Kimber- lite Xenolith (Dawson)	Kimber- lite Xenolith (Holmes)	Lens in Gneiss (Johann- sen)
$\begin{array}{c} \mathrm{SiO}_2 \\ \mathrm{MgO} \\ \mathrm{FeO} \\ \begin{pmatrix} \mathrm{Total} \ \mathrm{Fe} \\ as \ \mathrm{FeO} \end{pmatrix} \\ \mathrm{Fe_2O_3} \\ \mathrm{Al_2O_3} \\ \mathrm{CaO} \\ \mathrm{Na_2O} \\ \mathrm{K_2O} \\ \mathrm{Cr_2O_3} \\ \mathrm{NiO} \\ \mathrm{CoO} \\ \mathrm{TiO}_2 \\ \mathrm{MnO} \\ \mathrm{P_2O_8} \\ \mathrm{Ho} \\ \mathrm{Ho} \end{array}$	43.06 39.32 6.66 (8.15) 1.66 3.99 2.65 0.61 0.22 0.42 0.39 0.02 0.58 0.13 0.08 0.21	$\begin{array}{c} 44.89\\ 38.62\\ *8.49\\ (8.49)\\ 0.00\\ 3.99\\ 2.82\\ 0.35\\ 0.05\\ 0.40\\ \dagger\\ 0.28\\ 0.11\\ \end{array}$	43.98 42.00 7.54 (8.56) 1.13 2.35 2.00 n.d. n.d. n.d. n.d. n.d. n.d. n.d. n	$\begin{array}{c} 45.12\\ 37.97\\ *7.87\\ (7.87)\\ 0.00\\ 4.96\\ 3.10\\ 0.24\\ 0.06\\ 0.36\\ \dagger\\ 1\\ 0.23\\ 0.09\\ \end{array}$	$\begin{array}{c} 44.72\\ 40.48\\ *8.23\\ (8.23)\\ 0.00\\ 3.52\\ 2.03\\ 0.18\\ 0.07\\ 0.45\\ \dagger\\ \dagger\\ 0.18\\ 0.14\\ \end{array}$	$\begin{array}{c} 45.60\\ 32.51\\ 5.82\\ (9.34)\\ 3.92\\ 7.13\\ 3.66\\ 0.27\\ 0.18\\ 0.31\\ 0.13\\ 0.25\\ 0.17\\ 0.05\\ \end{array}$	41.32 36.37 9.54 (11.41) 2.08 4.85 4.30 0.65 0.06 0.51 n.d. 0.15 0.17 nil	44.22 41.42 6.94 (7.89) 1.05 2.92 2.37 0.07 nil 0.50 0.21 0.17 0.13 nil	$\begin{array}{c} 44.60\\ 40.45\\ *8.30\\ (8.30)\\ 0.00\\ 4.18\\ 1.72\\ 0.11\\ 0.02\\ 0.37\\ \dagger\\ \div\\ 0.16\\ 0.09\\ \end{array}$	$\begin{array}{c} 44.29\\ 40.74\\ 7.57\\ (8.17)\\ 0.67\\ 2.96\\ 2.55\\ 0.20\\ 0.01\\ 0.41\\ 0.31\\ n.d.\\ 0.14\\ 0.13\\ 0.02\\ \end{array}$	$\begin{array}{c} 45.16\\ 40.84\\ 7.16\\ (7.35)\\ 0.20\\ 2.99\\ 1.93\\ 0.55\\ 0.21\\ 0.20\\ 0.14\\ n.d.\\ 0.14\\ 0.28\\ 0.20\\ \end{array}$	44.32 40.11 7.72 (8.76) 1.16 2.96 2.66 0.16 0.07 0.31 0.27 n.d. 0.12 0.14 nil	44.10 41.63 7.33 (8.26) 1.03 2.78 2.15 0.25 0.25 0.25 0.25 0.25 0.23 n.d. 0.12 0.12 nil	45.58 42.60 6.41 (6.65) 0.27 2.41 2.10 0.24 1.11 0.09 n.d. 0.15 0.12 0.03	47.17 39.84 5.20 (6.96) 1.96 2.85 1.93 0.20 0.35 0.32 n.d. 0.32 n.d. 0.06 0.12 nil	44.01 40.04 4.53 (8.56) 4.48 3.01 3.34 n.d. n.d. 0.44 n.d. 0.15 tr n.d.
1120	100.00	100.00	99.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Olivine Enstatite Diopside Plagioclase Pargasite-Ed	enite	62 2 36	#	++ 03: 03: 03	+ \$\$ \$\$	++ % % % %	74 9 16	++ 02 02	64 23 12	+ 0 0 0	14 69 69	56-75 21-33 2-11	67–72 9–22 8–19	60 § §	60 ‡ ‡	62 26
Spinel Chromite Picotite Magnetite	949)	tr		٩	4		1	¶.	1	4	٩	0.9-2.9	2.1-3.2	8	3	2

TABLE 2. Comparison of Chemical Compositions and Mineralogy of Rocks Approaching the Pyrolite Composition

\* All Fe calculated as FeO in the moderately serpentinized Lizard rocks.

† Average Ni and Co contents, determined spectrographically, of Lizard

peridotites are 0.20 and 0.01%, respectively. Note: Analyses have been calculated to 100% anhydrous, but no adjustment has been made to the Fe<sup>++</sup>/Fe<sup>+++</sup> ratio. ‡ Major constituent, >30 %.

§ Minor constituent, >3%, <30%.

 $\P$  Accessory constituent, <3 %.

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indicative of widely differing pressure and temperature conditions of crystallization. In the following sections, evidence relating to the relative P-T stability fields of these assemblages is discussed.

3. The assemblage olivine + amphibole +accessory chromian spinel. Descriptions of granulitic or gneissic terrains containing metamorphosed ultrabasic bodies [Howie, 1955; Davidson, 1943; Eskola, 1952; Carstens, 1920] refer to assemblages of olivine + amphibole ('hornblende,' 'edenite') with, in addition, possibly orthopyroxene, clinopyroxene, or spinel, depending upon specific rock composition. These rocks, where analyzed, are richer in CaO, SiO<sub>2</sub>, and FeO than the chosen pyrolite composition. Nevertheless, they strongly suggest that in conditions equivalent to granulite and higher-grade amphibolite facies metamorphism in the crustal environment, ultramafic rocks of pyrolite composition may be characterized by the assemblage olivine + magnesian hornblende.

Two analyses of amphibole + olivine rocks possessing the pyrolite composition are recorded in Table 2. One is a partial analysis of an edenite olivinite from California [Johannsen, 1938, p. 411]. The other analysis quoted is from the Lizard (Cornwall) peridotite [Green, 1963]. This peridotite was emplaced as a high-temperature crystalline diapir during low-grade regional metamorphism. The assemblage olivine + amphibole characteristically occurs at contacts with hornblende granulite or brown hornblende amphibolite of the metamorphic aureole and in local retrogressive alteration of plagioclasebearing peridotite (cf. next section).

Tilley [1947] describes peridotite mylonites from St. Paul's rocks (mid-Atlantic ridge) which contain olivine + green-brown amphibole. Older analyses (quoted by Tilley) of the assemblage olivine + amphibole show essentially the same rock composition as is given in Table 2, column 8. Tilley notes that relics of an unmylonitized intergrowth of olivine + amphibole occur locally within the mylonite. Thus, in the coarsely crystalline rocks from which the mylonites were derived, there appear to have been representatives of both the assemblage olivine + amphibole and the assemblage olivine + pyroxene + spinel (cf. section 5). Hess [1960b] has sugtod that it heite from St Paul's

rocks may be tectonically exposed parts of the suboceanic mantle.

The examples quoted above show clearly that rocks of pyrolite composition may crystallize in a stable assemblage consisting of olivine  $\pm$  amphibole. An upper limit to the thermal stability of this assemblage is imposed by the dehydration of the amphibole. Under conditions where  $P_{\rm H,O} =$  load pressure, this may be as high as 1000°C. Where the water-vapor pressure is much less than the load pressure, i.e. in a waterdeficient environment, the stability field of the assemblage olivine  $\pm$  amphibole will be displaced to lower temperatures. *Ringwood* [1962b] has pointed out that these conditions may be realized in the uppermost suboceanic mantle.

If material of primitive pyrolite composition should exist below the oceanic Mohorovicic discontinuity, and, furthermore, if this region should be water deficient, containing between 0.5 and 0.7 per cent of water, then the assemblage olivine + amphibole would probably remain stable at levels of lower temperature (< 500°C).

4. The assemblage olivine + plagioclase + enstatite + clinopyroxene + accessory chronite. There are very few analyzed rocks of approximate pyrolite composition which display the mineral assemblage olivine + plagioclase + pyroxenes (hereinafter called 'plagioclase pyrolite'). Two such rocks are from the Lizard peridotite [Green, 1963] (Table 2, columns 4 and 5). This intrusive provides a particularly instructive example of the relationships between plagioclase pyrolite and pyroxene pyrolite. (The assemblage olivine + aluminous pyroxenes has previously been called 'transitional pyrolite' [Ringwood, 1962a, b], but the term 'pyroxene pyrolite' is preferred as more explicit.)

The Lizard peridotite consists of a coarsegrained, primary core, characterized by the assemblage olivine + aluminous enstatite (6 to 6.5 per cent Al<sub>2</sub>O<sub>3</sub>) + aluminous diopside (6.5 to 7 per cent Al<sub>2</sub>O<sub>3</sub>) + aluminous spinel. Detailed field and petrographic investigations [*Green*, 1963] lead to the conclusion that this body was derived from the mantle and that the coarse primary mineral assemblage mentioned above was formed in an initial, deep-seated crystallization of the body. The peridotite was subsequently intruded at a high temperature, perhaps between SOC<sup>2</sup> and 1000<sup>2</sup>C to a higher.

erustal level, resulting in the formation of a sh-grade metamorphic aureole in the country week. During this diapiric intrusion, a marginal sheath of the peridotite was mylonitized and merystallized. The resultant mineral assemblage consists of olivine + enstatite (2 per cent M<sub>2</sub>O<sub>3</sub>) + diopside (3 per cent Al<sub>2</sub>O<sub>3</sub>) + calcic plagioclase + chromite. This assemblage, corresponding to the 'plagioclase pyrolite' of Ringwood's [1962a] model, has clearly crystallized an equilibrium assemblage at moderate erustal depth and at a temperature probably in the range 700° to 1000°C. The plagioclase-bearing peridotite locally, under lower temperature and/or higher water pressure conditions, shows partial or complete retrogressive alteration to the assemblage olivine + amphibole.

The plagioclase has formed from lime, alumina, and soda, which were originally present in solid solution in the pyroxenes of the primary assemblage. The change in mineralogy has clearly been caused by recrystallization in the crust at a lower pressure than that under which the primary assemblage olivine + aluminous pyroxenes formed, probably in the mantle.

Brown's [1957] analysis of average peridotite accumulate in the Rhum complex comes close to the pyrolite composition but is distinctly higher in FeO, CaO, and Al<sub>2</sub>O<sub>3</sub> contents. Mineralogically it differs from the Lizard assemblages in lacking enstatite. Although the minerals in the Rhum peridotite are accumulated from a basaltic magma, it is considered that their retention at a high temperature during the accumulation of the overlying peridotite and allivalite would have caused reaction between the phases if the accumulated assemblage were tot stable at a high temperature, at shallow or moderate crustal depths, and in an anhydrous of low  $P_{\rm H_{2}O}$  environment.

The intrusive ultrabasic rock from Cyprus [Gass, 1958] consists of olivine phenocrysts set plagioclase, diopside, and hypersthene (see Table 2, column 6). Again a sequence of crystalbation is involved, and the composition of the magma during precipitation of each phase is bot known. The rock as a whole is much higher in Al.O. and lower in MgO than the other examples. The evidence from olivine gabbros, troctolites, and norites, although departing considerably from the rock composition proposed for pyrolite, is that the assemblage magnesian olivine + plagioclase + orthopyroxene + clinopyroxene is a stable one at high temperatures at crustal levels, particularly in an anhydrous environment.

The occurrence of a plagioclase pyrolite assemblage in the mantle will be limited by the breakdown of plagioclase at higher pressures as exemplified (in reverse) by the Lizard peridotite. Breakdown occurs in favor of jadeite and Tschermak's silicate, (CaMg)Al<sub>2</sub>SiO<sub>0</sub>, which go into solid solution in pyroxenes, forming highly aluminous varieties.

The experimental results of Robertson et al. [1957], Yoder and Chinner [1960, p. 80], Yoder and Tilley [1961], and Clark and de Neufville [1962] set an upper limit to the maximum pressure at which olivine + plagioclase + pyroxenes would be stable. It is improbable that this assemblage can exist above 20 kilobars, and the maximum pressure may be substantially less than this figure. Uncertainty arises because most experimental results deal only with the stability of end members of the plagioclase series. Anorthite and albite break down to different reaction products. Accordingly, intermediate plagioclase will be somewhat stabilized by the free energy mixing of the end members of the series.

On the balance of available evidence, it appears that plagioclase pyrolite may be stable at depths less than 50 km and temperatures in excess of 600° to 700°C in an environment of low water-vapor pressure. This assemblage may therefore occur in a rather small zone in the oceanic upper mantle as suggested by *Ringwood* [1962b]. The assemblage may be more important in regions of high heat flow, where the temperatures beneath the Mohorovicic discontinuity are higher than usual.

5. The assemblage olivine + aluminous enstatite + aluminous diopside  $\pm$  spinel. The constant mineralogy of the peridotite nodules in basalt has drawn comment from a number of authors, notably Ross et al. [1954], Hess [1960a], Wilshire and Binns [1961], and these authors, among others, have argued for their derivation from the mantle. The nodule contain dominant olivine, less abundant enstatite and diopside, and accessory spinel. Analyses of these minerals [Ross et al., 1954] from the nodules demonstrate the characteristic high Al<sub>2</sub>O<sub>3</sub> content of both ortho- and clinopyroxene and also the high MgAl-O, content of the spinels. The compositions of a typical nodule from California [Hess, 1960a], a nodule from olivine basalt at Mount Gambier, South Australia [Stanley, 1910], and of two averages of several nodules from each of two new South Wales localities [Wilshire and Binns, 1961] are given in Table 2. These analyses are strikingly similar in both major and minor constituents.

As discussed in the preceding section, the Lizard peridotite contains a primary core having a 'pyroxene pyrolite' assemblage (Table 2, column 9) and differs from the nodule compositions only in its higher  $Al_2O_3$  content. A detailed comparison [*Green*, 1963] of the compositions of the minerals of the Lizard peridotite with those of peridotite nodules argues convincingly for similar conditions of crystallization.

Except for its low K<sub>2</sub>O and Na<sub>2</sub>O contents the dunite mylonite from St. Paul's rocks [*Tilley*, 1947] has nearly the same composition as the peridotite nodules and garnet peridotites. The analysis given in column 8, Table 2, is of a mylonite containing both enstatite and diopside augen in fine, recrystallized olivine and brown, translucent spinel. Data on the  $Al_2O_3$  contents of the large pyroxenes would be particularly welcome, but, bearing in mind the rock composition and mineralogy, we can compare the rock most closely with the 'pyroxene pyrolite' assemblage.

From the experimental and field evidence discussed in the preceding section, it is clear that the characteristic assemblage olivine + aluminous pyroxenes + aluminous spinel has crystallized under greater load pressure than the plagioclase pyrolite assemblage. As implied by *Ringwood*'s [1962b] model, this assemblage may well occupy an extensive region in the upper mantle. As would be expected, the calculated density of the pyroxene pyrolite assemblage (about 3.32 g/cm<sup>s</sup>) is significantly higher than that of the corresponding plagioclase pyrolite assemblage (3.24 g/cm<sup>s</sup>).

6. The assemblage olivine +pyrope garnet + pyroxene(s). The three analyses of garnet peridotites given in Table 2 include two inclusions in African kimberlites [Dawson, 1962; Holmes, 1936] and one analysis from a garnet peridotite lens occurring in association with eclogite as lenses in gneiss in Switzerland [Johannsen, 1938, p. 422]. From their mineralogy, dotites within dunite in Amklovdalen, Norway [*Eskola*, 1921], may also approach this composition.

The Swiss garnet peridotite differs from the other two analyses in having a higher CaO content, and it differs mineralogically in lacking enstatite. Nevertheless, the analyses are remarkably similar to the analyses of peridotite nodules in basalt and to the pyrolite model composition.

The contrast in mineralogy between the aluminous pyroxene-bearing assemblage and the garnet-bearing assemblage must be attributed to different P-T conditions of crystallization. The absence of the assemblage olivine + pyrope garnet + pyroxene(s) (garnet pyrolite) in the Lizard peridotite sequence, and as nodules in basaltic rocks, compared with its characteristic occurrence in the diamond-bearing pipes, suggests that garnet pyrolites derive from greater depths in the mantle than the aluminous pyroxene + olivine assemblages.

Such a relationship would be expected up a crystallographic and general mineralogical grounds. *Thompson* [1948] has pointed out they high pressure strongly favors mineral semblages in which aluminum lies in octahedra coordination. Minerals in which aluminum occurs in tetrahedral coordination appear to be unstable at high pressure. The change in coordination from tetrahedral to octahedral is accompanied by a substantial increase in density due to closer packing.

In aluminous pyroxenes, approximately half of the Al atoms lie in tetrahedral coordination A change in coordination with resultant increasin density can be obtained if, under high prosure, the highly aluminous pyroxene break down into a low alumina pyroxene and pyroperich garnet. Transition from the pyroxene two rolite to garnet pyrolite appears to be due to this effect. The calculated density of garnet tworolite is 3.37 g/cm<sup>3</sup> as compared with 3.52 for pyroxene pyrolite.

The *P-T* conditions governing the transitient from pyroxene pyrelite to garnet pyrolite apnot known. *Ringwood* [1962b] has pointed out that garnet pyrolite requires higher pressure for its stability than eclogites, at corresponding temperatures. A possible boundary between the two assemblages, derived from indirect seturity evidence, was outlined in that paper. Hence, are

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	Olivine + Amphibole Assemblage a b		Plagioclase Pyrolite	Pyroxen a	e Pyrolite b	Garnet Pyrolite	
Olivine	65.0	57.6	71.9	61.4	65.3	65.2	
Normal Al2O3 Enstatite High Al2O3		17.6	6.5	16.8	15.6	7.8	
Diopside Omphacite			4.7	30 % Jd 70 % Di 15.3	30 % Jd 70 % Di 16.8	43% Jd 57% Di 11.4	
Hornblende Plagioclase (Ab44AN54) Spinel (high MgAl <sub>2</sub> O4 content) [70% pyrope]	31.8	21.9	13.6	5.9	(10 % 24)		
Garnet 12% almandine 6% grossular 6% uvarovite 6% andradite						13.3	
Rutile	0.6	0.5	0.6	0.6	0.6	0.6	
Chromite-magnetite Density, g/cm <sup>3</sup> H <sub>2</sub> O (wt %) in rock	2.6 3.25 0.7 9	2.3 3.28 60.5%	2.6 3.24	3.30	1.7 3.32	1.7 3.3	

TABLE 3. Calculated Modal Compositions and Densities for Ideal Pyrolite Composition of Table 1

In Table 3 two olivine  $\pm$  amphibole assemblages are calculated, one on the basis that plagioclase, clinopyroxene, and enstatite taxe been completely replaced by an amphibole (composition in mole per cent of 12% soda-tremolite, 12% cummingtonite, 12% achermakite, and 64% tremolite). The second assemblage is calculated using as a basic control the composition of an analyzed rablende from the Lizard olivine  $\pm$  amphibole assemblage (high in edenite substitution, with some cummingtonite and  $\pm$  betmakite substitution) and the presence of enstatite as in some examples of the Lizard peridotite.

I we pyroxene pyrolite assemblages are possible, depending on whether the pyroxenes, particularly the enstatite, can accomto-iate a high Al<sub>2</sub> O<sub>3</sub> content or whether this appears as spinel.

The calculated composition of the garnet compares well with that observed by Dawson in the garnet peridotite xenolith in timberlite previously discussed.

ording to the model, garnet pyrolite would ocupy an extensive region in the upper mantle, breetly underlying a zone of pyroxene pyrolite.

7. Modal compositions and densities inferred or the ideal pyrolite composition. In the first tion of this paper we arrived at a preferred bemical composition for a primitive mantle material. In later sections we have drawn atten-\* a to a variety of natural mineral assemblages that apparently are stable under different P-Tmoditions and in rock compositions close to that suggested for the mantle. In Table 3 we the calculated modal compositions (weight ier cent) and rock densities for analogous asmblages in the chosen mantle composition of T ble 1. The high content of Fe<sub>2</sub>O<sub>3</sub> in the chosen imposition (cf. footnote, Table 2) and its calrelation as magnetite, together with the calculaion of TiO<sub>2</sub> as rutile, introduce a bias toward shtly high values in the calculated densities. However, this is consistent for all the assemblages and does not affect the relative densities.

8. Discussion. The data we have collected show conclusively that rocks of peridotitic composition with low but essential  $Al_2O_3$ , CaO, and  $Na_2O$  crystallize in four distinct mineral assemblages, dependent upon the *P*-*T* conditions of crystallization.

- 1. Olivine + amphibole + accessory chromian spinel.
- 2. Olivine + plagioclase + enstatite + clinopyroxene + accessory chromian spinel.
- 3. Olivine + aluminous enstatite + aluminous clinopyroxene + spinel.
- Olivine + pyrope garnet + pyroxene(s).
  All these assemblages are dominated by olivine as the major mineral present.

The four mineral assemblages agree with those which were suggested in a model for the upper mantle proposed by *Ringwood* [1962*a*, *b*]. Furthermore, the inferred relative pressure and temperature conditions of formation of the assemblages are qualitatively consistent with that model. Significant aspects of that model may therefore now be considered verified by the evidence of the natural mineral assemblages discussed herein.

The primitive 'pyrolite' chemical composition of the mantle has been taken (somewhat arbitrarily) to be equivalent to a mixture of one part of basalt to three parts of dunite. The rocks discussed in this paper possess chemical compositions closely approaching that model. It should be emphasized, however, that any parent rock characterized by basalt-dunite ratios between 1:1 and 1:10 would probably be capable of crystallizing in each of the four mineral assemblages, according to the specific P-T conditions.

Accordingly, if ultrabasic rocks in this composition range do, in fact, predominate in the upper mantle, large-scale mineralogical zoning controlled by the P-T distribution will be inevitable. The upper mantle cannot, therefore, be regarded as a homogeneous region possessing a characteristic set of physical parameters (such as density and seismic velocity). Implications of this mineralogical zoning with respect to the presence or absence of a low-velocity zone, and to regional variations in seismic velocity profiles and surface heat flow, were outlined in previous papers [Ringwood, 1962a, b]. Further progress now awaits the direct experimental determination of the P-T fields of the four assemblages, as well as a better knowledge of the elastic properties of the individual minerals of these assemblages, as a function of temperature and pressure.

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