

Chemical variation among French ultramafic xenoliths—evidence for a heterogeneous upper mantle

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SUMMARY. Some 200 ultramafic xenoliths and their basaltic hosts from five French localities were studied. New analyses are presented, which show the five host-rocks to be nepheline- and olivine-normative. Seven bulk analyses of xenoliths from four localities, together with analyses of their constituent diopsides and, for six, of their orthopyroxenes, are also presented. Xenoliths from four occurrences appear to have equilibrated at pressures between about 8 to 18 kb at sub-basaltic solidus temperatures. Suites of xenoliths are chemically different. Histograms were used to determine compositions of depleted and 'undepleted' upper mantle. A suite of peridotite xenoliths from the Bultfontein kimberlite pipe is no less depleted in fusible oxides than xenoliths from two French localities. 'Undepleted' upper mantle is very similar to 'pyrolite' in composition, except that the latter has much higher TiO_2 , Na_2O , and K_2O contents. No xenolith encountered in this work has a bulk composition that could yield more than 12% oceanic tholeiite on partial melting.

THE search for representative samples of the upper mantle has been directed largely at ultramafic xenoliths from alkalic basalts and kimberlites and at ultramafic intrusions of non-cumulate origin. Most recent studies applied to mantle composition have concentrated on ultramafic xenoliths (Jackson and Wright, 1970; Kuno and Aoki, 1970; Chen, 1971; Kudo *et al.*, 1972), because these constitute fresh material directly derived from the mantle and apparently unaltered to any major degree during their passage to the surface. Although some dunitic xenoliths may be infusible residues from mantle anatexis and some pyroxenitic xenoliths may be of cumulate origin cognate with their host-basalt, it seems likely that lherzolitic xenoliths are actual mantle samples relatively undepleted in fusible components and unrelated to the enclosing host-basalts either chemically or isotopically (Leggo and Hutchison, 1968; Kleeman *et al.*, 1969; Cooper and Green, 1969; Paul, 1971; Kudo *et al.*, 1972; Zartmann and Tera, 1973).

A large number of ultramafic xenoliths from each of several widely spaced localities in the Massif Central, France, have been studied to see how much chemical variation occurs in samples from a single locality and whether regional differences in mantle chemistry can be demonstrated with certainty. A preliminary report on this work was given by Hutchison *et al.* (1970), and part of the work was summarized in a review paper by Harris *et al.* (1972). The present paper provides the detailed final results of this project.

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Between 18 and 43 xenoliths from each of five widely spaced localities (see fig. 1) have been analysed mainly by X-ray fluorescence techniques described in the appendix. A specimen of host-basalt from each locality has been analysed also. For comparison with the French ones, 15 peridotite xenoliths, collected by J. B. Dawson from the Bultfontein kimberlite pipe, were analysed. In addition, 3 analyses of garnet-peridotite xenoliths (Carswell and Dawson, 1970) bring to 18 the total number of analyses of specimens from this locality used in this work.

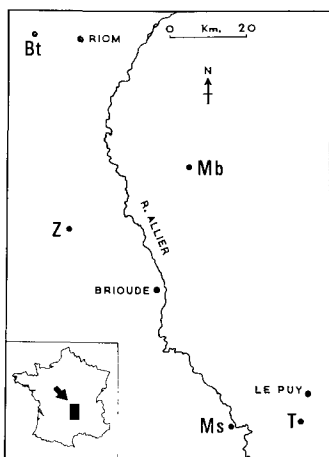


FIG. 1. French specimen localities. Bt: Puy Beaunit scoria cone. Z: Volcan de Zanière scoria cone. Mb: Montboissier plug. Ms: Monistrol d'Allier basalte du Rocher du Lion flow. T: Tarreyres scoria cone.

In the present paper, a brief discussion of the petrology and chemistry of the host-rocks is followed by a description of the suites of xenoliths. Mineralogical and chemical data on 7 spinel-lherzolite xenoliths are presented. Pyroxenes are used as *P* and *T* indicators and suggest that different xenoliths equilibrated under different physical conditions. Finally, histograms are used to deduce the compositions of the various types of mantle sampled in each locality.

Host-basalts. Puy Beaunit, Volcan de Zanière, and Tarreyres localities (see fig. 1) are scoria cones, whereas Montboissier is a plug and the Monistrol d'Allier xenoliths are found in a thick lava flow (for the last, see Vilminot, 1965). Apart from their varying vesicularity, the 5 host-basalts are similar. All have microphenocrysts of olivine and purplish-brown augite, the latter often zoned. The groundmass

is fine-grained and composed of feldspar laths, which are sometimes flow-aligned, small, elongate pyroxene crystals, grains of opaque ore, and a variable glass content. All the basalts contain micro-xenoliths or xenocrysts, which were undoubtedly in disequilibrium with their host-liquid. These have been derived either from the break-up of sialic basement rocks—e.g. quartz grains—or from ultramafic material—e.g. xenocrysts of orthopyroxene. The reaction product around quartz grains is normally a mass of acicular clinopyroxene crystals. In one case, the Montboissier plug, clots of calcic feldspar crystals may be the precursor of irregular patches of zeolite.

The basalts are chemically similar (see Table I); all are undersaturated, with olivine and nepheline in the norm. The presence of exotic quartz in the mode of the Puy Beaunit basalt is reflected in the SiO_2 content of 47.55%; this is about 2% higher than in the other basalts. All are members of the 'association sodique fortes' of Jung and Brousse (1958) and lie in the field of 'continental inclusion-bearing basalts' established by Forbes and Kuno (1967). The Tarreyres basalt is highly oxidized, with approximately equal amounts of FeO and Fe_2O_3 , a property reflected by its peridotite inclusions, many being discoloured by the presence of hematite. The low total of the analysis of the Basalte du Rocher du Lion (Ms) is almost certainly due to the presence of interstitial calcite; CO_2 was not determined.

The ultramafic xenoliths

These coarse-grained rocks are composed of olivine+orthopyroxene+clinopyroxene+spinel. Although the Ca-rich pyroxene is often rare, it is seldom absent; there are few true harzburgites. A small proportion of the xenoliths from Puy Beaunit have accessory brown mica, while many from Tarreyres have accessory yellow-green amphibole. Some xenoliths contain a little feldspar associated with spinel, amphibole,

TABLE I. *Chemical analyses of basaltic host-rocks*

	1	2	3a	3b	4a	4b	5
SiO ₂	47.55	45.02	45.63	45.20	43.52	43.0	42.75
TiO ₂	2.26	3.44	2.30	2.50	2.29	3.25	2.87
Al ₂ O ₃	16.08	15.19	15.03	13.40	12.15	12.10	13.71
Fe ₂ O ₃	3.11	3.06	2.86	5.40	2.44	4.10	6.19
FeO	7.82	8.00	7.84	7.10	8.94	7.50	6.11
MnO	0.20	0.18	0.19	0.25	0.21	0.17	0.19
MgO	6.97	7.50	8.44	7.90	13.15	12.40	10.46
CaO	10.07	10.59	8.95	9.20	10.30	9.75	10.53
Na ₂ O	3.42	3.82	3.94	3.90	3.31	3.50	3.22
K ₂ O	1.69	1.96	1.34	2.45	1.54	1.90	1.88
H ₂ O+	0.32	0.32	1.88	1.70	0.34	1.05	0.92
H ₂ O-	0.12	0.19	0.57	0.90	0.24	0.45	0.29
P ₂ O ₅	0.66	0.81	1.18	0.90	1.04	1.70	0.90
Sum	100.27	100.08	100.15	100.80	99.47*	100.87	100.02
<i>Molecular normative nepheline and olivine</i>							
Ne	4.2	12.3	6.3	—	13.5	—	11.4
Ol	13.2	11.7	18.2	—	24.9	—	14.4

1. Basalt bomb from Puy Beaunit scoria cone.
 2. Basalt bomb from scoria, Volcan de Zanière.
 - 3a, b. Basalt from pipe at Montboissier.
 - 4a, b. Basalte du Rocher du Lion, Monistrol d'Allier.
 5. Basalt bomb from scoria cone, near Tarreyres.
- * CO₂ detected, but not determined.

Analysts: J. Gronow, except for 3b and 4b. 3b, analysis by Taisne in Brousse (1961) p. 42, no. 77. 4b, analysis by Blot, in Vilminot (1965), Table III, no. 1.

or chrome-diopside. This feldspar is clearly a reaction product and not part of the primary assemblage. In hand-specimen, ultramafic xenoliths from each locality are distinctive.

Puy Beaunit. Most xenoliths are small and angular. Many are cut by thin basaltic veins up to 2 mm thick, which were removed prior to crushing for analysis. However, a few specimens have interstitial glass. These were rejected for analysis as it could not be readily determined if the glass were introduced from the host-basalt or if it were the result of partial melting in the peridotite itself. Most xenoliths contain negligible contents of clinopyroxene and so are harzburgitic. In thin-section, spinel is opaque or red-brown.

Several specimens are very coarse-grained and composed of olivine, orthopyroxene, and clinopyroxene in approximately equal proportions. The clinopyroxene of one such rock is an endiopside with no Al in six-fold co-ordination, suggesting that it equilibrated at low pressure. This is confirmed by the α_0 and β_0 parameters (O'Hara, 1967) of 48.7 and 2.5, respectively, which indicate that it crystallized or recrystallized in the presence of feldspar or spinel at about 1 kb pressure and 1200 °C. These pyroxene-rich rocks may be related to noritic xenoliths, which are found in approximately equal abundance, both types being subordinate to the harzburgitic ones. The former two types probably crystallized from a magma. The orthopyroxene of the norites exhibits incongruent melting to olivine granules plus brown isotropic glass.

Volcan de Zanière. A uniform suite of harzburgitic xenoliths occurs here. Specimens are small, sub-angular, and composed of whitish olivine and porphyroblastic brown orthopyroxene crystals, which may be longer than 1 cm. Some spinel and a small amount of Ca-rich pyroxene are always present.

Montboissier. The Montboissier plug carries a suite of xenoliths similar to that of the previous locality. However, in this instance they are usually large, rounded, and may be partly carbonatized. Montboissier xenoliths carry more pyroxene than those from the Volcan de Zanière, are partly serpentinized, and are therefore much darker in appearance.

Monistrol d'Allier. Of the five suites of French xenoliths studied, the most diverse appears to be from the Basalte du Rocher du Lion, near the village of Monistrol d'Allier. Ultramafic fragments range from angular and small to large and ovoid, with major axes up to 25 cm long. Some examples are close to dunite, but most are lherzolites with an olive-green spinel, which has, in some cases, reacted with clinopyroxene to form olivine, plagioclase, and opaque ore. A more common reaction is one between orthopyroxene and spinel, forming a mass of granular olivine and ore and other fine-grained material. Introduction of water has sometimes led to the alteration of orthopyroxene and serpentinization of olivine. The assemblage of basalt and xenoliths has been described in detail by Vilminot (1965).

Tarreyres. In this scoria cone occur mostly angular ultramafic fragments, the bulk being partly oxidized. However, in a roadside face on the south of the cone the xenoliths are pale yellow-green and unaltered. Although some are harzburgitic, many of the 42 specimens analysed are spinel-lherzolite, with some amphibole. In thin-section the spinel is brown to olive-green and the amphibole is pleochroic, pale straw-coloured to yellow-green. The spinel, amphibole, and pyroxenes may have reaction rims, those round amphibole being feldspar-bearing, whereas olivine is conspicuous in the others. It is possible that the amphibole is the result of reaction of spinel with H₂O from the host-basalt and SiO₂ from the pyroxenes.

In summary, most ultramafic xenoliths from the two southern localities (Monistrol d'Allier and Tarreyres) are true lherzolites, whereas those of the middle localities are close to harzburgite. The suite of xenoliths from the most northerly site (Puy Beaunit) includes a few true lherzolites and a few pyroxene-rich xenoliths, but comprises mainly harzburgitic and dunitic varieties; in addition, mafic fragments, norites, occur.

Mineralogy

The lherzolite inclusions have the composition olivine+aluminous pyroxenes+spinel, which is typical of such occurrences throughout the world (see Forbes and Kuno, 1967). The French specimens contain olivines in the range Fo_{87-94} (Harris *et al.*, 1972). In Table II are presented microprobe analyses of coexisting pairs of orthopyroxenes and clinopyroxenes, together with X-ray fluorescence analyses of the bulk rocks. Atomic ratios or molecular norms (after Barth, 1961), are also given.

Inspection of the table indicates that there is a positive correlation between Al_2O_3 contents of the bulk rocks and of their constituent pyroxenes. Thus Al_2O_3 content of their environment may be an influence on the Al_2O_3 content of pyroxenes, as suggested by Howie (1965). In the analysed specimens, this oxide is roughly equally divided between octahedral and tetrahedral sites. Orthopyroxene ranges from $En_{87.7-91.2}$, when the small wollastonite component (1 to 2 mol. %) is ignored. All the monoclinic pyroxenes are diopsides of the typical green variety with Cr_2O_3 from 0.44 to 1.01 wt % and all have a $CaAl_2SiO_6$ component, which reaches 10 mol. % in T15. This pyroxene also has the highest jadeite component, 6.4 mol. %, when the atomic proportions are converted to the pyroxene components of Kushiro (1962), i.e., with Na assigned to aegirine, chrome-acmite, and jadeite, in that order.

The temperature of equilibration of the xenoliths can be estimated from the degree of solid solution between diopside and enstatite (Davis and Boyd, 1966; Boyd, 1973; Wagner and Luth, 1974), and the pressure from the alumina content of the enstatite if the latter is saturated in alumina, in the presence of spinel or garnet (MacGregor, 1974). Alternatively, pressure and temperature can be estimated conveniently from the composition of the diopside (O'Hara, 1967); such estimates are given in Table II.

Different methods give different results. For most of the analysed clinopyroxenes (Table II), the molecular ratio $Ca/(Ca+Mg)$ is close to, or greater than, 0.5, suggesting temperatures of less than 900 °C. Even the specimen (Z1) with the lowest ratio apparently equilibrated at only slightly higher temperature. For most of the clinopyroxenes, the semi-empirical method of Wood and Banno (1973) does not yield markedly higher temperatures. The empirical enstatite geothermometer of Boyd and Nixon (1973) gives a range of temperature from 1090 to 1240 °C (average about 1140 °C), and the enstatite geothermometer of Mysen (1973), from 950 to 1110 °C (average about 1020 °C).

For his geobarometer, MacGregor (1974) suggests that enstatite in equilibrium with diopside has about 2 wt % less Al_2O_3 than enstatite on the enstatite-pyroxene join. Correcting for this, 3.6 % (plus 2 %) Al_2O_3 in the enstatite of spinel-lherzolite corresponds to a pressure of equilibration of 16 kb if the T were 1000 °C, and to 22 kb if the T were 1100 °C, these temperatures being higher than the temperatures of equilibrium found by MacGregor (1974) for spinel-lherzolites in general.

The pressure-temperature grid of O'Hara (1967) is sensitive to the oxidation state of iron (Griffin, 1973). Using the measured FeO and Fe_2O_3 contents of the diopsides, a pressure range of 7 to 18 kb (15 kb average) and a temperature range, 750 to 1200 °C (1025 °C average), are indicated. However, the Fe_2O_3 contents seem high. This

TABLE II. For commentary, see text. Locality symbols as on fig. 1.

	Bulk rock analyses							Clinopyroxene				
	1	2	3	4	5	6	7	1	2	3a	3b	
	Bt3	Z1	Z3	Mb9	Mb42	T10	T15	Bt3	Z1	Z3	Z3	
SiO ₂	44.3	43.9	44.8	42.8	44.7	43.1	44.5	53.6	52.1	51.9	51.2	
TiO ₂	0.01	0.02	0.03	0.01	0.01	0.08	0.09	0.06	n.d.	0.11	0.11	
Al ₂ O ₃	1.04	1.33	2.31	1.48	2.26	3.22	4.05	2.87	4.26	4.70	5.31	
Cr ₂ O ₃	0.45	0.40	0.47	0.33	0.43	0.40	0.38	1.01	0.95	0.44	0.65	
Fe ₂ O ₃	1.15	1.31	1.39	1.93	1.59	1.66	1.70	1.22	1.03	2.33	2.41	
FeO	7.50	7.30	7.00	6.95	6.11	7.11	6.60	1.31	2.09	1.15	1.15	
NiO	0.29	0.31	0.27	0.33	0.27	0.26	0.23	0.05	n.d.	n.d.	n.d.	
MnO	0.12	0.11	0.12	0.11	0.11	0.12	0.12	0.08	n.d.	n.d.	n.d.	
MgO	43.8	44.7	41.9	44.5	40.0	39.9	38.7	16.0	16.4	16.1	15.9	
CaO	1.61	1.01	2.13	0.92	2.64	2.80	3.34	23.3	21.2	22.0	21.9	
Na ₂ O	0.05	0.06	0.11	0.04	0.09	0.21	0.26	0.61	0.86	1.02	1.02	
K ₂ O	0.01	0.01	0.01	0.01	0.01	0.01	0.01	n.d.	n.d.	n.d.	n.d.	
Sum	100.33	100.46	100.54	99.41	98.22	98.87	99.98	100.11	98.89	99.75	99.65	
Molecular Norms							Ions per six oxygen atoms					
Ab	0.5	0.5	1.0	0.5	1.0	1.5	2.0	Si	1.944	1.909	1.889	1.868
An	2.3	3.0	5.3	3.5	5.3	7.3	9.0	Al ^{iv}	0.056	0.091	0.111	0.132
Wo	1.8	0.6	1.6	0.2	2.6	2.0	2.4	Al ^{vi}	0.067	0.093	0.091	0.096
En	18.0	16.0	19.6	14.2	24.0	15.0	18.6	Ti	0.002	—	0.003	0.003
Fs	1.6	1.6	1.8	1.2	2.0	1.2	1.4	Cr	0.029	0.027	0.013	0.019
								Fe ²⁺	0.033	0.028	0.064	0.066
Fo	68.1	70.8	63.6	72.6	58.8	64.8	59.4	Fe ³⁺	0.040	0.064	0.034	0.035
Fa	6.3	6.0	5.4	5.7	4.5	6.0	5.1	Ni	0.002	—	—	—
								Mn	0.002	—	—	—
Mt	0.4	1.2	1.3	1.8	1.5	1.7	1.6	Mg	0.863	0.895	0.870	0.861
Ct	1.0	0.4	0.4	0.3	0.4	0.5	0.4	Ca	0.903	0.832	0.856	0.857
Il	—	—	—	—	—	—	0.2	Na	0.043	0.061	0.072	0.072
								K	—	—	—	—
Mg/(Fe+Mg)%	90.1	90.4	90.1	90.1	90.4	89.2	89.5	WXY	1.984	2.000	2.003	2.009
								%Al ^{iv}	45.5	49.5	55.0	57.9
Olivine	Fo ₉₀ *	Fo _{88.2}	Fo _{88.2}	Fo _{88.2}	Fo _{89.5} †	—	—	En	46.9	49.2	47.7	47.3
								Fs	4.1	5.1	5.4	5.6
								Wo	49.0	45.7	46.9	47.1
								α _c	53.5	50.0	52.1	52.3
								β _c	3.6	4.5	5.2	6.1
								P(kb)	12	7	16	18
								T(°C)	750	1200	1050	1050
								α _c §	52.6	49.4	50.5	50.6
								β _c §	2.7	3.8	3.6	4.3
								P(kb)	6	4	5	7
								T(°C)	900	1200	1100	1150

* Microprobe analysis.

† X-ray fluorescence analysis.

‡ By X-ray diffraction.

§ α_c and β_c calculated assuming all Fe in the ferrous state.

could be due to secondary oxidation of the clinopyroxene or to underestimation of FeO. If a low original Fe₂O₃ content is assumed, temperatures about 50 °C higher and pressures about 50 % lower are obtained.

It must be stressed that if unmixing has occurred in the pyroxenes, microprobe analyses do not give the pressure and temperature of initial crystallization, but of the unmixing. For example, exsolution lamellae are clearly visible in thin section in the T10 clinopyroxene, so that microprobe analysis will give the *P* and *T* that obtained during the formation of the lamellae. Analysis (by D. K. P.) of a bulk clinopyroxene separate from a xenolith (DW15) from Dreiser Weiher (Frechen, 1963) and analysis

P and *T* are derived from the α_c and β_c parameters of O'Hara (1967)

Orthopyroxene Analyses											
4	5	6a	6b	7	2	3	4	5	6	7	
Mb9	Mb42	T10	T10	T15	Z1	Z3	Mb9	Mb42	T10	T15	
52.8	52.4	50.6	49.6	52.3	55.5	54.5	55.7	55.4	55.0	56.0	SiO ₂
0.08	0.07	0.36	0.42	0.48	n.d.	n.d.	0.03	<0.01	0.08	0.09	TiO ₂
4.12	4.69	6.37	6.60	6.89	2.86	3.60	3.54	3.79	4.37	3.95	Al ₂ O ₃
0.77	0.85	0.74	0.83	0.65	0.43	0.35	0.40	0.47	0.33	0.23	Cr ₂ O ₃
n.d.	n.d.	2.96	n.d.	1.80	2.82	n.d.	n.d.	n.d.	5.10	2.78	Fe ₂ O ₃
2.88	2.62	1.39	6.27	1.58	3.18	6.29	6.33	6.40	3.14	4.38	FeO
0.07	0.05	0.05	0.05	0.05	n.d.	n.d.	0.12	0.11	0.10	0.10	NiO
0.07	0.07	0.09	0.14	0.09	n.d.	n.d.	0.14	0.15	0.10	0.10	MnO
15.8	15.7	15.1	14.0	14.6	33.2	31.5	32.4	32.1	31.8	32.5	MgO
23.1	23.2	20.8	20.2	20.6	0.56	0.94	0.62	0.66	0.69	0.65	CaO
0.70	0.70	1.41	1.47	1.88	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Na ₂ O
0.01	0.01	0.00	0.00	0.00	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	K ₂ O
100.40	100.36	98.87	99.58	100.92	98.55	97.18	99.28	99.08	100.71	100.78	Sum
1.916	1.900	1.843	1.840	1.874	1.931	1.935	1.935	1.930	1.886	1.914	Si
0.084	0.100	0.157	0.160	0.126	0.069	0.065	0.065	0.070	0.114	0.086	Al ^{iv}
0.092	0.101	0.117	0.128	0.165	0.048	0.086	0.080	0.086	0.063	0.073	Al ^{vi}
0.002	0.002	0.010	0.012	0.013	—	—	0.001	—	0.002	0.002	Ti
0.022	0.024	0.021	0.024	0.019	0.012	0.010	0.011	0.013	0.009	0.006	Cr
—	—	0.081	—	0.048	0.074	—	—	—	0.132	0.072	Fe ³⁺
0.087	0.080	0.042	0.194	0.048	0.093	0.187	0.184	0.186	0.090	0.125	Fe ²⁺
0.002	0.002	0.001	0.001	0.001	—	—	0.003	0.003	0.003	0.003	Ni
0.002	0.002	0.003	0.004	0.003	—	—	0.004	0.004	0.004	0.005	Mn
0.853	0.850	0.822	0.773	0.780	1.721	1.667	1.678	1.666	1.626	1.656	Mg
0.898	0.901	0.832	0.803	0.791	0.021	0.036	0.023	0.025	0.025	0.024	Ca
0.050	0.049	0.099	0.105	0.130	—	—	—	—	—	—	Na
—	—	—	—	—	—	—	—	—	—	—	K
2.008	2.011	2.028	2.044	1.998	1.969	1.986	1.984	1.983	1.954	1.966	WXY
47.7	49.3	57.3	55.6	43.3	59.0	43.0	44.8	44.9	64.4	54.1	%Al ^{iv}
46.4	46.4	46.7	43.5	46.7	90.2	88.2	88.8	88.6	86.5	88.0	En
4.8	4.5	7.2	11.2	5.9	8.7	9.9	10.1	10.1	12.1	10.7	Fs
48.8	49.1	46.1	45.3	47.4	1.1	1.9	1.2	1.3	1.4	1.3	Wo
—	—	52.1	—	52.4	—	—	—	—	—	—	
—	—	7.2	—	6.2	—	—	—	—	—	—	
—	—	18	—	18	—	—	—	—	—	—	
—	—	1050	—	1050	—	—	—	—	—	—	
52.3	52.8	49.8	48.8	51.0	—	—	—	—	—	—	
3.7	4.3	5.0	5.2	4.8	—	—	—	—	—	—	
9	15	9	10	12	—	—	—	—	—	—	
1000	900	1200	1200	1100	—	—	—	—	—	—	

Pyroxene analyses by microprobe, analyst A. L. Chambers.

Bulk rock analyses by X-ray fluorescence and neutron activation, analysts, R. Hutchison and D. K. Paul.

by electron probe (by A. L. C.) of the same mineral, indicate that the clinopyroxene crystallized first at about 1250 °C and 7 kb, but re-equilibrated at a lower temperature, 1100 °C and similar pressure, when estimated by the method of O'Hara (1967).

O'Hara (1967) suggested that spinel-lherzolite xenoliths equilibrated within the melting interval of basalt. With the exception of a few high values obtained by the method of Boyd and Nixon (1973), estimates of temperature of equilibration of the French xenoliths lie below the melting interval of basalt. However, it is possible that the pyroxenes originally formed at magmatic temperatures, with subsequent exsolution at lower temperatures; thus O'Hara's data can be reconciled with those presented here. Because they recrystallized, under conditions in which basalt is solid,

the spinel-lherzolite xenoliths could not have been precipitated by the magmas that brought them to the surface, a fact substantiated by Sr isotopic disequilibrium between host and xenoliths (Leggo and Hutchison, 1968). Equilibration of spinel-lherzolite with a magma must have predated eruption by some hundreds of millions of years to allow time for growth of radiogenic Sr.

O'Hara and Mercy (1963) observed that olivines of garnet-peridotite are less magnesian than their coexisting orthopyroxenes, whereas the opposite is true of the olivines of spinel-lherzolites. Because of this, they suggested that the four phases of the spinel-bearing assemblage had not been in equilibrium, and postulated the former presence of a fifth phase, basaltic liquid. The 'purely speculative drawings' of Olsen and Bunch (1970) suggest that the distribution of Mg between coexisting olivine and orthopyroxene may be temperature-dependent. From their fig. 4 it appears that an olivine of about Fo₉₀ should be in equilibrium with an orthopyroxene of about En₉₂ at 600–700 °C, and with one of about En₈₈ at 1100–1200 °C. This is consistent with the data on pyroxenes presented above. Analysed olivine and orthopyroxene of specimen Mb42 are Fo_{89.5} and En_{89.7} (see Table II), suggesting equilibration above 700 °C and below 1100 °C, and in agreement with the figure of 900 °C obtained from O'Hara's (1967) parameters.

The analyses presented here indicate that the mineral assemblages of xenoliths from four French localities last equilibrated at temperatures below the solidus of basalt. It is likely that the xenoliths first equilibrated with a magma but subsequently re-equilibrated at lower temperature during a magmatic cycle some hundreds of millions of years before eruption. Specimens from four localities apparently equilibrated at 8 to 18 kb indicating 25 to 55 km depth and in the spinel-lherzolite field (see O'Hara, *et al.*, 1971, fig. 6).

Chemical composition of the upper mantle—preliminary discussion

The upper mantle is almost certainly peridotitic, but different regions of it may have had differing histories resulting in regional compositional differences. Indeed, some explanations of the high ⁸⁷Sr/⁸⁶Sr ratios sometimes found in alpine-type peridotites require a complex mantle history.

It is useful, therefore, to see if there is any independent check or external evidence for the relationship between xenolith composition and mantle composition. One possibility is to derive mantle composition from meteorite data (Ringwood, 1966*a, b*), but this suffers from three difficulties.

We cannot be certain which class of chondritic meteorite most closely approximates terrestrial composition. Indeed, the most recent work of Ganapathy and Anders (in prep.) derives a bulk composition for the earth by mixing the seven components of chondrites in the proportions found on earth, these proportions differing from those in chondrites. However, to estimate proportions, it is necessary to know certain terrestrial abundances, e.g. U content, or inter-element ratios, e.g. Mn/Fe²⁺, and so the investigation is circular to some extent.

Secondly, geophysicists increasingly suggest that the mantle may be chemically layered (e.g. Richter and Johnson, 1974), with an increase in mean atomic weight

with depth in the earth, presumably due to an increase in Fe/Mg ratio. The calculation of the composition of the upper mantle from that of the whole mantle or whole earth cannot be done until the extent of chemical layering is known.

Thirdly, the 'pyrolite' compositions derived from a chondrite model and from empirical considerations (3 parts peridotite to 1 part basalt) largely coincide for major elements but cannot do so for others, for example the radioactive elements U and Th. In effect, the 'pyrolite' model requires that the lower mantle be depleted in radioactive elements without significant change in major element abundances.

The content of radioactive elements in xenolithic material compared with levels of radioactivity calculated from mantle heat-flow should provide some assessment of the extent of chemical layering. However, the uncertainties are great. One assessment is that a uniform content of U, Th, and K, at the concentrations in lherzolite xenoliths, down to 900 km depth in the earth could provide the terrestrial heat-flow (Harris *et al.*, 1972), while Harris (1974) has decided that mantle heat-flow is consistent with a lherzolithic composition.

A different approach is to use theoretical considerations to see if changes in mantle composition with time and place are likely. It has been suggested that the composition of Archaean ultrabasic rocks such as peridotitic komatiite differ somewhat from modern ultrabasic rocks and xenoliths, indicating a primitive mantle richer in CaO and of higher Fe/Mg ratio than modern upper mantle (Viljoen and Viljoen, 1969). Present day processes of ocean floor spreading and the subduction of sub-oceanic crust must impose heterogeneity on the mantle. Is this permanent, or do homogenization processes (diffusion, magmatism, etc.) restore a uniform composition? There are no relevant data.

A probable conclusion is that present day upper mantle is likely to be heterogeneous, especially in its degree of depletion of the fusible (basaltic) components; the least depleted mantle is probably located immediately beneath the oldest cratons. In addition, as the oldest cratons are regions of low geothermal gradient, thermal arrest within the mantle of ascending magma is most likely to occur in these regions. At the opposite extreme, sub-oceanic mantle is likely to undergo the most frequent convective recycling and to be the most depleted in fusible components. Also, in regions of high geothermal gradient (sub-oceanic mantle), the ease of escape of magmatic fluids is likely to be highest, so local additions of fusible components within the mantle are least likely.

The best, and, indeed, the only real evidence for mantle composition and regional heterogeneity must be direct observation and analysis of mantle-derived samples, namely, ultramafic rocks and xenoliths.

Interpretation

On the basis of their bulk chemistry, an attempt is made at classifying xenoliths as depleted 'residua', as 'undepleted' or as 'enriched' in fusible components. It is again stressed that the term 'undepleted' is used for reasons of brevity and that it may be applied to xenoliths that are depleted to some (unknown) extent. From all the analyses summarized in Table III, for each locality frequency histograms for the various oxides

were drawn, of which those for MgO are taken as an example (fig. 2a). Although each of the populations of xenoliths is internally varied, variance tests indicate that for all oxides except SiO₂ and Cr₂O₃ there is 'significant' or 'highly significant' variation amongst the five groups, i.e. that the populations are different and that each locality has its own chemically distinctive suite of ultramafic xenoliths. This was stated by Hutchison *et al.* (1970) for Al₂O₃ only. The Puy Beaunit and Tarreyres populations

TABLE III. *Ultramafic xenoliths: mean compositions, minima, maxima, and standard deviations*

	Puy Beaunit				Volcan de Zanière				Montboissier			
	Min.	Mean	Max.	$\hat{\sigma}$	Min.	Mean	Max.	$\hat{\sigma}$	Min.	Mean	Max.	$\hat{\sigma}$
SiO ₂	39.3	44.0	47.7	1.7	41.8	43.5	46.7	1.2	41.6	44.1	47.9	1.1
TiO ₂	<0.01	0.04	0.18	0.04	<0.01	0.03	0.13	0.03	<0.01	0.02	0.10	0.01
Al ₂ O ₃	0.63	1.63	3.70	0.84	0.88	1.73	3.20	0.51	1.14	1.97	2.89	0.38
Cr ₂ O ₃	0.36	0.47	1.03	0.15	0.38	0.44	0.54	0.05	0.33	0.46	0.59	0.06
Fe ₂ O ₃	0.56	1.40	2.09	0.36	1.08	1.47	2.13	0.25	1.33	1.95	2.60	0.30
FeO	6.30	7.43	10.78	0.98	5.92	6.65	7.30	0.40	5.29	5.94	6.95	0.36
NiO	0.22	0.27	0.33	0.03	0.25	0.29	0.32	0.02	0.22	0.27	0.33	0.02
MnO	0.11	0.13	0.26	0.04	0.11	0.12	0.14	0.01	0.11	0.11	0.13	0.00
MgO	38.7	41.9	46.0	2.2	38.85	42.75	45.5	1.5	38.1	41.6	44.6	1.5
CaO	0.24	1.62	3.50	1.05	0.63	1.51	2.68	0.55	0.92	2.15	3.28	0.58
Na ₂ O	0.02	0.11	0.31	0.09	0.05	0.12	0.83	0.05	0.04	0.10	0.41	0.07
K ₂ O	<0.01	0.04	0.13	0.05	<0.01	0.03	0.08	0.03	<0.01	0.04	0.31	0.06
Sum	97.42	99.04	101.07	1.1	97.52	98.64	100.54	0.9	97.39	98.71	101.58	1.0
	Monistrol d'Allier				Tarreyres				Bultfontein			
	Min.	Mean	Max.	$\hat{\sigma}$	Min.	Mean	Max.	$\hat{\sigma}$	Min.	Mean	Max.	$\hat{\sigma}$
SiO ₂	43.1	44.6	45.9	0.7	42.7	44.1	46.3	0.7	41.8	44.3	47.2	1.3
TiO ₂	<0.01	0.08	0.15	0.03	<0.01	0.07	0.16	0.03	0.01	0.05	0.16	0.04
Al ₂ O ₃	0.88	3.13	5.85	1.02	1.19	2.77	4.70	0.86	0.38	1.74	3.55	0.88
Cr ₂ O ₃	0.34	0.41	0.46	0.04	0.28	0.43	0.58	0.07	0.25	0.41	0.62	0.09
Fe ₂ O ₃	0.63	1.27	1.92	0.29	0.80	1.45	2.29	0.36	1.46	2.35	2.99	0.43
FeO	5.71	6.64	7.34	0.39	5.69	6.65	8.92	0.62	3.29	4.09	4.85	0.47
NiO	0.15	0.25	0.32	0.03	0.20	0.26	0.30	0.02	0.22	0.28	0.34	0.03
MnO	0.11	0.11	0.13	0.01	0.10	0.11	0.15	0.01	0.07	0.10	0.13	0.02
MgO	32.3	39.4	44.6	2.3	35.2	40.5	44.3	2.0	36.1	41.2	46.0	2.3
CaO	0.70	3.12	7.78	1.31	0.71	2.58	4.79	0.95	0.44	1.28	3.36	0.90
Na ₂ O	0.04	0.24	0.40	0.07	0.07	0.22	0.65	0.11	0.05	0.14	0.38	0.03
K ₂ O	<0.01	0.04	0.10	0.02	<0.01	0.01	0.07	0.01	0.01	0.23	1.04	0.30
Sum	98.34	99.29	100.12	0.7	97.65	99.15	100.54	0.8	99.04	100.76*	100.97	0.74

* Includes 4.59 % H₂O.

of xenoliths have bi-modal MgO distributions; the Montboissier population has a single mode at 40.5 wt % MgO, the peak lying between the modes of the first-mentioned groups. The harzburgitic inclusions of the Volcan de Zanière generally have the highest MgO contents of the French populations, being unimodal at 43 %, whereas the lherzolites of Monistrol d'Allier have their single mode at 39 %. The Bultfontein xenoliths cover the whole range, but may also be bi-modal. Since the steps in the histograms, 1 % MgO, are larger than the precision for each measurement ($2\hat{\sigma} = 0.65$), the bi-modal distributions are real. From the over-all variation illustrated

in fig. 2a, two distinct groups of xenoliths can be recognized, one with MgO greater than 40 %, the other with MgO less than 40 wt %. Since 'undepleted' or 'enriched' mantle should have lower MgO contents than 'residua', the figure of 40 % MgO may

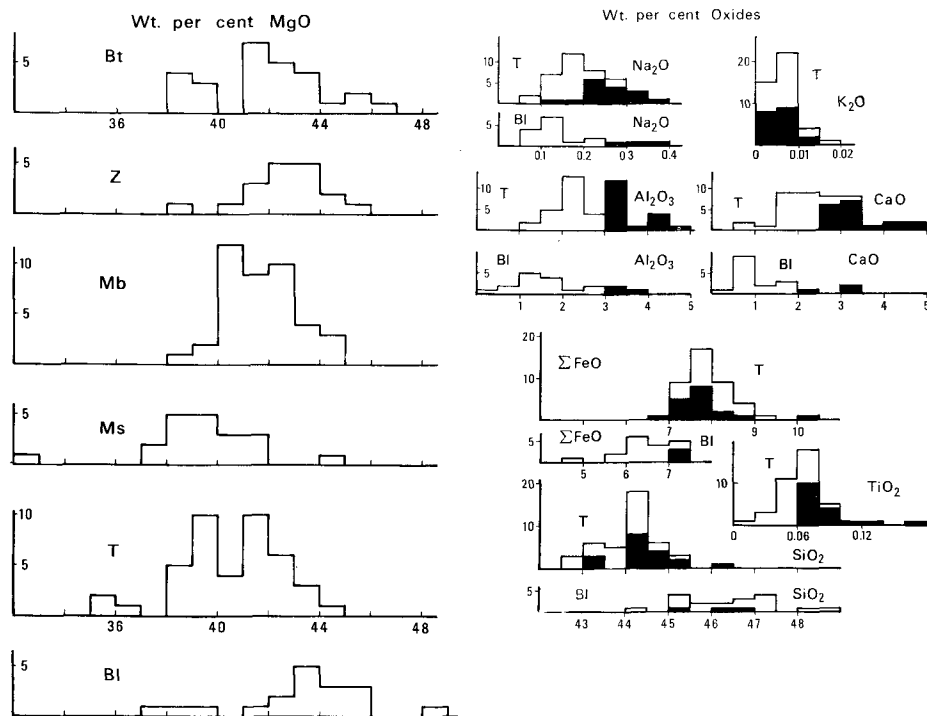


FIG. 2. (a) MgO distribution in each locality studied. Symbols as in fig. 1, with in addition, Bl = Bultfontein. (b) Distribution of other oxides in Tarreyres and Bultfontein samples. Cr₂O₃, NiO, and MnO show little variation (see Table III) and are omitted. TiO₂ and K₂O were probably introduced into Bultfontein peridotites during kimberlite emplacement; concentrations may not represent mantle composition and are omitted from the fig. Bultfontein analyses have been recalculated water-free. No correction has been made for reduced mass-absorption of X-rays due to the presence of water and low total iron in the Bultfontein samples; this is reflected in the high sums of these analyses (see Table III). Consequently, there is probably a systematic error of +1 per cent MgO and +0.5 per cent SiO₂ in the Bultfontein figures. In depleted Bultfontein xenoliths, the modal values of SiO₂ and MgO are probably close to 46.5 and 43.0 % respectively, i.e. slightly lower than in Table IV (no. 12).

represent a division between residua and the others. From fig. 2a, residua greatly outnumber possible 'undepleted' or enriched mantle xenoliths in the material sampled by the eruptions.

Xenoliths with MgO less than 40 % are now examined in an attempt at subdividing them into 'undepleted' and enriched categories. Histograms illustrating the frequency distribution of various fusible oxides, total iron as FeO, and SiO₂ for the Tarreyres and Bultfontein populations are shown in fig. 2b. Specimens with MgO less than 40 % are shaded. One such xenolith has total iron as FeO in excess of 10 %, Al₂O₃ 4.0 %;

CaO 4.38%; TiO₂ 0.16%; Na₂O 0.31%; and MgO 35.2%. The sum of the full analysis is 99.57 (see Table IV, no. 11). The $Mg \times 100 / (Mg + Fe)$ molecular ratio of this xenolith, T33, is 85.8; in the remainder of the Tarreyres specimens it ranges from 88.8 to 91.2. T33 is probably the result of magmatic enrichment of Fe, Ti, and other fusible oxides. This interpretation differs fundamentally from that of Kuno and Aoki (1970), who investigated suites of ultramafic xenoliths from world-wide occurrences.

TABLE IV. Modal compositions of ultramafic xenoliths; for commentary, see text. 'Modal' refers to the 'mode' of frequency distributions as in fig. 2, and is not to be taken in the petrological sense

	Beaunit		Zanière		Montboissier		Monistrol		Tarreyres		Bultfontein		
	1	2	3	4	5	6	7	8	9	10	11	12	13
	Mode	Undepl.	Mode	Undepl.	Mode	Undepl.	Depl.	Undepl.	Depl.	Undepl.	Pptd.	Depl.	Undepl.
SiO ₂	44.8	44.8	43.3	46.7	44.0	45.8	44.25	45.0	44.25	44.25	44.1	47.0	46.2
TiO ₂	0.01	0.10	0.02	0.01	0.01	0.02	0.09	0.09	0.05	0.07	0.16	0.02	0.09
Al ₂ O ₃	1.25	3.27	1.75	3.20	2.25	2.70	2.50	3.50	2.25	3.25	4.00	1.25	3.36
Cr ₂ O ₃	0.47	0.43	0.44	0.54	0.46	0.56	0.41	0.41	0.43	0.43	0.57	0.40	0.56
Fe ₂ O ₃	1.50	0.98	1.25	0.14	1.75	1.80	1.25	1.25	1.25	1.25	1.59	2.50	2.54
FeO	7.25	7.00	6.75	5.95	5.75	5.50	6.75	6.75	6.50	6.75	8.92	4.25	4.94
NiO	0.27	0.24	0.29	0.25	0.24	0.24	0.25	0.25	0.26	0.26	0.20	0.28	0.25
MnO	0.13	0.11	0.12	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.13	0.10	0.13
MgO	41.5	38.9	43.0	38.9	40.5	39.5	41.0	39.0	41.5	39.5	35.2	43.5	38.4
CaO	1.25	3.21	1.25	2.68	2.25	2.80	2.5	3.25	2.00	3.25	4.38	0.75	3.07
Na ₂ O	0.08	0.23	0.13	0.14	0.08	0.10	0.20	0.28	0.18	0.23	0.31	0.13	0.32
K ₂ O	0.01	0.05	0.01	0.06	0.02	0.02	0.03	0.035	<0.01	<0.01	0.01	0.08	0.47
Sum	98.52	99.32	98.31	98.68	97.42	99.15	99.34	99.92	98.78	99.35	99.57	100.26	100.33
$\frac{100 \text{ Mg}}{\text{Mg} + \text{Fe}}$	89.7	89.9	90.8	91.0	90.9	90.9	90.4	89.9	90.5	90.0	85.8	92.3	90.5

These authors found gradational relationships only, and arbitrarily selected specimens with high Fe:Mg ratios (i.e. low $Mg \times 100 / (Mg + Fe)$ ratios) as representative of undepleted upper mantle. However, one essential property of undepleted upper mantle is that it can produce a basaltic liquid fraction on partial melting. The experimental work of Green and Ringwood (1967) and Green and Hibberson (1970) has shown that a natural tholeiite and an olivine-basalt have olivine or orthopyroxene as liquidus phases at pressures from 13 to 18 kb. In this pressure range the experimentally produced liquidus phases are more magnesian-rich relative to iron than the xenoliths chosen by Kuno and Aoki (1970) as 'undepleted'. Conversely, partial melting of upper mantle of Kuno and Aoki (1970) type would be expected to produce a liquid more enriched in iron than the basalts investigated by Green and Ringwood (1967) and Green and Hibberson (1970); the evidence from basalts indicates that their parental mantle has a $Mg \times 100 / (Mg + Fe)$ molecular ratio close to 90, thus sustaining our interpretation of T33 as 'enriched'. There are no major textural differences between this specimen and the others, but it has small grains of opaque ore whereas irregular masses of green-brown spinel are typical of most xenoliths from this locality. The opaque ore of T33 is probably chromite, as evidenced by the high (0.57%) Cr₂O₃ content of the bulk xenolith.

Apart from the single specimen just described, the MgO-poor Tarreyres xenoliths form a coherent group. Fig. 2*b* shows that they have the highest contents of fusible oxides and is therefore a graphical expression of the negative correlation of MgO with TiO₂, Al₂O₃, CaO, Na₂O, and SiO₂ (see Harris *et al.*, 1972). From the modal values of the different oxides on these histograms are derived the compositions of Tarreyres depleted residuum and of 'undepleted' upper mantle shown in Table IV (nos. 9 and 10). The approach outlined here is essentially that of I. G. White (1967) and of Harris *et al.* (1967), but the larger numbers of analyses performed in this study have enabled us to distinguish between the two types of mantle.

The other suites of xenoliths have been treated in exactly the same way. Like Tarreyres, the Monistrol d'Allier suite has a high proportion of 'undepleted' specimens but in this instance their K₂O content is about 0.035 % compared with about 0.01 % for Tarreyres material. Seven of the 28 Puy Beaunit xenoliths have MgO less than 40 %, but of these four are either enriched in fusible oxides or have been contaminated by their host-basalt. The mean composition of the remaining three is presented in Table IV (no. 2) as an approximation to 'undepleted' upper mantle beneath Puy Beaunit. The five xenoliths from Montboissier and one from the Volcan de Zanière having MgO less than 40 % are poorer in Na₂O, CaO, and TiO₂ than 'undepleted' mantle from the three other localities, suggesting strong depletion in the mantle sampled by these two eruptions—see Table IV, nos. 6 and 4, respectively.

Of the 18 analysed xenoliths from the Bultfontein kimberlite, 10 are garnet-lherzolite of which 3 are considered to be 'undepleted', i.e. 30 % of the garnet-lherzolites or 17 % of all the specimens analysed. Since Dr. J. B. Dawson attempted to collect specimens representative of the various types occurring at Bultfontein (*pers. comm.*), the more abundant garnet-lherzolites are under-represented in our sample and so the figure of 30 % 'undepleted' upper mantle is probably close to the truth. Chen's (1972) analyses indicate that the Bultfontein xenoliths may be even more refractory than our estimate. However, his analyses are less precise than those of this study and at variance both with these and with the atomic absorption analyses of Carswell and Dawson (1970). When present, percentages of 'undepleted' xenoliths in the French suites are: Monistrol d'Allier, 55 (11 of 20), Tarreyres, 40 (17 of 42), Puy Beaunit, 11 (3 of 28). Hutchison *et al.* (1970) argued that the five French host-basalts are so similar in bulk chemistry and in Rb/Sr and ⁸⁷Sr/⁸⁶Sr ratios that they were probably derived by the same process acting at the same depth. Thus, differences between the different suites of xenoliths probably reflect lateral rather than vertical changes in the bulk chemistry of the upper mantle beneath the Massif Central. In addition, there is no evidence from the pyroxenes of the xenoliths to suggest that 'residual' and 'undepleted' types equilibrated under different *P* and *T* conditions, contrary to Boyd's (1973) findings for garnet-lherzolite xenoliths of southern Africa. Tarreyres 'undepleted' upper mantle is lower in K₂O (see Hutchison, 1971), and probably lower in SiO₂ and richer in MgO than 'undepleted' Monistrol d'Allier upper mantle, which is similar to that beneath Puy Beaunit. The most refractory residual mantle of the French suites is that of the Volcan de Zanière, but the Bultfontein depleted xenoliths are lower in total iron, have a higher Mg × 100/(Mg + Fe) molecular

ratio and so the latter appear to be the more refractory. Since the Bultfontein material is partly serpentinized it is possible that this has affected the bulk composition. However, SiO_2 , total Fe, and MgO do not correlate with H_2O content, which ranges from 2.9 to 6.8 wt %, suggesting that serpentinization has not affected bulk composition of major elements. The data obtained in this study indicate that Bultfontein upper mantle has higher MgO and SiO_2 and lower total iron content than Massif Central upper mantle.

The specimens from Bultfontein are derived from the upper mantle beneath the ancient South African craton, so it is possible that their low total iron and high MgO contents are the result of intense depletion during strong early heating, as discussed above. Enrichment of such residua in basaltic elements could have produced the 'undepleted' mantle represented by the three garnet-lherzolite xenoliths. Enrichment in Rb of peridotite blocks in kimberlite was shown by Allsopp *et al.* (1969) to date from the time of emplacement of the kimberlite. The high and variable K_2O content of the Bultfontein xenoliths is almost certainly the result of contamination from the kimberlitic magma and is therefore unrelated to upper mantle composition. Thus, for some minor elements, garnet-peridotite xenoliths in kimberlite are not our best samples of upper mantle, so that O'Hara's (1970, p. 244) statement that 'Garnet-lherzolite nodules in kimberlite provide the best available model of the primitive upper mantle composition' is not completely true.

Conclusion

Garnet-lherzolite xenoliths from the Bultfontein kimberlite pipe are no less depleted in fusible oxides than spinel-lherzolite xenoliths in several French occurrences. The French specimens do tend to be poorer in SiO_2 and are in a less highly oxidized state. 'Undepleted' upper mantle beneath Monistrol d'Allier is similar in chemical composition to 'undepleted' mantle material from Bultfontein. Differences in bulk chemistry between the different French suites of xenoliths have been established statistically.

TiO_2 contents of both garnet-bearing and spinel-bearing lherzolite show that 'undepleted' varieties can yield a maximum of 9 % of oceanic tholeiite or 4 % of alkalic basalt by partial melting before this oxide is exhausted. The first figure is slightly higher than that (6 %) of Harris *et al.* (1972), who used the mean composition of all analysed Monistrol d'Allier xenoliths on which to base their estimate. The highest figure for TiO_2 in an 'undepleted' xenolith is 0.15 wt %, and for Na_2O , 0.40 %. Thus the values in Ringwood's pyrolite (1966a) have not been found (0.71 and 0.57 % for TiO_2 and Na_2O , respectively) and no ultramafic material encountered in this study could yield more than 15 % of oceanic tholeiite by partial melting. However, major element composition and $\text{Mg} \times 100 / (\text{Mg} + \text{Fe})$ molecular ratios of our 'undepleted' mantle are in excellent agreement with the hypothetical pyrolite composition (Ringwood, 1966a).

Acknowledgements. We reiterate the acknowledgements of Hutchison *et al.* (1970). In addition, we thank Mr. C. J. Elliot for performing atomic absorption analyses, Drs. A. L. Graham and K. A. Rodgers for discussion and criticism of the text, and Mr. R. F. Symes for assistance in writing the section on microprobe analysis.

Appendix—analytical techniques

Microprobe analysis. An A.E.I., SEM 2 instrument was used, with an accelerating voltage of 20 kV, current of about 0.2 mA, and metal, oxide, and silicate standards. Corrections for the physical factors governing X-ray generation were computed as outlined by Sweatman and Long (1969), with an extra factor added to allow for the non-normal incidence of the electron beam. FeO was determined on about 10 mg of separated grains by the volumetric method of Wilson (1960).

Precision ranges from about $\pm 1\%$ for a major element such as Si or Ca, down to about $\pm 8\%$ for a minor, low-atomic-number element such as Na. As a check on accuracy, the E₃ diopside (Nixon *et al.*, 1963) was analysed (cf. Table V, 1a–1d). In addition, R.H. analysed

TABLE V. *Analyses of two chrome-diopsides*

	1a	1b	1c	1d	2a	2b
SiO ₂	54.61	55.3	55.8	54.8	52.3	52.4
TiO ₂	0.23	0.17	0.17	0.16	0.48	0.56
Al ₂ O ₃	1.30	2.08	1.91	1.91	6.89	6.96
Cr ₂ O ₃	0.92	0.86	0.90	0.88	0.65	0.62
FeO	4.04	3.35	3.49	3.40	3.20	3.00
MnO	0.10	0.11	0.12	n.d.	0.09	n.d.
MgO	16.20	16.2	16.8	16.3	14.6	14.6
CaO	20.88	21.2	19.8	20.2	20.6	20.1
Na ₂ O	1.28	1.26	1.33	1.13	1.88	1.66
K ₂ O	0.12	0.05	0.04	n.d.	—	n.d.
Sum	99.68	100.6	100.4	98.8	100.74*	[100]

Total Fe calculated as FeO. * Includes 0.05% NiO.

1. E₃ diopside. 2 T15 diopside.

1a. 'Wet' analysis by M. H. Kerr, in Nixon *et al.* (1963).

1b. Microprobe analysis by Boyd (1968).

1c. Microprobe analysis by A. L. Chambers (unpubl.), performed at Leeds.

1d. Microprobe analysis by R. Hutchison (unpubl.), performed in the British Museum (Natural History).

2a. Microprobe analysis by A. L. Chambers, Table II, no. 7, this work.

2b. Microprobe analysis by R. Hutchison (unpubl.), performed in the British Museum (Natural History). Due to problems in inserting the grain-mount for an S.E.M. 2 instrument into a 'Geoscan', this analysis produced a low total of 94.1. However, when recalculated to 100%, as shown, it is clearly within experimental error of analysis 2a.

The groups of analyses show excellent agreement, the only major discrepancy being between the Al₂O₃ and FeO figures for 'wet' and microprobe analyses of the E₃ diopside. The 'wet' figures may be the result of misapportioning Al and Fe in the R₂O₃ precipitate, the Al₂O₃ having been obtained by difference.

the T15 diopside using the instrument and procedure of the British Museum (Natural History) (see Table V, 2a and 2b). The excellent agreement within the two sets of analyses indicates a high degree of accuracy in the microprobe analyses presented in Table II.

Bulk rock analysis. For convenience in handling a large number of specimens, X-ray fluorescence (X.R.F.) was selected as the best technique. Ten xenoliths were chosen for use as standards and analysed in duplicate using largely 'classical' techniques, by F. Buckley of Leeds, and R.H. For X.R.F., aliquots of rock powder were fused with a lithium-carbonate/lithium-tetraborate mixture in gold-plated Pt crucibles, to produce glass discs suitable for

insertion into the Phillips 1212 automatic X-ray spectrometer. The discs were prepared as in the method of Norrish and Chappell (1967), but no heavy absorber was added, to allow emission of sufficient X-rays for determination of minor Cr_2O_3 , NiO, and MnO, in addition to SiO_2 , Al_2O_3 , total Fe as Fe_2O_3 , MgO, and CaO. The ten standard rocks were used to draw a calibration curve for each of these eight oxides. By chance, the standards were rich in MgO, (41.0–44.6 %), poor in Al_2O_3 (0.92–2.35 %), and fairly poor in CaO (0.26–3.56 %). Atomic absorption (A.A.) analyses indicate that the calibration for MgO holds down to 32 % and for CaO up to 7.78 %—cf. X.R.F. and A.A. figures in Table VI. To check the

TABLE VI. Comparison between atomic absorption (a) and X-ray fluorescence (b) analyses of 5 xenoliths

	1		2		3		4		5	
	a	b	a	b	a	b	a	b	a	b
SiO_2	45.4	44.1	46.8	46.3	45.1	44.2	46.5	45.9	45.4	44.5
TiO_2	0.10	0.08	0.16	0.12	0.10	0.07	0.21	0.15	0.15	0.11
Al_2O_3	4.10	3.92	4.45	4.48	3.00	2.91	5.80	5.85	3.95	3.95
Cr_2O_3	0.41	0.47	0.29	0.32	0.40	0.43	0.35	0.37	0.38	0.41
Fe_2O_3	1.58	0.88	1.45	1.24	1.14	1.18	2.58	1.92	2.17	0.75
FeO	6.59	6.89	6.41	6.26	6.83	6.66	5.69	5.71	5.98	6.97
NiO	0.23	0.23	0.20	0.22	0.25	0.27	0.14	0.15	0.23	0.23
MnO	0.13	0.11	0.13	0.11	0.12	0.11	0.15	0.12	0.12	0.11
MgO	38.2	38.4	36.0	36.4	41.0	40.3	30.7	32.3	38.4	38.3
CaO	3.10	3.09	4.25	4.13	2.80	2.81	7.71	7.78	3.55	3.47
Na_2O	0.26	0.22	0.41	0.36	0.28	0.25	0.48	0.40	0.36	—
K_2O	0.00	0.004	0.00	0.005	0.01	0.008	0.08	0.10	0.015	0.04
<i>Sum</i>	<i>100.10</i>	<i>98.39</i>	<i>100.55</i>	<i>99.95</i>	<i>101.03</i>	<i>99.20</i>	<i>100.39</i>	<i>100.75</i>	<i>100.70</i>	<i>98.84</i>
Total iron as Fe_2O_3	8.90	8.54	8.57	8.20	8.73	8.58	8.90	8.27	8.82	8.51
$\frac{\text{Mg} \times 100}{\text{Mg} + \text{Fe}}$	89.5	90.0	89.3	90.0	90.3	90.3	87.2	88.6	89.6	90.0

Analysts: A.A.; C. J. Elliott. X.R.F.; R. Hutchison and D. K. Paul. 1. T21, 2. T29, 3. T36, 4. Ms9, 5. Ms10.

For most oxides there is good agreement. SiO_2 determination is the least precise major element measurement by A.A. and the results are consistently higher than for X.R.F. The higher A.A. total iron figures may be due to enhanced absorption in the presence of large excesses of MgO. In columns 'b' Na_2O was determined by neutron activation by D. K. Paul.

Al_2O_3 calibration, this oxide was determined (by R.H.) in three Al_2O_3 -rich xenoliths by the method of Pritchard (1965), and the X.R.F. figures were found to be low. A new calibration curve was therefore drawn. In Table VI there is good agreement between revised X.R.F. figures for Al_2O_3 and those obtained later by A.A.

Precision. Duplicate analyses of seventeen xenoliths, representing all French localities and Bultfontein, were performed in order to estimate precision. $2\hat{\sigma}$ for a single measurement is: for SiO_2 , 0.52; for Al_2O_3 , 0.16; for Cr_2O_3 , 0.01; for NiO, 0.00; for MnO, 0.00; for MgO, 0.65; for CaO, 0.04; for total Fe as Fe_2O_3 , 0.15.

TiO_2 and K_2O were determined by X.R.F. on undiluted briquetted rock powders, calibration curves having been established using a 'spiking' technique. From counting on the standards, precision ($2\hat{\sigma}$) for each measurement is much better than 0.005.

Na was determined by neutron activation similar to the method of Schroeder and Winchester (1962). One sample analysed after each of seven irradiations had a mean Na_2O content of 655 ppm, with $2\hat{\sigma} = 73$ ppm. The contribution from ^{27}Al and ^{24}Mg , which may

also produce ^{24}Na , was measured using a synthetic mixture with Mg and Al contents like those in peridotites; γ radiation from the mixture was equivalent to 5.5 ppm Na_2O , a figure considered insignificant compared with Na_2O in the samples. Aliquots of rock powder from 0.15 to 0.25 g were weighed and sealed into polythene capsules for irradiation. Capsules that leaked necessitated repeated measurement but, unluckily, some repeats were also unsuccessful, hence the absence of a figure for Na_2O in Table VI, no. 5b. Standards used were kindly donated by Professor E. A. Vincent of Oxford, and the measurements were made in the Geology Department, University of Manchester, by D.K.P., on the invitation of Dr. J. Esson. Analyses of French samples appear in full in Paul (1970).

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