Rare Earth Geochemistry of Fused Ophiolitic and Alpine Lherzolites

II. Beni Bouchera, Ronda and Lanzo

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Abstract. Partial fusion hypotheses have been proposed for the origin of lherzolite-harzburgite alpine peridotite associations. Analyzed lherzolites from Othris, Ronda, Lanzo and Beni Bouchera, have light REE depleted to chondritic REE abundances, and clinopyroxenes contain most of the REE relative to depleted olivine and orthopyroxene. Variation in the level of REE enrichment within these lherzolites indicates mantle heterogeneity probably caused by partial melting processes. The Beni Bouchera spinel lherzolite and the Othris plagioclase lherzolite are the best candidates for relatively "undepleted" mantle based on REE studies. Fractional fusion calculations (15-25%) reveal that partial melts have REE characteristics somewhat similar to oceanic tholeiites. Conversely, computed source peridotites from oceanic tholeiites (Schilling, 1975) are similar to the alpine lherzolites reported here. Alpine lherzolites are, however, depleted in trace elements (K, Rb, Sr and Ba, Menzies and Murthy 1976). Since the lherzolites have an undepleted major, minor and REE chemistry close to that of pyrolite, the lost trace element-rich fraction must represent a small degree of melting. It is proposed that alpine lherzolites are residue left after the loss of a nephelinitic/alkalic fraction, $([Ce/Yb]_N = 2.0 - 4.01)$ representing a small degree of partial fusion. This labile fraction may have existed as an intergranular phase or hydrous mineral prior to melting.

1. Introduction

A. General

In the Mediterranean area, tectonite or metamorphic ultramafic rocks occur in three distinct geological environments (Fig. 1). The first major occurrence takes the form of large massifs of peridotite, known as alpine peridotites. Secondly, peridotites occur within ophiolitic complexes as foliated lherzolites and harzburgites which form a basement for the accumulation of crustal cumulate dunites,

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Fig. 1. Distribution of peridotite massifs, ophiolitic peridotites and xenolithic localities in the Mediterranean region (see Nicolas and Jackson, 1972, for further information and references concerning the smaller squares)

lherzolites, wehrlites, etc. The third major occurrence is in the Massif Central district of France, where abundant peridotite xenoliths are to be found in alkali basalt flows and scoria cones.

Recent models proposed by Ringwood (1966) and Green and Ringwood (1967), indicate that the least depleted peridotite is very similar to their estimate of primary mantle composition, based on a hypothetical mixture of alpine peridotite and an oceanic basalt. The least depleted is normally a lherzolite which contains 5% diopside in addition to olivine, orthopyroxene and either plagioclase, garnet or spinel. Substantial amounts of partial melting of these lherzolites, in either the plagioclase, spinel or garnet lherzolite stability field, leads to the production of a harzburgite residue. This partial fusion model is supported by the experimental work of Kushiro (1971). It is therefore interesting to examine the least refractory peridotite as potential source material for basalts.

B. Rare Earth Chemistry

Frey (1966) studied the REE geochemistry of a variety of peridotitic rocks and, in later investigations (Frey et al., 1968, 1971; Frey, 1969, 1970), he included peridotites from the Mediterranean area. Since then, many of the classic alpine peridotite and ophiolite localities in the Mediterranean have been re-investigated (Kay and Senechal, 1976, 1975; Montigny et al., 1973; Loubet et al., 1975; Menzies, 1974, 1976a, b, c; Menzies et al., 1975). Most of the work on alpine peridotites recorded the mild (lherzolite) or severe depletion (harzburgite) in light REE. The nature of the REE profiles within the alpine harzburgites and lherzolites is very much controlled by the REE content of diopside, since orthopyroxene and olivine contain low REE abundances. Relative to chondritic REE

	i	2	3	4	5	6	7	8	9	10	11
SiO ₂	41.94	41.75	44.35	43.61	42.55	42.88	43.55	43.87	38.83	42.42	43.63
TiO,	tr		0.14	0.06	0.16	0.04	0.04	0.04	0.02	0.06	0.11
Al ₂ O ₃	2.78	4.80	3.64	2.93	2.50	1.72	2.96	2.38	0.82	0.48	1.85
Cr_2O_3	0.15	tr	0.33	0.39	0.36	0.21	0.36	0.01	0.08	0.48	0.42
Fe ₂ O ₃ ^a	0.98	1.25	0.59	1.09	1.72	2.03	2.09	2.18	2.47	0.83	2.48
MnO	0.06	0.17	0.13	0.11	0.12	0.07	0.14	0.14	0.12	0.16	0.16
MgO	43.06	37.10	38.75	29.86	39.89	42.81	39.29	41.11	44.13	46.95	42.58
CaO	0.64	3.70	3.29	2.66	2.42	1.12	1.77	0.87	1.65	0.74	2.15
Na ₂ O	0.12	0.50	0.26	0.26	0.17	0.03	0.06	0.04	0.06	0.0	0.14
K ₇ Õ	0.03	_	_	0.01	_	_		tr	tr	0.01	0.02
$H_{2}O^{+}$	3.06	4.20	0.67	1.89	2.99	1.94	2.39	2.34	2.72		_
H ₂ O ⁻	0.17	0.12	0.06	0.15	0.16	0.24	0.17	0.22	0.18		
P.O.	0.17	0.12		_		0.01	0.02	0.02	0.16		
NiO			0.27	0.26	0.26			0.08	0.08	0.30	0.28
SO ₃ –		_	0.12	0.03	_						
CO ₂	-	0.20									
Total	100.86	99.95	100.13	100.05	100.26	99.89	99.87	100.26	99.47	100.00	100.00

Table 1. Major, minor and trace element chemistry of alpine harzburgites and lherzolites

1. and 2= Beni Bouchera (after Kornprobst, 1966)

3.-5=Ronda (after Dickey, 1970)

6.-9 = Lanzo (after Boudier, 1972)

10=Othris harzburgite (average of 7 after Menzies and Allen, 1974)

11 = Othris lherzolite (average of 6)

^a Total iron as Fe₂O₃

abundances, the latter two minerals are characteristically light REE depleted or have U-shaped profiles, whereas diopside typically contains up to $10 \times$ chondritic REE abundances and has a flat profile with slight depletions in light and/or heavy REE.

C. Major, Minor and Trace Element Chemistry

The major, minor and trace element chemistry of alpine lherzolites and harzburgites has been described in detail elsewhere (Kornprobst, 1966; Dickey, 1970; Boudier and Nicolas, 1972; Menzies, 1974; Menzies and Allen, 1974; Menzies, 1976c). A table of typical analyses of harzburgites and lherzolites is provided, with examples from Beni Bouchera, Morocco; Ronda, Spain; Lanzo, Italy; and Othris, Greece (Table 1). These analyses are taken from the literature and do not represent the samples analyzed here and, as such, no evaluation can be made of chemistry in relation to terminology.

Harzburgites tend to be highly refractory in nature, resulting from a predominance of highly forsteritic olivines and magnesian orthopyroxenes. Dunites and harzburgites are characterized by high MgO, NiO, Cr_2O_3 , and low Al_2O_3 , CaO, Na₂O, K₂O, and TiO₂. Certain of these elements can be concentrated in the harzburgites, e.g., Al_2O_3 , in the orthopyroxene phase, whereas the high Al_2O_3 content of the lherzolites is the result of larger modal amounts of plagioclase, spinel or garnet.

Lherzolites contain $\geq 5\%$ diopside and plagioclase (garnet or spinel), in conjunction with olivine, orthopyroxene and spinel. Consequently, the chemistry is less refractory with lower MgO content and higher concentrations of TiO₂ alkalis and calcium.

D. Strontium Isotope Geochemistry

Any simple genetic correlation of alpine peridotites and basalts, either via partial melting or fractionation is incompatible with published strontium isotopic analyses (Roe et al., 1965; Stueber, 1965; Hurley, 1967; Bonatti et al., 1970). Recently, however, Graham and Ringwood (1971) and Ringwood (1975) postulated disequilibrium fusion as an explanation for the marked discrepancy in isotopic composition, between alpine peridotites (87 Sr/ 86 Sr=0.707-0.727) and oceanic lavas $({}^{87}\text{Sr}/{}^{86}\text{Sr}=0.702-0.704)$. Partial justification of a disequilibrium melting model is the existence of minerals, in apparent isotopic disequilibrium, within peridotite nodules (Stueber and Ikramuddin, 1974; Dasch and Green, 1975; Burwell, 1975; Basu and Murthy, 1976). However, Hofmann and Hart (1975) and Nelson and Dasch (1976) suggest (after consideration of available high temperature and pressure diffusion data) that isotopic disequilibrium between minerals in xenoliths is favoured at sub-solidus temperatures by the low diffusion rates of Sr. At higher temperatures the increased diffusion rates and presence of a melt would effectively homogenise the isotopic composition of co-existing mineral phases. Further justification for a disequilibrium melting model (Beswick, 1976; O'Nions and Pankhurst, 1974) is the existence of alpine peridotites with highly radiogenic strontium isotopic compositions.

However, recent studies (Menzies and Murthy, 1976, 1977, in prep.) of mineral separates from three alpine lherzolites have shed new light on this problem. One of the lherzolites from Beni Bouchera contains co-existing minerals with isotopic compositions in the range of oceanic tholeiites and, as such, could well represent sub-oceanic lithosphere. Lherzolites from Lanzo and Ronda have clinopyroxenes with isotopic compositions similar to basalts but the olivines are more radiogenic than in Beni Bouchera. This may be a secondary (mobility of Rb or introduction of radiogenic Sr) or a primary (apparent isochron relationships?) feature. Future work will help to elucidate such problems. In conclusion, it can be said that the true isotopic identity of alpine peridotites lies in the fresh primary minerals and not in peridotites which (a) contain serpentine, formed as a result of interaction of olivine with seawater or groundwater, and, (b) which contain only the more radiogenic minerals-viz. olivine and orthopyroxene. Trace element relative abundance data (K, Rb, Sr and Ba) reveals that, in all cases, the analyzed lherzolites are slightly depleted relative to "pyrolite" models (Menzies, 1976; Menzies and Murthy, 1977).

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Name	Туре	Country rock	Peridotite types	Meta- morphic layers	Magmatic layers	General references
Beni Bouchera, Morocco	Alpine peridotite	Paleozoic- Triassic	Harzburgite, dunite and spinel lherzolite	Ortho- pyroxenite	Garnet pyroxenite	Kornprobst (1969, 1966) Conquere and Kornprobst (1971) Dickey (1970)
Ronda, Spain	Alpine peridotite	Paleozoic and younger rocks	Harzburgite, dunite and garnet, spinel and plagioclase lherzolite	Ortho- pyroxenite	Garnet pyroxenite and olivine gabbro	Dickey (1970) Dickey et al. (1976) Obata (1976), Loomis (1972, 1975)
Lanzo, Italy	Alpine peridotite	Palezoic- Mesozoic metam- orphics	Harzburgite, dunite and spinel and lherzolite	Ortho- pyroxenite	Gabbro and clino- pyroxenite	Boudier (1972), Boudier and Nicolas (1972, 1976)
Othris, Greece	Ophiolite	Triassic- Jurassic limestones	Harzburgite, dunite and spinel and plagioclase lherzolite	Ortho- pyroxenite	Olivine gabbro and clino- pyroxenites	Hynes et al. (1972), Hynes (1972), Welland (1972), Nisbet (1974), Menzies (1973, 1974), Menzies and Allen (1974)
Troodos, Cyprus	Ophiolite	Triassic- Jurassic sedimentary- volcanic rocks	Harzburgite, dunite and plagioclase lherzolite	Ortho- pyroxenite	Gabbro and clino- pyroxenite	Gass (1967), Moores and Vine (1971), Greebaum (1972), Lort and Matthews (1972), Gass and Smewing (1973), Allen (1975), George (1975)

Table 2. Summary of the geology of alpine and ophiolitic massifs

2. Geologic Setting

(Geologic data are summarized in Table 2 and petrographic descriptions of the analysed samples are provided in Appendix A.)

A. Alpine and Ophiolitic Peridotites

1. Plagioclase lherzolites. The peridotites of Lanzo, Troodos and Othris (Fig. 1) (Boudier, 1972; Boudier and Nicolas, 1972, 1976; Menzies, 1973; Menzies and Allen, 1974) equilibrated in the plagioclase peridotite field and are in contact with greenchist facies rocks. The Othris and Troodos peridotites constitute the sub-oceanic mantle portion of two ophiolites and are associated with an oceanic crustal section of volcanic and plutonic rocks. No such extrusive rocks are associated with the Lanzo massif. Boudier (1972) and Menzies (1973) reported the existence of gabbroic segregations within these massifs in association with lherzolite and harzburgite. They interpreted this association to mean that a fertile lherzolite had been melted to generate a melt fraction (in situ gabbroic dikes) and a refractory residue (harzburgite). Lherzolite, however, remained unmelted in certain portions of the Lanzo, Troodos and Othris complexes. 2. Spinel Lherzolites. The Ronda and Beni Bouchera massifs contain primarily spinel lherzolite with sub-ordinate amounts of plagioclase and garnet lherzolite in the case of Ronda (Obata, 1976). Loomis (1972) suggested that the Ronda massif was emplaced at high temperature after having recrystallized along a decreasing P-T gradient. Such a decreasing P-T gradient is supported by the existence of lherzolites from three different stability fields. Dickey (1970) initially interpreted Ronda in terms of fusion of a peridotite massif, with subsequent recrystallisation and decompression. Magmatic layers within the massif were believed to represent in situ partial melt. More recent data indicate that the massif formed via a more complex multi-stage model, involving perhaps both fractional fusion and fractional crystallisation (Dickey et al., 1976). Kornprobst (1969) suggested that the Beni Bouchera massif predominantly formed in the garnet lherzolite field and underwent fusion after adiabatic uplift. The existence of garnet (a high pressure mineral) and the lherzolite-harzburgite association encouraged Kornprobst to propose that in Beni Bouchera one sees the "results of anatectic melting of an aluminous peridotite which originated within the upper mantle".

3. Lherzolite Xenoliths. Spinel lherzolite xenoliths occur within scoria cones, alkali basalt flows and volcanic plugs of the Massif Central district, (Fig. 1) France (Harris et al., 1967; Harris et al., 1972; Hutchison et al., 1970; Hutchison, 1970; Leggo and Hutchison, 1968; Hutchison et al., 1975). Lherzolite xenoliths are included in this study, since their major, minor and trace element chemistry is similar to that of relatively undepleted mantle (Hutchison et al., 1975) and to various alpine lherzolites.

3. Rare Earth Element Analyses

A. Procedure

Aliquots of powdered samples were analyzed for rare earth elements (REE), Na, Sc, Cr, Fe, Co, Ni, Hf, Ta, and Th by instrumental neutron activation analysis (INAA) in the laboratories of the Lunar and Planetary Sciences Division of the Johnson Space Center. Samples were irradiated for 28 to 42 h in the Texas A&M nuclear reactor, at a neutron flux of $\approx 8 \times 10^{12} n/cm^2/s$. Analytical procedures were similar to those reported by Denechaud et al. (1970), Allen et al. (1970), Helmke et al. (1973), and Haskin et al. (1974). USGS standard rocks BCR-1 and DTS-1 were used as irradiation monitors. Values for those secondary standards have been previously determined by radiochemical neutron activation analysis in this laboratory. Table 3 lists elemental concentrations of BCR-1 and DTS-1 as determined in this laboratory. Precision has been determined by repeated analysis of Knippa basalt and DTS-1 to be better than $\pm 5\%$ for all elements except Ni, Yb, Lu and Hf. Estimated uncertainties in accuracy are <1.5% for all elements except Tb, Hf and Ta (Jacobs et al., 1977, in prep.).

B. Results

A harzburgite (least fertile) and lherzolite (most fertile) were analysed from each massif. Data on the mineral separates and whole rocks are summarized in Table 4 and Figures 2 and 3. The errors on each analysis (10 values) are also summarized on Table 3. Data from Menzies (1976c) are included for comparison.

Diopsides (Figs. 2, 3, and 4). Diopside from the Beni Bouchera, Ronda and Lanzo complexes vary from $2.0-12.0 \times$ chondrite. The profile is an inverted U-shape. Slight depletion in light and heavy REE is evident in all three localities. REE in diopsides from the Massif Central xenoliths vary from $0.9-12.0 \times$ chondrite. All the analysed diopsides have flat REE abundances patterns, or, they are light REE depleted.

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Element	Uncertainty %	Our value for BCR-1 ^a (Except where noted)
Fe as FeO	+ 2	12.2
Na ₂ O	+2	3.35
Cr as Cr ₂ O ₃	+2	(.313) DTS-1 value
Sc	$\frac{-}{\pm}2$	31.6
Со	± 4	36.0
Ni	$\pm 10 - 50$	(2390) DTS-1 value
Hf	± 8	5.2
Та	± 11	(0.91) Lit. value Flanagan (1973)
Th	± 10	(6.0) Lit. valve Flanagan (1973)
La	± 2	25.2
Ce	± 8	54.2
Sm	<u>+</u> 3	6.80
Eu	± 4	1.97
Tb	± 9	1.15
Yb	± 5	3.48
Lu	±5	0.526

Table 3. Measured analytical uncertainties and results of analyses of BCR-1 and DTS-1 $\,$

^a Used as irradiation monitor values

Orthopyroxenes (Figs. 2 and 3). Orthopyroxenes from the alpine localities are slightly $(.4 \times)$ to heavily depleted $(.04 \times)$ in light REE and the heavy REE converge on a value of $1 \times$ chondrite for Lu.

Olivines (Figs. 2 and 3). Olivines from the alpine localities have either U-shaped profiles or they are very depleted in light REE relative to chondritic REE abundances. The Beni Bouchera olivine has a relatively flat profile in relation to the heavily depleted Ronda profile and the U-shaped profile of the Lanzo olivine.

Harzburgites (Figs. 2, 3 and 5). The harzburgite-dunite REE profile is dominated by the modal amount of olivine relative to orthopyroxene since no significant plagioclase or clinopyroxene is present. Since olivine and orthopyroxene have light REE depleted profiles the whole rocks should reflect this. In many cases the marked light REE depletion may be further enhanced by the effects of serpentinization (Shih, 1972; Frey, 1969). The Ronda harzburgite is relatively flat in REE profile relative to the heavily LREE depleted profile of the Lanzo and Beni Bouchera and harzburgites and dunites.

Lherzolites (Figs. 2, 3 and 5). The relative enrichment level of the lherzolites is controlled by the modal amount of, and the REE content of, the diopside phase, since all analyzed lherzolites are a mixture of olivine, orthopyroxene and diopside. Only in the case of Othris might the minor amounts of plagioclase increase the light REE.¹

¹ A characteristic feature of many alpine peridotites is the partial or complete replacement of plagioclase by a hydrogrossular-zoisite assemblage. Consequently, analysis of plagioclase in the Othris and Lanzo samples was impossible. It can only be assumed that plagioclase would increase the LREE very slightly

Table 4. Kale earth element concentrations in albine, ophiolitic and xenolithic i
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				-	-					
		La	Ce	(Nd)	Sm	Eu	Tb	(Ho)	Yb	Lu
Othris ^a Greece	G1 lherzolites (separates below)	-	0.80		0.17	0.09	0.05		0.28	0.03
	lherzolite		0.54		0.18	0.06	0.05		0.30	0.07
	G2 dunites			(0.04)	0.01	0	_	(0.02)		_
	G3 olivine	0.90	0.86	(0.54)		0.05	0.05	0	0.49	0.09
	G4 orthopyroxene		0.88		0.10	0.08	0.08	(0.34)	0.90	0.10
	G5 clinopyroxene	1,16	2.00	(4.44)	1.72	0.58	0.42	(0.85)	1.82	0.31
Troodos Cyprus	T1 lherzolite ^a	0.29	0.15	-	0.03	0.01	0.01	(0.04)	0.19	0.01
	T2 harzburgite ^b	0.02	0.04	(0.03)	0.01	0.01	_		0.02	_
Lanzo	L1 lherzolite	0.06	0.55		0.13	0.04	0.03			
Italy	lherzolite ^a		0.72		0.22	0.10			0.32	0.06
	L2 dunite	0.01	_		0.01	_	-		0.09	0.01
	L3 olivine	0.02	-		0.01	0.003	_		0.12	
	L4 orthopyroxene		_		0.03				0.10	0.04
	L5 clinopyroxene	0.82	4.42		1.03	0.26	0.23		0.26	0.09
Beni Bouchera	B1 lherzolite	0,45	1.34		0.34	0.18	-		0.36	0.08
Morocco	B2 dunite	0.05			0.01	0.01	_		0.134	0.02
	B3 olivine	0.05	0.18		0.04	0.02			0.12	0.02
	B4 orthopyroxene	0.14	_		0.063	0.022	_		0.17	0.04
	B5 clinopyroxene	1:97	5.86		2.011	0.83	0.53		1.76	0.20
Ronda	R1 lherzolite	0.092	_			0.05	— .		0.12	0.02
Spain	R2 dunite	0.03	0.07		0.03	0.01	_		0.02	0.001
	R3 olivine	-			0.01	0.01			0.15	
	R4 orthopyroxene	0.04	_		0.03	_	0.02		0.13	0.03
	R5 clinopyroxene	0.73	3.48		0.81	0.32	0.19		0.72	0.10
Massif Central	Mc1 eglazine-cpx.	0.31	1.83		0.74	0.42	0.36		1.02	0.13
France	MC2 roche de lion-	3.02	6.18		1.52	0.55	0.30		1.91	0.23
	cpx.									
	MC3 vissac-cpx.	1.40	3.82		1.61	0.79	0.57		2.22	0.35
	MC4 vissac-cpx. ^a	2.19	3.46		1.33	0.54	0.36		1.34	0.23
Chondrite ^c		0.33	0.88	(0.60)	0.18	0.06	0.04	(0.07)	0.20	0.03
	$> 1 \text{ ppm}^{d}$	5-10%	≦8%	. /	≦3%	≦5%	≦10%	. /	≦5%	≦5%
	0.1-1 ppm	≦25%	8.20%		3-20%	5-20%	10-25%		5-30%	5-20%
	<0.1 ppm	>25%			>25%	>20%	>25%		> 30%	> 20%

a after Menzies (1976c)

After Kay and Senechel (1976) After Haskin et al. (1968) Ъ

с

đ Sigma values

N.B. = All minerals are separated from the lherzolite listed at the top of each group



Fig. 2. Rare earth distribution in alpine plagioclase lherzolites and constituent minerals. Othris data is after Menzies (1976c). The "recalculated" line represent a mass balance recalculation using model analyses and mineral data

The Beni Bouchera lherzolite has a flat middle to heavy REE (MREE-HREE) profile $1.5-2.5 \times$ chondrite with a minor depletion in light REE. In the Ronda lherzolite the level of REE abundance is approximately $1.0 \times$ chondrite. The Lanzo lherzolite has an approximate chondritic REE abundance at $0.6-0.8 \times$ chondrite with depletion in the light REE (La).

Recalculated lherzolite (Figs. 2 and 3). The mixture 15:25:60 = clinopyroxene: orthopyroxene: olivine, is used as an ideal lherzolite mineralogy, since it is a close approximation to the modes of the analyzed lherzolites.

Mass balance comparison of actual and recalculated lherzolites (Figs. 2 and 3) helps in evaluating whether or not the REE content of the analyzed lherzolite can be explained simply in the terms of the observed mineralogy. Occasionally discrepancies are discovered between the two (Early, 1975, in prep.) and therefore require the presence of an intergranular phase. In the case of the lherzolites from Lanzo, Beni Bouchera and Ronda only minor discrepancies exist between the actual and the recalculated lherzolite. The presence of minor plagioclase in the Othris lherzolite would contribute to the light REE discrepancy.



Fig. 3. Rare earth element distribution in alpine spinel lherzolites and constituent minerals. The "recalculated" line represents a mass balance recalculation using modal analyses and mineral data

C. Comparative Diopside Data

The diopside phase of mantle tectonite peridotites contains a significant proportion of the strontium, rubidium and other LIL elements, and the major proportion of the REE. During fusion, the diopside contributes to the low melting fraction and, as such, must contain a significant amount of the magmatophile elements. Comparative REE data from oceanic (Shimizu and Hart, 1973–1974), alpine (Frey, 1969) and ophiolitic lherzolites are provided in Figure 4. The variety of diopside REE content is reflected in the diversity of lherzolites. Diopsides vary in REE profile from light REE enriched (Varne and Graham, 1971; Frey and Green, 1974), to light REE depleted (Menzies, 1976c). Diopsides from xenoliths, when plotted on a La/Sm versus Yb diagram, show a greater range in La/Sm than diopsides from alpine lherzolites and, as such, are less uniformly depleted. The alpine lherzolite clinopyroxenes have a La/Sm ratio is less than 1.5. However, the alpine lherzolites and cumulate peridotites display a greater range in Yb than the diopsides from xenoliths. Rare Earth Geochemistry of Fused Lherzolites. II

	La	Се	Sm	Eu	Tb	Yb
(1) Beni Bouche Morocco	ra,					
Clinopyroxene Orthopyroxene Olivine	0.29 0.03 0.03	0.88 [0.08] ^a 0.11	0.30 0.02 0.02	0.12 0.01 0.01	0.08 [0.01] [0.01]	0.26 0.04 0.07
	0.35 (1.08) ^b	1.07 (1.21)	0.34 (1.87)	0.14 (2.01)	0.10 (2.12)	0.37 (1.88)
(2) Ronda, Spai	n					
Clinopyroxene Orthopyroxene Olvine	0.11 0.01 —	0.52 [0.03] —	0.12 0.01 	0.05	0.03	0.11 0.03 0.09
	0.12 (0.36)	0.55 (0.62)	0.13 (0.72)	0.05 (0.72)	0.03 (0.68)	0.23 (1.14)
(3) Lanzo, Italy						
Clinopyroxene Orthopyroxene Olivine	0.12 - 0.01	0.66 - -	0.15 0.01 —	0.04 - -		0.04 0.02 0.07
	0.13 (0.39)	0.66 (0.75)	0.16 (0.88)	0.04 (0.57)	(-)	0.13 (0.65)

Table 5. Rare earth element concentrations in recalculated lherzolites.Recalculated Lherzolite(Model = Clinopyroxene:Orthopyroxene:Olivine = 15:25:60

^a extrapolated or interpolated values

^b normalised to chondrite

REE content and profile characteristics of diopsides in xenoliths (Fig. 4) mimic those of the host lherzolite. Diopsides from xenoliths are characterized by a large range in La/Sm ratio, whereas diopsides from alpine and oceanic lherzolites are characterized by chondritic or light REE depleted profiles.

4. Partial Melting Processes

A. Theoretical Considerations

Equations for trace element behavior during fractional melting (Schilling and Winchester 1967; Shaw, 1970) have been applied to the origin of terrestrial (Gast, 1968; Schilling, 1975) and lunar basalts (Shih et al., 1975; Weill et al., 1974). Varne and Graham (1972) used the theoretical treatment of Shaw (1970) in calculations involving a hornblende-clinopyroxene lherzolite from Ataq, South Yemen. Similarly, Menzies (1976a, b, c,) and Menzies et al. (1975) used these



Fig. 4. Rare earth element distribution in diopsides from alpine, oceanic and xenolithic lherzolites. Data is from various sources-lherzolite xenoliths (Menzies, 1976c); alpine lherzolites (Menzies, 1976c, this study; Frey, 1969; Philpotts et al., 1972) and an oceanic lherzolite from Shimizu and Hart (1973-74). The shaded areas in the lower figure cover the analyses from the Mediterranean (Menzies, 1976c) and the Lizard (Frey, 1965). Diopsides with REE characteristics similar to those separated from the Lizard peridotite and an oceanic lherzolite, have been found in alpine lherzolites from the Klamath Mountains, California (Menzies et al., 1977)

equations to assess the potential of various peridotites as source material for tholeiitic basalts. The equations of Shaw (1970) are used here to calculate the REE content of partial melts and residual peridotites. A variety of D values for mineral/liquid pairs (Schnetzler and Philpotts, 1970; Philpotts and Schnetzler, 1970; Shih, 1972), source modal mineralogies (Schilling, 1975) and generated liquids were used in the computations. The data that will be discussed involve the lherzolite models of Schilling (1975). The residual harzburgite (80:20-olivine:orthopyroxene) is computed using the distribution coefficients of Shih (1972). [See Appendix B.]

B. Computed Residues and Liquids in Spinel and Plagioclase Lherzolites

1. Residues. Calculated residues from 10-30% partial melting of the peridotites are all depleted in light REE (Fig. 5). Some of the low melting residues are

(1976c)



similar in REE content to unmelted lherzolites. There is an apparent similarity between the residue left after a low degree of melting of the Beni Bouchera lherzolite and the unmelted Lanzo or Ronda lherzolites. The Lanzo and Beni Bouchera residual peridotites are both heavily depleted in light REE, while the Ronda harzburgite has an approximately chondritic REE abundance at $0.1 \times$ chondrite. A similar residual peridotite was reported from the Troodos massif (Kay and Senechel, 1976).

2. Liquids. Liquids produced by melting of these alpine lherzolites are similar in REE characteristics to oceanic basalts. An oceanic basalt composite is provided for comparison (Schilling, 1975) (Fig. 5). Partial melting of $\geq 15-25\%$ would generate a basalt similar in heavy REE to a tholeiite. Certain tholeiites (Frey et al., 1974), however, are believed by Schilling (1975) to require a more light REE depleted source than any of the possible sources reported here.

Although the liquids generated by partial melting of alpine lherzolites have the REE characteristics of oceanic tholeiites, the level of enrichment may be somewhat lower, due to a more picritic composition. Picritic liquids are believed, from experimental work, to be the partial melts in equilibrium with the host peridotite (O'Hara, 1968). Such melts represent a minor part of ophiolitic lava piles (Gale, 1973) and certain samples have a REE concentration of $3.0-5.0 \times$ chondrite (Blanchard et al., 1976). Such picrites commonly contain a high proportion of olivine euhedra, spinel, orthopyroxene and clinopyroxene phenocrysts. Komatiites can also be used in estimates of the REE composition of mantle sources since they are believed to represent high degrees of partial melting. Moreover, most ultramafic lavas are very similar in REE profile to initial mantle melts, since olivine fractionation does not change the REE profile significantly, only the level of enrichment.

5. Sub-Oceanic Mantle

Ophiolites and alpine peridotites may provide a petrological insight into the constitution of the sub-oceanic mantle if one accepts that ophiolites represent fragments of oceanic crust. The dominant rock within the mantle sections is undoubtedly harburgite and dunite with very minor amounts of plagioclase and spinel lherzolites. Any interpretation of the origin of such peridotites depends on the preservation of textures. Textural data in such peridotites are somewhat complicated by (a) textural features related to partial melting (Menzies, 1973; Dick, 1975); (b) possible cumulus processes in segregating basalts: (c) subsiding cumulates from ridge areas (Dickey, 1975); (d) multiple phases of intrusion (Allen, 1975); and (e) recrystallisation and deformation.

Ophiolitic suites contain an oceanic crustal section of volanic and plutonic rocks (Gass, 1968; Moores and Vine, 1971) and a lower metamorphic peridotite section (Bezzi and Piccardo, 1971; Davis, 1963). These tectonite lherzolites and harzburgites are interpreted as sub-oceanic mantle. In Troodos and Othris the mantle section exists as plagioclase (and spinel) lherzolite below a cap of oceanic crustal rocks. Experimental studies (Green and Ringwood, 1967; Herzberg, 1972) indicate that the uppermost mantle in sub-oceanic areas (15–35 km) should be a plagioclase bearing peridotite. At depth this becomes unstable and forms spinel lherzolite (35-70 km) and eventually garnet lherzolite (65–100 km). The spinel and plagioclase lherzolites exposed in alpine peridotites and ophiolites are possible candidates as source material for tholeiitic basalts because of their generally undepleted chemistry (Menzies and Allen 1974, Dickey 1970, Boudier 1972). There is little reason to believe that the garnet peridotites exposed in alpine massifs (Dickey et al., 1976) are potential source material, Garnet incorporates the heavy REE and if it remains in the residue left after melting the generated liquids would be enriched in light REE unlike tholeiitic lavas. It is well known that the MOR tholeiite are characterised by LREE depleted abundance patterns (Frey et al., 1968; Kay et al., 1970) and that the source for such material must also be depleted in light REE. The source of alkali basalts will not be discussed since it is outwith the scope of this paper and many of the recent models (Schilling, 1973, 1975) are incompatible with Sm/Nd studies (DePaolo and Wasserburg, 1976; Richard et al., 1976). It is known, however, that small degrees of melting (<1%) of alpine lherzolites produces light REE enriched liquids.

Sub-oceanic mantle is believed by Schilling (1975) to be light REE depleted. a conclusion compatible with REE data on ophiolitic and alpine tectonite peridotites (Menzies, 1975, 1976a, b, c; Loubet et al., 1976). Alpine lherzolites may therefore represent sub-oceanic mantle. In any discussion of sub-oceanic mantle. particularly the source material for tholeiitic magmas, one is faced with the inevitable question, "Is the light REE depletion the result of an earlier melting episode?". Gast (1968) and Tatsumoto et al. (1965) have already suggested that the light REE depletion observed in tholeiitic layas indicates that the source for tholeiites could be a residue left after partial melting of a source with a chondritic (flat) REE pattern. Richard et al. (1976) reported Sm/Nd data which strongly supports this suggestion. They further suggest that the degree of melting was large or that the melting occurred at low pressure (or both). Ringwood (1975) however, suggested that a small degree of melting would explain the discrepancy between alpine peridotites (light REE depleted) and an ideal pyrolite composition. He suggested that the addition of 1% nephelinite to the light REE depleted Lizard peridotite would produce an ideal mantle composition. Ringwood (1975) noted that the existence of such nephelinitic liquids at low degrees of partial melting is compatible with experimental data. Whether the light REE depletion is the result of large or small degrees of melting awaits further geochemical and isotopic studies.

Chemical analyses of alpine peridotites (e.g. Menzies and Allen, 1974; Dickey, 1970; Boudier, 1972; Frey, 1969; Menzies, 1976; Loubet et al., 1976) reveal that in the case of many lherzolites the chemistry is similar to estimates of primary mantle composition except for deficiencies in trace elements (Menzies and Murthy, 1976a, b, 1977). The loss of these trace elements (K, Rb, Sr, Ba, U etc) must represent a small degree of partial melting since the residue is close to pyrolite in composition. This led Menzies and Allen (1974) to tentatively suggest that alpine lherzolites may have experienced a small degree of partial melting. Calculations of liquids in equilibrium with clinopyroxenes, and calculations of the REE composition of small degrees of melt generated from alpine lherzolites (using the technique in section 4) reveals that in all cases the liquid is light REE enriched. Application of the equations of Shaw (1970), at less than 1% melting, produces light REE enriched liquids with $(Ce/Yb)_N =$ 2.0-4.0. Similarly, calculations of liquids co-existing with the clinopyroxenes, using solid-liquid partition coefficients, reveals the existence of liquids enriched in light REE and possibly alkalis.

It can be tentatively suggested that such a fraction may have once existed within the peridotite framework as a hydrous mineral or intergranular phase. Since this represents part of the low-melting fraction it will be removed at low degrees of melting. Mobility of such a low melting fraction (light REE and alkali enriched) within the mantle may help explain the existence of light REE enriched refractory material (Frey and Green, 1974). Basu and Murthy (1977 in prep.) suggested that a hydrous, trace element rich phase, like kaersutitic amphibole, exists within the mantle. When mobilised this amphibole produces a trace element rich liquid which will mix with other melts produced by large degrees of melting. One can speculate that the lack of trace elements in otherwise undepleted alpine lherzolites may also be the result of loss of a low melting fraction which once existed as a hydrous mineral or intergranular phase. However, the existence of hydrous minerals within the mantle continues to be the source of much debate (O'Nions and Pankhurst, 1974; Hart and Hofmann, 1974; Beswick, 1976).

6. Conclusion

In this paper and elsewhere (Menzies, 1976c; Menzies et al., 1975, 1977), mineral and whole rock studies of plagioclase and spinel lherzolites have added to our understanding of the origin of the REE variability in mantle peridotites, the possible degrees of partial melting required to generate basaltic liquids (light REE depleted or chondritic REE abundances), the types of liquids that can be generated, and the significance of the residual material. It certainly appears that alpine lherzolites and harzburgites have REE contents appropriate for source and residual materials involved in the production of tholeiitic laves. As such, alpine bodies may represent fragments of oceanic lithosphere. The features observed in this study are compatible with the observations and conclusions of Schilling (1975), Loubet et al. (1975) and Shih (1972). Schilling calculated the REE composition of source peridotites using oceanic basalt data. Recent strontium isotopic studies (Menzies and Murthy, 1976, 1977 in prep.) have to some extent resolved the apparent isotopic discrepancy between oceanic tholeijtes and alpine peridotites. These new data appear to be compatible with a simple mantle origin, unlike the previous more complex models (Stueber, 1965).

The following conclusions can be drawn from the REE analyses: (1) The majority of analyzed lherzolites have either chondritic or light REE depleted abundance profiles. The least depleted lherzolite is the Beni Bouchera lherzolite. Such a source would contain $2.0 \times -2.5 \times$ chondrite REE. (2) The variation in the relative level of REE enrichment or depletion in all of these lherzolites is inferred to be a result of partial melting processes. Alpine and ophiolitic lherzolites are uniformly depleted relative to xenoliths. As yet, no light REE enriched alpine or ophiolitic lherzolites have been reported. (3) The refractory material (harzburgite or dunite) is depleted in light REE. The exceptional example with enrichment in the light REE is, perhaps, produced by mobility of a primary interstitial "fluid" mobilized during the melting of the lherzolite (<5%) or a secondary fluid involved in serpentinization. (4) The degree of melting necessary to generate a basaltic liquid is compatible with the degree of melting required to generate residua from the source lherzolite. For example,

if we accept Beni Bouchera as a suitable source lherzolite, and, a liquid at $10 \times$ chondrite as a reasonable estimate of a basaltic liquid, then generation of such a liquid requires approximately 17% melting. Above 25% melting, generated partial melts are similar in REE characteristics to the source lherzolite although levels of enrichment do differ. The range of melting required to generate liquids with basaltic REE abundances is compatible with experimental data, 10–30%. (5) Utilization of a 60:25:15 mode (olivine:orthopyroxene:clinopyroxene) indicates that the actual and recalculated lherzolites, though differing in minor details of their profile, are similar. Any La discrepancy between the actual and recalculated lherzolite is probably due to loss of La (and other labile elements) during serpentinization. (6) The diversity in computed liquids, from a chondritic REE abundance to a liquid depleted in light REE, is compatible with the variation observed in oceanic basalts. All such liquids can be generated between 10-30% melting. (7) Computed equilibrium partial melts (<1% fusion) are light REE enriched ((Ce/Yb)_N=2.0-4.0). It is proposed that removal of such alkalic or nephelinitic liquids (LREE enriched) may account for the lack of K, Rb, Sr and Ba within the lherzolites. Consequently, alpine lherzolites may represent the residue left after a small degree of melting. Prior to melting this labile fraction may have occurred as a hydrous mineral or intergranular phase within the lherzolite framework.

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Appendix A

Beni Bouchera, Morocco. Serpentinized lherzolite containing clear clinopyroxene, highly altered olivine, large megacrysts of orthopyroxene and minor amoeboid chromian spinels.

Ronda. Lherzolite dominated by serpentinized olivines containing orthopyroxene crystals and interstitial diopside grains. The diopside is concentrated into "layers".

Lanzo. Lherzolite containing clinopyroxene as a small interstitial phase. Orthopyroxenes are elongated megacrysts in a matrix of large olivine grains and comminuted olivine-orthopyroxene grains. Plagioclase (<1%) and diopside are intergrown and occasionally plagioclase (hydrogrossular?) surrounds spinel grains.

Othris. Lherzolite containing partially serpentinized olivine interstitial clinopyroxenes and orthopyroxene. Minor interstitial plagioclase (now an isotropic assemblage of hydrogrossular and ziosite) is visible.

Appendix B

	Plagioclase	Source						
		Clino-	Ortho-	Olivine				
(1)	15	17	17	51				
(2)		15	25	60				
(3)	Garnet 14	12	17	57				
		Eutectic Liquid						
	Plagioclase	Clino-	Ortho-	Olivine				
(1)	50	28	11	11				
(2)		55	20	25				
(3)	Garnet 47	47	3	3				

The peridotite models used in the partial melting computations were recalculated using the REE mineral data from this study. The mineral data was combined in various proportions:

(1) Plagioclase Peridotite. (2) Lherzolite. (3) Garnet Lherzolite [Garnet 187-Philpotts et al. (1972)]

All harzburgites recalculated to an ideal 80% olivine and 20% orthopyroxene mix.

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