

Geochemistry of spinel peridotite inclusions in basalts from Sardinia

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Abstract

The spinel peridotite inclusions in basalts from Sardinia are upper-mantle residues affected by metasomatism which led to an enrichment particularly of U and light *REE*. The metasomatism took place prior to the recrystallization which produced the primary mineral assemblage of the inclusions. The compositional variations imply that the xenoliths are residual after at least two melting events.

KEYWORDS: spinel, peridotite, basalts, Sardinia, rare earth elements.

Introduction

IN principal, elemental abundances of the upper mantle may be provided by analyses of basalts which are thought to be partial melts from the mantle, and/or by analyses of ultramafic rocks which represent mantle material. In practice, it is very difficult to reconstruct the composition of the mantle because of the superimposed effects of various processes on the distribution of trace elements (De Paolo, 1983). In particular, numerous recent studies have shown that many xenoliths were contaminated and/or metasomatized by fluids rich in incompatible elements such as light rare-earth elements and U. However, additional trace element data are needed to better understand and constrain such processes.

This paper deals with the distribution of trace elements in ultramafic xenoliths that occur in Plio-Quaternary alkali basalts from Pozzomaggiore, Sardinia (Italy), in order to discuss the origin of these inclusions and put constraints on the upper-mantle composition beneath Sardinia.

Petrology

Plio-Quaternary alkali olivine basalts from Pozzomaggiore, north-western Sardinia (Italy) frequently contain xenoliths of spinel peridotite. A detailed description of the petrography and

mineral chemistry of the ultramafic xenoliths and their host basalts were given by Albuquerque *et al.* (1977) and Dostal and Capedri (1976) and thus only a brief summary is outlined below.

The most basalts are porphyritic. The phenocryst phases are olivine, clinopyroxene and plagioclase which are enclosed in a groundmass of glass, olivine, clinopyroxene, plagioclase and Fe-Ti oxide.

The peridotite xenoliths range in size from 10 to 20 cm. They contain a typical four-phase mineral assemblage of olivine, orthopyroxene, clinopyroxene and spinel although the modal proportions of the minerals in the individual xenoliths are somewhat variable. Most xenoliths are spinel lherzolite but some are olivine pyroxenite. No hydrous phases such as amphibole or phlogopite were observed. The small amount of glass in some xenoliths is considered to be the product of internal melting and it occurs in association with clinopyroxene or in reaction rims around spinel. The various geothermometers based upon the composition of the minerals gave low values suggesting subsolidus re-equilibration (Albuquerque *et al.*, 1977).

Analytical notes

Thirteen ultramafic xenoliths were selected from a set of samples studied by Albuquerque

TABLE 1 Transition element contents (in ppm) in separated minerals of spinel peridotite inclusions

Mineral	Clinopyroxene					Orthopyroxene				Olivine				
	Ref.	72	92	94	107	111	72	92	107	111	72	92	94	107
Sample	1	4	5	10	12	1	4	10	12	1	4	5	10	12
Sc (ppm)	68	74	69	64	88	19.4	17.5	15.6	24.6	2.9	2.3	1.7	2.2	3.2
V	165	283	290	256	251	69	102	94	103	10	10	10	10	10
Cr	6615	7000	6400	5800	7600	3470	3000	2600	3680	126	79	107	95	143
Co	27	22	22	23	25	58	59	61	62	136	143	136	145	140
Ni	415	364	309	356	366	770	760	770	725	2980	2960	2470	2980	2920
Cu	2	7	7	5	4	1	3	1	1	2	3	5	4	2
Zn	9	7	11	9	11	27	28	29	28	41	40	46	42	45

Corresponding major element data are given in Dostal and Capedri (1976). Ref. - original sample numbers of Albuquerque et al. (1977) and Dostal and Capedri (1976).

TABLE 2 REE, Th and Hf contents (in ppm) in clinopyroxene

Sample	La	Ce	Sm	Eu	Tb	Yb	Lu	Th	Hf
1	0.66	1.8	0.23	0.08	0.05	0.17	0.025	0.1	0.1
4	1.40	4.5	1.16	0.49	0.34	1.63	0.276	0.2	0.6
5	18.7	52.1	6.34	1.70	0.62	1.45	0.228	1.3	0.9
10	7.71	17.2	1.39	0.48	0.32	1.49	0.242	0.7	0.4
12	4.23	11.3	1.18	0.40	0.23	0.76	0.120	0.1	0.5

et al. (1977) and Dostal and Capedri (1976). From five of these xenoliths, the constituent minerals—olivine, orthopyroxene and clinopyroxene—were separated and analysed for trace elements. V, Cr, Co, Ni, Cu and Zn were determined by atomic absorption. Rare-earth elements (REE), Th, Hf and Sc in clinopyroxenes and Sc in whole-rocks were analysed by instrumental neutron activation. The precision and accuracy of the analytical methods were given by Dostal et al. (1983). REE in whole-rocks were determined by a radiochemical neutron activation method described by Savoyant et al. (1984). In general, the precision of all these methods is better than 10%. The values for the mineral phases are the averages of two determinations.

The minerals were separated by magnetic and heavy liquid methods and by handpicking using a binocular microscope. The separates were subsequently washed in 2NHCl and again hand-picked under a binocular microscope. The purity

of the pyroxenes and olivine was optically estimated to be better than 99%.

Geochemistry

Mineral phases. The trace-element data for several mineral phases separated from the xenoliths are given in Tables 1 and 2. The distribution of Sc, Cr, Co and Ni in pyroxenes and olivines of the ultramafic xenoliths is similar to that described in detail by Stosch (1981) from a suite of spinel peridotite xenoliths. The concentration of Co and Ni in the minerals of the various xenoliths remains nearly constant whereas Sc and Cr abundances are variable. In each mineral phase, Zn shows little variation while Cu varies by a factor of 3. This range of variation is mainly due to analytical error at such low concentration levels. Compared to major constituent minerals, the higher Zn contents in whole-rocks may be related to the occurrence of spinel which is enriched in Zn by

a factor of 20–50 relative to olivine (Dupuy and Leblanc, 1984). However, the low Cu content in spinel (Dupuy and Leblanc, 1984) cannot account for its high abundance in the whole-rock. This Cu content is higher than that in the major constituent minerals and may be due to the presence of submicroscopic grains of sulphides. The V content decreases from clinopyroxene through orthopyroxene to olivine while Zn increases in this direction.

The partition coefficient values (*K*) for olivine/orthopyroxene and clinopyroxene/orthopyroxene (Table 3) vary within a small range and are

TABLE 3 Average partition coefficient values

	$K_{\text{olivine/orthopyroxene}}$	$K_{\text{clinopyroxene/orthopyroxene}}$
Sc	0.14 (0.01)	3.8 (0.4)
V		2.6 (0.2)
Cr	0.034 (0.006)	2.1 (0.2)
Co	2.34 (0.07)	0.40 (0.04)
Ni	3.91 (0.07)	0.49 (0.04)
Zn	1.50 (0.08)	0.32 (0.06)

bracketed values - standard deviation

similar to those reported by Stosch (1981) (coefficients of variation are <10%, except for $K^{\text{ol/opx}}$ of Cr which is probably affected by the presence of spinel in olivine). It is noteworthy that $K^{\text{cpx/opx}}$ for Ni, V, Co, Cu and Cr are nearly identical to that of pyroxenes from granulitic rocks (Liotard and Dupuy, 1980) suggesting subsolidus re-equilibration under conditions similar to those of the lower crust.

The distribution of REE in clinopyroxene is shown in Fig. 1. Like U (Dostal and Capedri, 1976), the REE content is highly variable among individual samples and a positive correlation exists between U and light REE (LREE) (Fig. 2). The homogeneous distribution of U tracks within mineral phases (Dostal and Capedri, 1976) implies that REE may also be uniformly distributed in the minerals. Two types of chondrite-normalized REE patterns have been identified among the clinopyroxenes: (a) LREE-enriched patterns with La/Yb > 4, typical of clinopyroxene belonging to group Ia of Stosch and Seck (1980); (b) a LREE-depleted pattern (sample 4) with La/Yb < 1 similar to clinopyroxene of group Ib (Stosch and Seck, 1980).

A comparable range of LREE-enriched patterns has also been described by Frey and Green

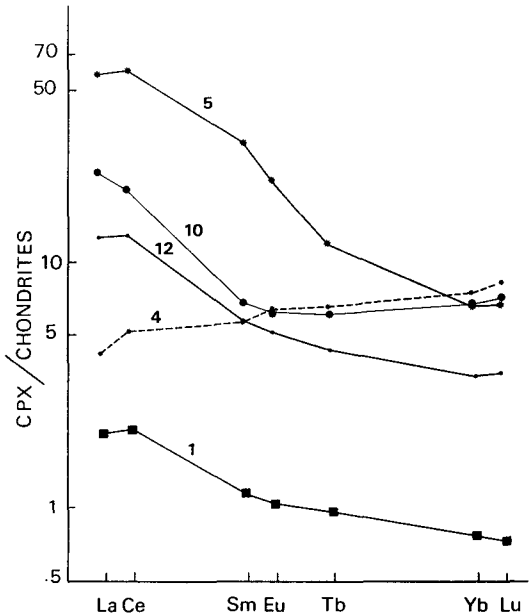


FIG. 1. Chondrite-normalized REE abundances in clinopyroxenes of the spinel peridotite xenoliths from Sardinia.

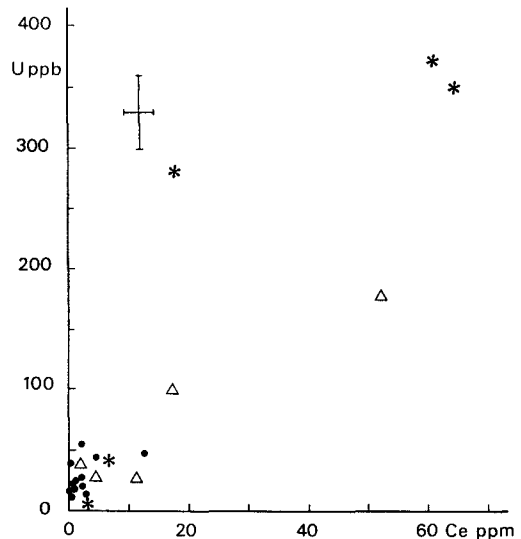


FIG. 2. U vs. Ce diagram. Full circles—inclusions from Sardinia; triangles—clinopyroxene from Sardinian inclusions; stars—clinopyroxene from Victorian inclusions (Frey and Green, 1974). Error bars correspond to two standard deviations. U data on Sardinian inclusions are from Dostal and Capedri (1976).

TABLE 4 Major and trace element compositions of peridotite xenoliths

Ref. Sample	122 13	72 1	101 6	92 4	111 12	94 5	105 8	109 11	79 2	84 3	107 10	106 9	101-P 7
SiO ₂	40.63	44.18	42.93	42.54	43.81	41.20	43.90	43.34	44.95	45.15	44.90	45.95	50.34
Al ₂ O ₃	0.30	0.65	0.99	1.07	1.11	1.29	1.31	1.54	1.95	2.00	2.48	2.79	3.04
Fe ₂ O ₃	9.05	8.14	8.50	9.39	8.39	9.22	9.14	8.55	8.64	8.72	8.69	8.79	4.30
MnO	0.12	0.12	0.12	0.13	0.13	0.14	0.15	0.12	0.13	0.14	0.13	0.14	0.09
MgO	48.86	44.91	44.90	46.15	44.84	43.81	44.06	44.65	40.90	400.74	40.70	38.74	24.60
CaO	0.25	0.44	1.47	0.50	0.86	3.18	0.94	1.16	2.20	1.40	2.09	2.54	14.65
Na ₂ O	0.03	0.02	0.10	0.06	0.08	0.22	0.10	0.05	0.16	0.15	0.21	0.17	0.46
K ₂ O	0.01	0.01	0.05	0.01	0.04	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.05
TiO ₂	0.01	0.01	0.05	0.03	0.04	0.07	0.02	0.03	0.02	0.04	0.05	0.11	0.13
P ₂ O ₅	0.02	0.02	0.06	0.03	0.02	0.06	0.04	0.01	0.03	0.03	0.02	0.02	0.05
H ₂ O ⁺	0.03	0.04	0.02	0.04	0.02	0.02	0.04	0.06	0.15	0.12	0.03	0.13	0.06
H ₂ O ⁻	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.10	0.02	0.02	0.02	0.26
Σ	99.33	98.56	99.21	99.97	99.36	99.24	99.73	99.54	99.24	98.52	99.34	99.41	99.02
Sc (ppm)	3.7	6.8	6.9	5.9	9.1	11.1	8.4	9.3	11.5	9.3	11.2	13.8	35.7
V	15.	32.	39.	32.	52.	62.	36.	58.	54.	51.	64.	82.	156.
Cr	1240.	3400.	1940.	1210.	3350.	2600.	2355.	3410.	2500.	2130.	2190.	2665.	6200.
Co	127.	114.	112.	120.	111.	113.	112.	114.	108.	109.	105.	104.	44.
Ni	2820.	2440.	2400.	2500.	2320.	2100.	2330.	2340.	2100.	2140.	20.85.	1870.	860.
Cu	2.	9.	6.	7	3.	12.	3.	3.	11.	10.	8.	8.	7.
Zn	67.	68.	67.	74.	68.	76.	81.	67.	67.	65.	56.	59.	52.
La	.32	.072	1.26	.270	1.52	5.79	.83	.54	.227	.418	1.07	.49	3.22
Ce	.58	.145	2.08	.495	2.75	12.64	2.22	1.02	.332	.590	2.05	1.09	4.73
Nd		.94	.24	1.00	5.94	1.40	.38	.32	.90	.67	2.11		
Sm	.045	.009	.188	.053	.171	1.15	.339	.068	.058	.083	.164	.194	.507
Eu	.012	.003	.048	.018	.048	.265	.089	.021	.025	.028	.048	.062	.148
Tb	.006	.023	.015	.017	.110	.060	.016	.021	.018	.039	.040	.081	
Yb	.021	.009	.087	.086	.060	.273	.149	.087	.190	.086	.229	.194	.389
Lu	.003	.002	.017	.016	.011	.045	.027	.027	.035	.016	.041	.037	.080
Σ* (ppb)	16	16	55	19	14	48	20	18	40	22	27	24	44

*U data (ppb) from Dostal and Capedri (1976). Ref - original sample numbers of Albuquerque et al. (1977) and Dostal and Capedri (1976).

(1974) from lherzolite inclusions in Victorian basanites. According to Nagasawa *et al.* (1969), Menzies (1983) and Frey (1983), the *LREE* enrichment in diopside from spinel peridotite xenoliths reflects mantle enrichment events. As also evident in other areas (Frey and Green, 1974; Frey and Prinz, 1978), the clinopyroxene *REE* patterns are reflected in those of the whole-rock inclusions, with the exception of one sample. The clinopyroxene of sample 4 has *LREE*/heavy *REE* (*HREE*) less than the chondritic ratio, whereas the whole-rock shows a relative *LREE* enrichment. A similar feature has been encountered in the Dreiser Weiher peridotite xenoliths (Stosch and Seck, 1980) and attributed to surface contamination. Sample 4 was probably also contaminated since a mass balance calculation for U indicates that only about 30% of this element is present in the mineral phases (Dostal and Capedri, 1976).

Whole-rocks. The major element composition of the ultramafic xenoliths ranges between harzburgitic and lherzolitic, with the exception of sample 7 which is a pyroxenite (Table 4). The rocks have a composition typical of ultramafic inclusions in alkali basalts characterized by high [Mg]¹

¹ [Mg] = Mg/(Mg + Fe²⁺) with Fe³⁺/Fe²⁺ taken to be 0.15.

ratios (0.91–0.93) and low Ti, Na and K contents (Aoki and Suwa, 1977; Maaloe and Aoki, 1977). In the studied rock suite there is a continuous variation trend for several elements. In particular, Al₂O₃ shows a distinct positive correlation with CaO, Na₂O and TiO₂. The pyroxenite differs from the other samples by having a higher SiO₂ but lower MgO contents. Comparable pyroxenites have been encountered in several other regions (Tracy, 1980; Griffin *et al.*, 1984) and are considered to be cumulates (Frey and Prinz, 1978; Irving, 1980).

With the exception of Cu which is depleted in the samples studied relative to the earth mantle content (Jagoutz *et al.*, 1979) the other transition elements are strongly correlated with the major elements. Sc and V are positively correlated with Al₂O₃, while Ni, Co and to a lesser extent Zn are negatively correlated with Al₂O₃. Cr correlates negatively with Ni (except in sample 1, 11 and 12, where the more erratic variation of Cr is probably due to the heterogeneous spinel abundance) and behaves like Sc and V relative to Al₂O₃. The pyroxenite differs from the other ultramafic samples in its higher Cr, and V and lower Ni and Co contents.

The samples display large variations in *REE* distribution patterns (Fig. 3) similar to those

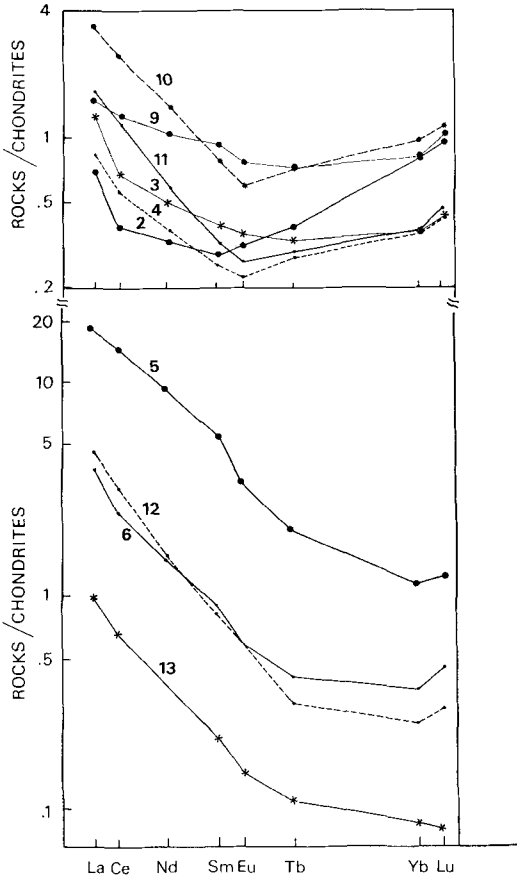


FIG. 3. Chondrite-normalized REE abundances in the spinel peridotite xenoliths from Sardinia.

observed in ultramafic xenoliths from other localities (Menziés, 1983; Frey and Prinz, 1978; Aoki and Suwa, 1977). Overall, the inclusions are enriched in *LREE* relative to *HREE*, but this enrichment is highly variable and is especially marked in samples 5, 6, 12 and 13 (La/Yb ratio ranges between 14 and 25). Other samples display U-shaped patterns with relative depletion in the middle *REE* region and a $(Tb/Yb)_n$ ratio < 1 . The *HREE* are correlated with Al_2O_3 and/or CaO (Fig. 4). A positive correlation also exists between *HREE* and Sc and V, but *LREE* do not show similar relationships. Xenoliths and low Al_2O_3 have high *LREE* contents (e.g. samples 5 and 12) and no correlation between *LREE* and CaO is apparent (Fig. 5). On the other hand, *LREE* correlate with U, especially in clinopyroxene (Fig. 2).

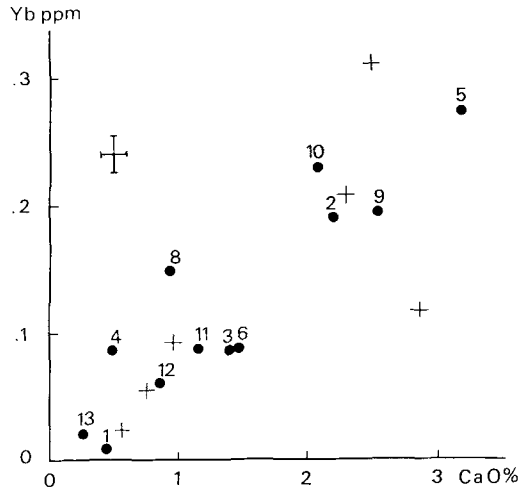


FIG. 4. Yb vs. CaO diagram for spinel lherzolite inclusions. Full circles—inclusions from Sardinia except for sample 7 (pyroxenite); crosses—inclusions from Western Victoria (Frey and Green, 1974). Error bars correspond to two standard deviations.

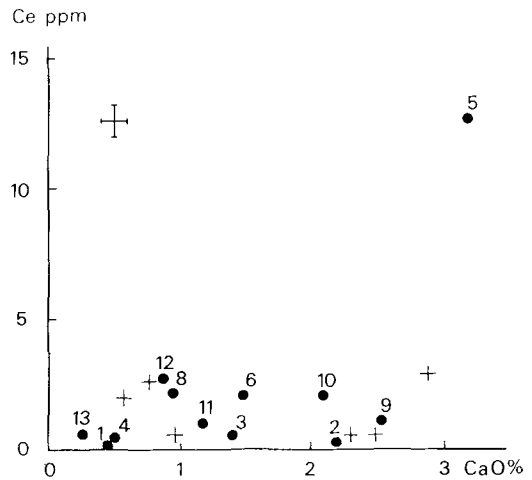


FIG. 5. Ce vs. CaO diagram for spinel lherzolite inclusions. Symbols as in Fig. 4.

Discussion

Spinel harzburgite and lherzolite inclusions are considered to be residues of upper-mantle material after the removal of basaltic melt. This is consistent with the depletion of the less refractory major elements Al, Ca, Ti, Na, K and incompatible elements such as Yb, Sc and V in our samples.

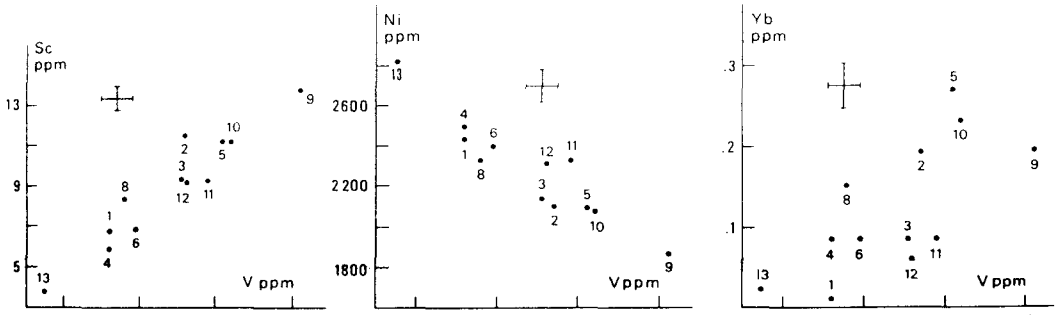


FIG. 6. Variations of Sc, Ni and Yb plotted against V in the spinel peridotite xenoliths from Sardinia. Error bars correspond to two standard deviations.

In contrast, the *LREE* are frequently enriched relative to *HREE* (Figs 4 and 5). Similar features reported for ultramafic inclusions from other areas (Menzies, 1983; Frey, 1983; Frey and Prinz, 1978; Maaloe and Aoki, 1977) have been attributed to metasomatic processes involving a liquid or a fluid phase highly enriched in *LREE*. Additional evidence for the metasomatic introduction of these elements is provided by other geochemical data and petrographic observations. Sample 5, which has the highest total *REE* abundances, is relatively enriched in Na and Ca (Table 4) and depleted in Al. The high Ca and Na content cannot be explained by processes based only on crystal-liquid equilibria but also implies secondary enrichment of both elements. In addition, this and some other inclusions contain small amounts of glass unrelated to the host basalts (Albuquerque *et al.*, 1977). Such glass is encountered in the inclusions from Victorian basanites (Frey and Green, 1974) and is considered to be formed by the breakdown of amphibole during the ascent of the inclusions. Its occurrence, therefore, may indicate the previous presence of amphibole which probably resulted from the impregnation of the upper-mantle material by a hydrous fluid.

From the data on U abundances, Dostal and Capedri (1976) concluded that the Sardinian xenoliths were contaminated by a fluid highly enriched in U. The correlation between *LREE* and U in both whole-rocks and clinopyroxene (Fig. 2) suggests that the *LREE* were also affected by this contamination process. A similar correlation of La with U was found by Frey and Green (1974) in the Victorian xenoliths. The pyroxenite, which has a high U and *REE* concentrations as the enriched ultramafic inclusions, may represent a cumulate affected by a metasomatic process. The homogeneous distribution of U tracks in the

minerals (Dostal and Capedri, 1976) implies that the inclusions were contaminated before or during their recrystallization, prior to their incorporation into the host basalts which are not genetically related to the inclusions.

Except for a few samples (4, 7, and 8) which were most affected by the enrichment mechanism, the other xenoliths display a positive correlation among Al, Ti, Na, Ca, Sc, V and *HREE* and all these elements are negatively correlated with Ni, Co and Zn (e.g. Fig. 6). These variations may suggest that the different xenoliths have been produced by variable degrees of partial melting. This hypothesis has been evaluated quantitatively on the basis of Yb vs. Yb/Sc fractionation by the total equilibrium equation of Shaw (1970) which relates the concentration of elements in the xenoliths (C_x) and the bulk partition coefficients (D) to the abundances in the source (C_0) and degree of partial melting (F). Two sets of partition coefficients corresponding to different temperatures (Ray *et al.*, 1983) were used in the calculations (Fig. 7). In addition, spinel has been omitted from the calculation due to the very low partition coefficients for Yb and Sc and the small modal proportions. The calculated compositions of the residue display a distinct fractionation trend for each set of partition coefficients. The trend is steeper for low values of coefficients (curve I). The other trends (II-V) were obtained using the high value set. The composition of the source for trend I was assumed to be pyrolitic (Stosch and Seck, 1980) while for the other trends, it was taken as already residual after previous extraction of the melt. A comparison with the calculated fractionation trends (Fig. 7) shows that the analysed xenoliths were not derived from a single source by a variable degree of melting. Fig. 7 suggests that at least two different source rocks were required

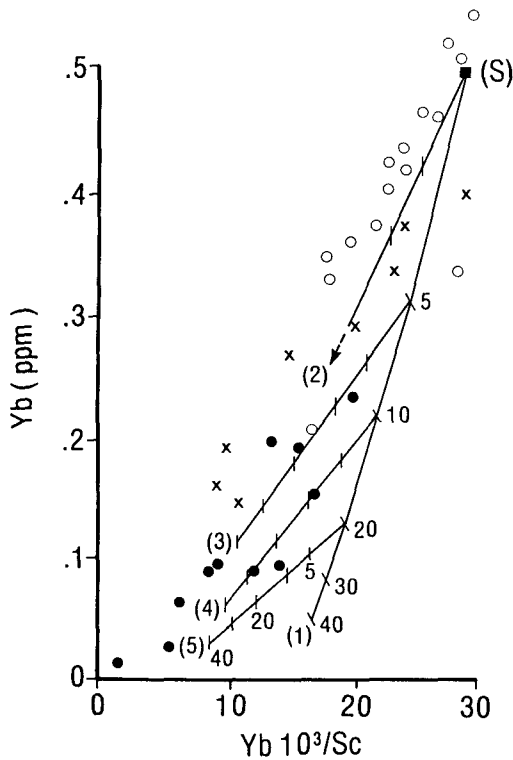


FIG. 7. Variations of Yb vs. Yb/Sc in the spinel peridotite xenoliths from Sardinia (●), Hoggar (Dupuy *et al.*, 1986) (○) and Dreiser Weiher (Stosch and Seck, 1980) (×). For comparison, the calculated compositions of the residue after partial melting are shown. Curve I represents the calculated path of the residue from the pristine upper mantle using low values of partition coefficients whereas curves II–V correspond to the residue derived from the previously depleted mantle using high partition coefficients. The parameters of melting are: partition coefficients for Yb from Stosch and Seck (1980), those of Sc (after Ray *et al.*, 1983); high values of partition coefficients— $cpx/l = 2.0$, $opx/cpx = 0.28$, $op/cpx = 0.040$; low partition coefficients— $cpx/l = 0.45$, $opx/cpx = 0.24$, $ol/cpx = 0.025$.

curve	C_0		X_0		
	Yb	Sc	Cpx	Opx	OI
I	0.5	16.6	0.21	0.30	0.49
II	0.5	16.6	0.21	0.30	0.49
III	0.31	12.4	0.20	0.30	0.50
IV	0.22	9.7	0.19	0.30	0.51
V	0.13	6.5	0.16	0.31	0.53

C_0 —composition of the source (in ppm), X_0 mineral proportions in the source. Mineral proportions in the melt: 0.40 Cpx, 0.25 Opx and 0.35 Ol.

and that both sources might have been already residual after a previous episode of extraction of

basaltic magma. The data on peridotite xenoliths from Dreiser Weiher (Stosch and Seck, 1980) and Hoggar (Dupuy *et al.*, 1986) have also been plotted on Fig. 7 for comparison. The xenoliths from each locality display distinct sub-parallel fractionation patterns suggesting that they were affected by the same processes as Sardinian xenoliths, probably by two partial melting events. However, there are differences among the various localities. Fig. 7 indicates that the first melting stage was the most extensive among the Sardinian xenoliths whereas the xenoliths from Hoggar were hardly affected and had nearly pyrolytic composition before the second melting event.

Conclusions

The spinel peridotite xenoliths from Sardinia underwent a complex evolution. Despite the absence of hydrous minerals such as amphibole, all studied xenoliths were affected by metasomatic processes to variable degrees. This contamination by a fluid phase enriched in U and LREE took place before or during recrystallization which produced the primary mineral assemblage of the inclusions. The xenoliths were subsequently accidentally incorporated into basalts which are not genetically related to them.

The fractionation of elements such as Al, Na, Ca, Ni and Co indicates that the inclusions are upper-mantle residues after different degrees of melting of different sources. Assuming that the original upper mantle had pyrolytic composition, the variations of trace elements in the peridotite xenoliths imply at least two stages of partial melting. Similar variation trends are shown by peridotite xenoliths and suggest a similar evolution, i.e. the peridotite xenoliths in various localities underwent multi-stage melting events.

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