

MAJOR AND TRACE ELEMENTS (+ Sr ISOTOPIC) GEOCHEMICAL CHARACTERISTICS OF THE MID-ATLANTIC RIDGE PERIDOTITES AND THE NATURE OF THE UPPER MANTLE

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ABSTRACT

A geochemical study (major and trace elements $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic composition) of peridotites collected during ODP Leg 109 drilling on the flanks of the Mid Atlantic Ridge (M.A.R.) ($23^{\circ} 10' \text{N}$), is presented. Like most abyssal peridotites, the samples have suffered variable degrees of serpentinization. Analysis of the data permits one to distinguish at least two stages of serpentinization. The first one was induced by a $^{87}\text{Sr}/^{86}\text{Sr}$ isotopically enriched fluid interpreted as low temperature unevolved sea water. The fluid corresponding to the second stage was less $^{87}\text{Sr}/^{86}\text{Sr}$ isotopically enriched, and could correspond to high temperature seawater which evolved through fluid/rock interactions. The data support a residual nature of these mantle peridotites, with compositional characteristics intermediate between slightly depleted orogenic lherzolites and highly depleted ophiolitic harzburgites.

Keywords: Lherzolites, harzburgites, MAR, mantle, serpentinization

INTRODUCTION

During the Ocean Drilling Project Leg 109, Hole 670 A was drilled into a peridotite body previously reported as outcropping on the flanks of the MAR ($23^{\circ}10'\text{N}$) in a normal fault system. The rocks recovered consist in a limited but interesting sequence of harzburgites with a variable degree of serpentinization (Shipboard Scientific Party, 1988, Site 670).

Outcrops of peridotites have been found beneath all oceans, where they are variably distributed, most of them are exposed along the large fracture zones associated with transform faults (Vema, Romanche fracture zones along the axial rift valley, or at some distance from the axial rift valley in relatively young oceanic crust (probably representing faulted blocks), or in sections from trenches at the margin of ocean basins (Puerto Rico Trench) (Bonatti and Hamlyn, 1981; Dick et al, 1984). In the Atlantic ocean they appear to occur rather frequently (Bonatti and Hamlyn, 1981; Michael and Bonatti 1985a, b, Juteau et al, 1990) and various reasons for this wide occurrence of peridotite outcrops in the Atlantic have been advanced (Karson et al., 1987; Dicket al, 1984; Juteau et al; 1990).

Mantle peridotites cover a large range of compositions, from lherzolitic (in alpine or orogenic bodies) to harzburgitic (in ophiolite

bodies) (Nicolas and Jackson, 1972; Boudier and Nicolas, 1986). These two types of peridotite display significantly different rare earth element (REE) patterns: slightly depleted light REE patterns for the first group with heavy REE contents of about twice chondritic abundance and highly depleted REE contents in the second group, with patterns often displaying a V shape with a significant light REE enrichment (Loubet et al., 1975; Frey, 1982, Ottonello, 1980; Ottonello et al., 1984 a,b; Pallister and Knight, 1981, Frey et al 1985, Menzies, 1984.). These two types of peridotite are classically interpreted as residual, resulting from a variable degree of partial melting (from low for the orogenic lherzolites to high for the harzburgitic ophiolites). The origin of the light REE enrichment of the highly depleted harzburgites gives rise to various interpretations (melt contamination, metasomatism, serpentinization). Prinzoffer and Allegre (1985) are of the view that this enrichment implies a disequilibrium type of melting process.

Abyssal or ocean floor peridotite compositions also extend over most of the range of mantle peridotites. With the exception of some highly depleted peridotites from oceanic trenches (Bonatti and Michael, 1989), these abyssal peridotites usually display slightly to moderately depleted

compositions, and do not reach the high depletion of the ophiolite harzburgites (Dick and Bullen, 1984; Michael and Bonatti, 1985b). According to the Leg 109 Preliminary Report (Shipboard Scientific Party, 1988) these M.A.R. peridotites might be residual, and apparently display intermediate to relatively depleted compositions.

The above suggests that Leg 109 peridotites collected on the M.A.R. could be interesting in several respects;

1. If these rocks are residual, they will provide information on the structure and composition of the oceanic mantle below the Mid-Atlantic Ridge and possibly on the genetic relationships between the ridge basalt and the peridotitic mantle.

2. Differences or analogies between alpine peridotite bodies, ophiolite bodies and oceanic crust-mantle sections have not been very clear. The main difficulty is due to lack of the entire oceanic crustal exposures from basaltic floor to mantle depth. These rocks, representing part of an oceanic crust, will shed more light to the uncertainty earlier raised.

3. If we assume that these peridotites are residual, they will also provide information on the fusion processes which affected these segments "en route" to the surface. The fusion processes within the mantle with respect to the origin and nature of the magmas formed, whether in equilibrium or not (Prinzoffler and Allegre, 1985); and the way the magmas are extracted and transported to the surface (McKenzie, 1984, and Spera, 1980 and Nicolas, 1986) has given rise to several proposals. These residual rocks are of paramount importance for the analysis of the fusion processes because they may enable a direct identification of the primary magmas. This task is extremely difficult with magmas found at the surface because the emitted magmas largely represent, an accumulation of numerous patches of primary magmas which suffered fractional crystallization before their eruption.

Like most peridotites found on the ocean floor, the samples collected are affected by varying degrees of serpentinization (here always more than 30%). Prior to an analysis of the conditions of melting of these rocks on the basis of some trace elements, it was assumed that the effects of the serpentinization process on the behaviour of these elements was very significant. This appears to be particularly necessary for the REE which are classically used for genetic modeling. These elements are classically considered as relatively less

affected than other elements by this process but this remains to be demonstrated in each particular case.

In this article we (a) present the geochemical data obtained on these Leg 109 peridotites (including analysis of the major elements, trace elements (including REE) and Sr isotopic compositions); (b) discuss, on the basis of these data, the origin and nature of these rocks; (c) analyse the mechanism and effects of the serpentinization process on the behaviour of some trace elements.

ANALYTICAL TECHNIQUES

The major elements, (except for Na and K), were measured by X-Ray Fluorescence (XRF) on a Siemens X-ray Spectrometer in the Toulouse University Petrological laboratory using fused pellets with the classical heavy absorber method. Na and K were analysed by flame spectrometry at the Geochemical Laboratory of Toulouse University (GLTU). Volatile elements were determined by loss on ignition at 1000°C. Analytical accuracy (and precision) is considered to be better than 2%

XRF spectrometry using pressed powder pellets (with a 10% weight binder) was used to analyze certain trace elements (Ti, V, Cr, Co, Ni, Nb, Zr). Matrix, instrumentation as well as interference and enhancement effects were corrected by computation with methods developed by Bougault et al., (1977). Selected international rock standards (Nancy CRPG standards) were used for calibration. Analytical accuracy for trace elements other than Nb was within 5% to 10% for concentrations higher than 20 ppm. This accuracy was ± 2 ppm at lower concentrations.

REE, Rb, Sr, and Ba concentrations were measured by isotope dilution at the GLTU on a modified CAMECA THN 206 MASS SPECTROMETER. Accuracy for these analyses was estimated at approximately 2%. Chemical separation of the elements was carried out on a AG 50 W (200-400 mesh) cationic ion exchange column. Sr was separated from Ca using ammonium citrate as a complexing agent (Birck and Allegre, 1978). REE were separated for mass spectrometry in three fractions on a HDEHP (Di(2ethylhexyl) orthophosphoric acid) column (Richard et al., 1976).

Sr isotopic composition measurements were performed on a Finnigan 261 automatic multicollector mass spectrometer at the GLTU. NES 987 Standard was measured with a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71020 ± 0.00002 ($2\sigma/\sqrt{N}$). Mass discrimination effect was corrected by normalizing the $^{88}\text{Sr}/^{86}\text{Sr}$ ratio

TABLE 1: List of the Leg 109 peridotite samples analyzed with their estimated degree of serpentinization.

SAMPLE	Estimated Serpentinization (%)
5 - 1 - 6 (37 - 39)	30
5 - 2 - 9 (73 - 75)	40
5 - 2 - 13 (100 - 103)	50
5 - 2 - 15 (116 - 118)	90
6 - 1 - 3 (16 - 19)	30
6 - 1 - 5 (30 - 34)	50
9 - 1 - 2 (12 - 14)	100

to a value of 8.375209.

RESULTS

Leg 109 peridotite samples analyzed from Hole 670 A are listed in Table 1 with their estimated degree of serpentinization. Major element, minor element, REE contents and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios are shown in Tables 2, 3 and 4 respectively.

Major element composition

Major element abundances are reported (on a water-free basis) in various diagrams (CaO/MgO , $(\text{Al}_2\text{O}_3/\text{MgO})$, $(\text{Al}_2\text{O}_3/\text{CaO})$, $(\text{Al}_2\text{O}_3/\text{TiO}_2)$ (Fig.1) and compared with the fields of compositions of mantle peridotites

from different geodynamic environments: the peridotites from the Ronda orogenic body (Frey et al., 1985), the spinel lherzolites from Zabargad island outcropping in a preoceanic rift (Bonatti et al., 1986), and highly depleted ophiolitic harzburgites. The Ronda peridotites look very interesting for reference, as their composition extends over a large range of compositions from slightly to highly depleted rocks. The Zabargad peridotites plot in this field at the slightly depleted pole.

Minor element composition

In a manner similar to major elements, the contents of compatible trace elements (such as Ni, Co, and Cr) or moderately incompatible elements (such as Y or Yb, two elements which have close geochemical affinities) also fall within the typical composition range of mantle peridotites. In the (Ni, MgO) diagram of Fig.2a and in the (CaO, Yb) diagram of Fig.2b, the Leg 109 peridotites are compared again with the compositions of the other classical mantle peridotite types and compared as well in Fig.2b with some previously studied abyssal rocks (data from Frey; 1985).

REE composition

REE compositions are plotted in the usual chondrite normalized representation (Fig.3). The La and Ce contents of four samples are not reported. This is because they were initially polished with CeO_2 powder and as a

 TABLE 2: Major element contents of 23° 10' N MAR Leg 109 peridotites
Leg 109

	P5-2-9 73 - 75	P5 - 2 - 13 100 - 103	P5 - 2 - 15 116 - 118	P6 - 1-3 16 - 19
SiO_2	36.79	36.77	36.96	37.60
TiO_2	0.03	0.03	0.03	0.03
Al_2O_3	1.56	1.36	1.64	1.76
Fe_2O_3^*	8.23	8.47	7.94	8.12
MnO	0.10	0.08	0.08	0.08
MgO	39.43	39.95	39.34	39.40
P_2O_5	0.03	0.02	0.02	0.02
CaO	1.62	1.12	0.89	1.20
K_2O	0.02	0.01	0.02	0.09
Na_2O	0.13	0.19	0.15	0.17
H_2O	12.93	13.32	13.52	12.62
Total	100.87	101.32	100.59	101.09

*Total Fe as Fe_2O_3

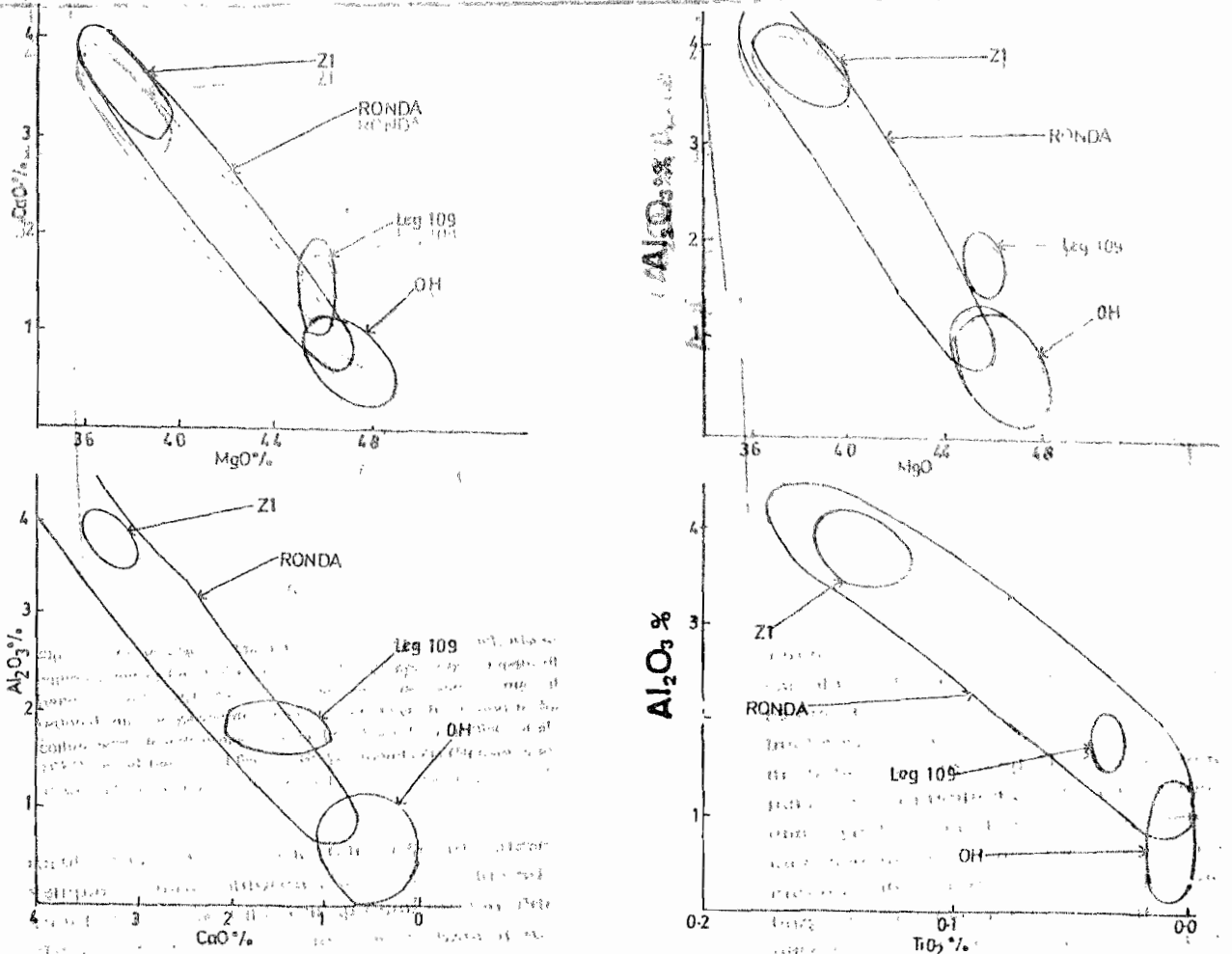


Fig. 1. (MgO,CaO), MgO,Al₂O₃, CaO,Al₂O₃, (TiO₂,Al₂O₃) compositions of Leg 109 peridotites. The composition domains of typical mantle peridotitic rocks covering the whole range of residual mantle peridotite compositions have been drawn for comparison: Ronda orogenic herzolites field (Ronda) (Prey et al. 1985), spinel herzolites from Zabargad island (ZI) (Bonatti et al. 1986) and the field of highly depleted ophiolitic harzburgites (OH).

result the La and Ce contents of these samples were unfortunately contaminated. Estimates show that this procedure did not affect the elemental compositions, except for Ce, and to a lesser extent La. Three more samples, which did not undergo this polishing treatment, were consequently analyzed in order to obtain the entire REE spectrum. In addition, in two of these additional samples, two different pieces were analyzed. Results of these analyses are shown in fig.3b. The two pieces analyzed in the sample p6-1-5 (30-34) show rather equivalent compositions but those analyzed in the sample p9-1-2 (12-14) have compositions which differ significantly. In this last sample, one of the pieces displays compositions significantly lower than all of the other rocks, but with a roughly parallel REE pattern. This sample is highly serpentinized and these peculiar

variations of the REE contents could be explained by a significant variation in this sample of the percentage of the REE bearing phase at a small scale.

In figure 4, the Leg 109 peridotites REE patterns are compared with those from other main types of mantle peridotites. Generally, it can also be seen that the REE patterns are intermediate between the slightly depleted orogenic herzolites and the highly depleted harzburgites. However, the patterns are very different. With the exception of the second piece of the p6-1-5 (30-34) sample, the REE patterns of all these Leg 109 peridotites are rather similar and are characterized by heavy to intermediate REE contents between 0.3 and 0.5 times that of chondrites and a significant relative depletion of the light REE. A break in the patterns occurs at the Nd level with a variable degree of enrichment from Nd to La. This enrichment is slight in samples p6-1-5, but relatively strong in one piece of the p9-1-2 sample.

⁸⁷Sr/⁸⁶Sr ratio
⁸⁷Sr/⁸⁶Sr isotopic ratios are well above

Fig.2 Trace element compositions of Leg 109 peridotites

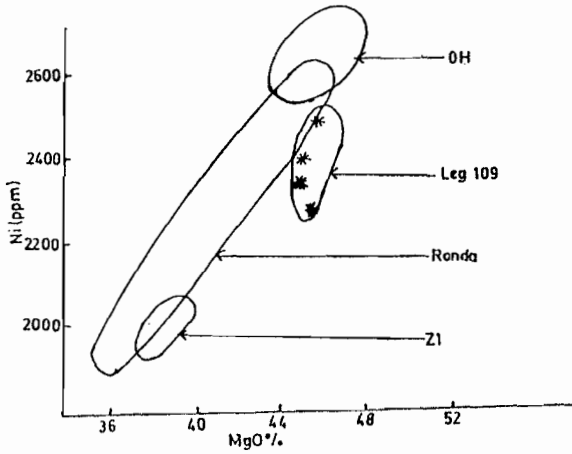


Fig.2a: (MgO, Ni) composition of Leg 109 peridotites. The same mantle peridotite fields as those reported in fig.1 have been drawn for comparison. (See fig. 1 for comments).

two poles of composition of the mantle peridotites (for example, the Al_2O_3 content of these NAOP range from 0.7% to 3%). The Leg 109 peridotites appear to be situated in the mean range of these NAOP.

In the (CaO, Yb) diagram of Fig.2b, the Leg 109 peridotite compositions are compared with the compositions of other abyssal peridotites from the Atlantic and Indian oceans previously studied (Frey, 1985). The Leg 109 peridotites plot in this diagram in the domain of the abyssal rocks and more specifically close to the field of composition of some abyssal peridotites from the Indian ocean. The very large range of CaO content appears to be a characteristic of the abyssal peridotites which might result from (a) a distinctive nature of these rocks (cumulates) or (b) a CaO mobilization following

Fig.2a.

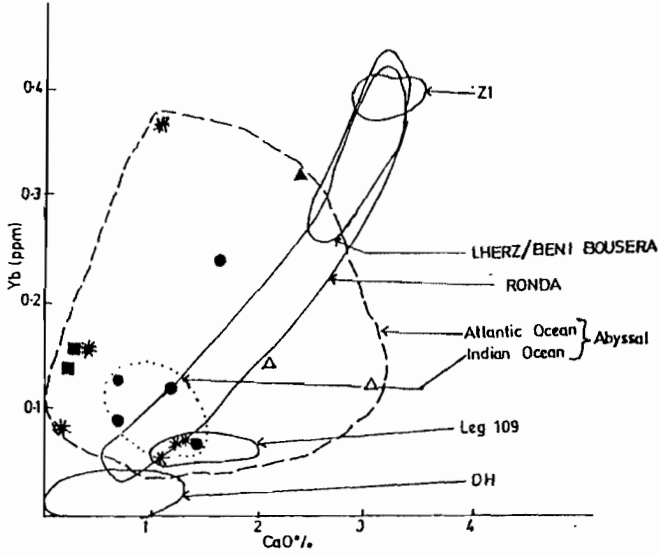


Fig.2b: (CaO, Yb) composition of Leg 109 peridotites compared with different mantle peridotite types and some abyssal peridotites. The following mantle peridotites have been drawn in this diagram: Ronda orogenic peridotite field (Frey et al., 1985), Lherz and Beni Bouchera orogenic peridotite field (Loubet, 1976). Highly depleted ophiolitic harzburgites, Abyssal peridotites from the Indian and Atlantic oceans (Frey, 1985).

those of N MORB lavas emitted in this region of the Atlantic Ocean, which are generally considered to be similar to those of the underlying mantle. Serpentinized peridotites, however, display classically high isotopic ratios, generally attributed to interaction with sea water.

LEG 109 AND ABYSSAL PERIDOTITE COMPOSITIONS

As shown recently by Bonatti and Michael (1989), the abyssal North Atlantic Ocean peridotites (NAOP) display a large range of compositions extending between the

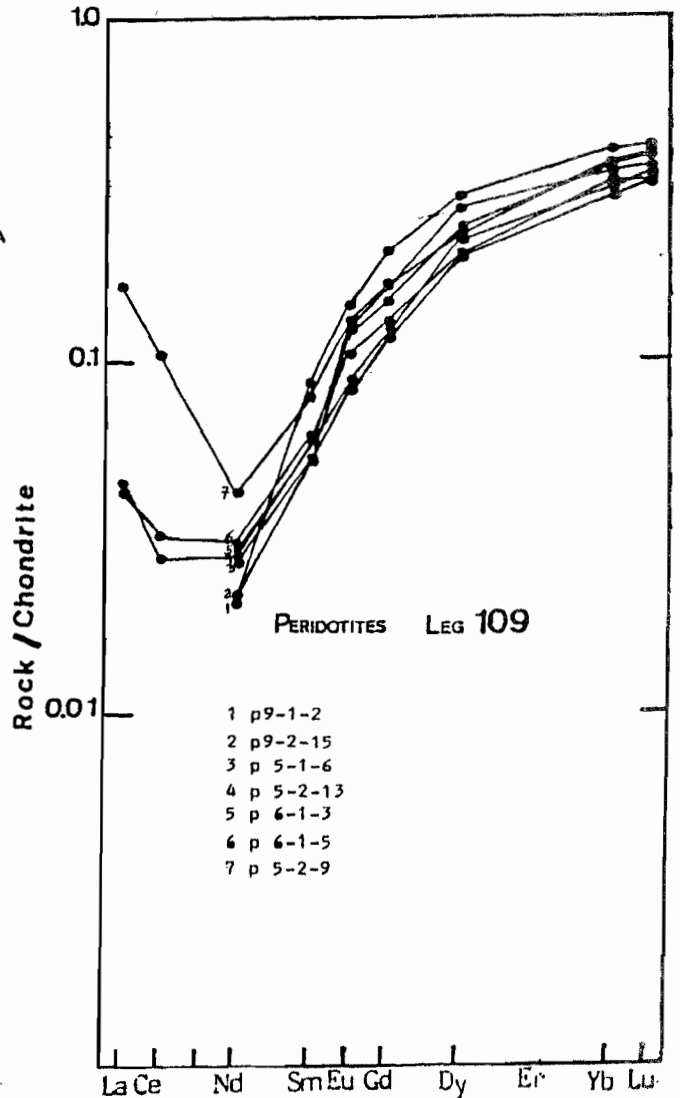


Fig.3a: REE content of Leg 109 peridotite samples plotted in the classical chondrite normalized representation (the two additional bfts analyzed in the samples P9-1-2 and P6-1-5, being excluded)

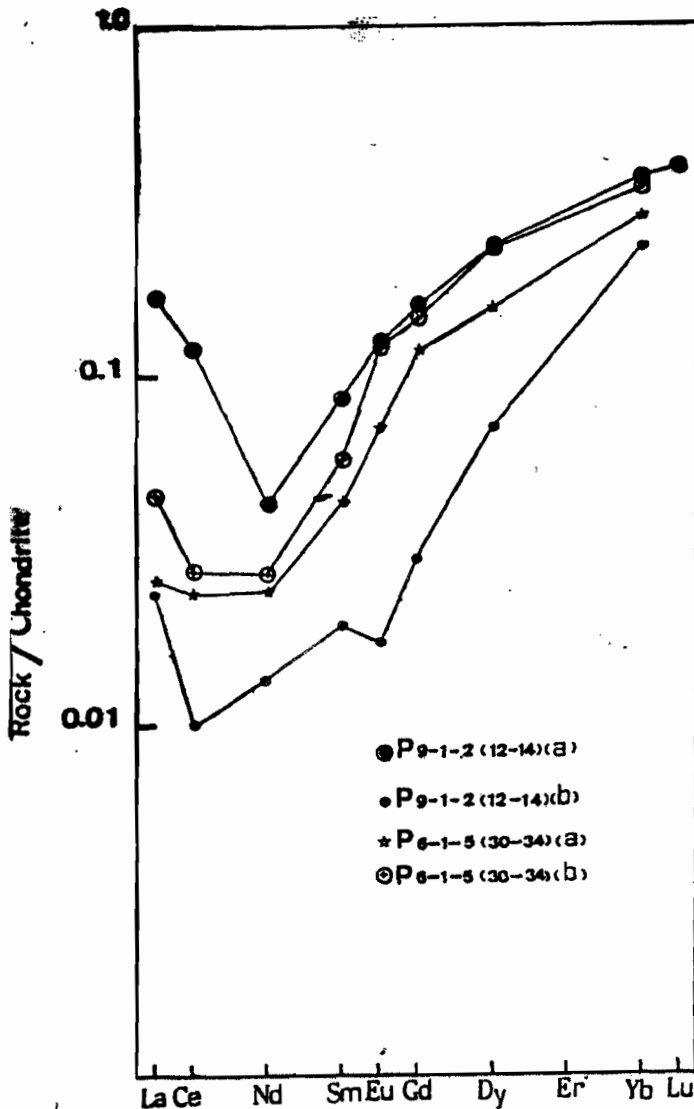


Fig.3b: REE content of the samples P9-1-2 and P6-1-5 with the additional bits analyzed in each of these samples.

serpentinization processes. Compared to Yb, Leg 109 peridotites display also large variations in their CaO content. As will be demonstrated shortly, CaO mobilization induced by a serpentinization process could explain this phenomenon.

EFFECTS OF SERPENTINIZATION ON MAJOR ELEMENT, REE AND ⁸⁷Sr/⁸⁶Sr COMPOSITIONS.

Major element composition, ⁸⁷Sr/⁸⁶Sr isotopic ratio and Sr element content.

The few rocks analyzed display a high degree of variability in degree of serpentinization (Table 1). This is ideal for the understanding of the behaviour of some elements during this process.

TABLE 3: Minor element contents of 23° 10'N MAR Leg 109 peridotites

XRF: X-Ray Fluorescence
ID: Isotope dilution

	Ti	V	Cr	Co	Ni	Zn	Ba	Rb	Rb	Nb	La	Ca	Sr	Sr	Sr	Nd	Zr	Sm	Eu	Gd	Dy	Y	Yb	Lu
	XRF	XRF	XRF	XRF	XRF	XRF	ID	XRF	ID	XRF	ID	ID	XRF	ID	ID	ID	XRF	ID	ID	ID	ID	XRF	ID	ID
P5-1-6							0.00	0	0.01		0.013	0.027	0.92	0.92	0.92	0.018		0.012	0.008	0.033	0.060		0.060	0.011
P5-2-9	156	59	2362	123	2369	46	2.98	0.830	0.02	0.590			0.00	1.11	1.11	0.015	12	0.010	0.009	0.040	0.073	4.200	0.068	0.013
P5-2-13	156	51	1893	135	2489	37	0	5.390	0.13	0.000			0.03	1.34	1.34	0.019	7	0.016	0.010	0.053	0.090	2.600	0.074	0.014
P5-2-15	156	62	2350	120	2275	35	4.00	1.260	0.01	1.360			2.28	1.79	1.79	0.013	11	0.010	0.006	0.029	0.060	1.900	0.055	0.011
P6-1-3	156	64	2721	120	2329	51	0.02	2.340	0.01	0.740			0.77	1.09	1.09	0.017	112	0.011	0.006	0.033	0.064	2.500	0.077	0.015
P6-1-5(a)							1		0.005		0.014	0.022	1.02	1.02	1.02	0.016		0.011	0.009	0.038	0.071		0.065	0.012
P9-1-2(a)							0.44	0.007	0.007		0.051	0.095	1.76	1.76	1.76	0.025		0.016	0.009	0.041	0.070		0.068	0.013
P9-1-2(b)							0				0.007	0.0079				0.008		0.0036	0.001	0.0076	0.0152		0.0442	
P6-1-5(b)												0.0189				0.014		0.0082	0.005	0.0363	0.0470		0.0350	

For the few rocks analyzed, a significant CaO decrease is noticed with increasing degrees of serpentinization (Fig.5a). The mobility of calcium through this process has been advocated (See Shipboard Scientific

TABLE 4: ⁸⁷Sr/⁸⁶Sr composition of 23° 10'N MAR Leg 109 peridotites.

	⁸⁷ Sr/ ⁸⁶ Sr	2 Sigma %
P5-1-6	0.706581	± 0.0051
P5-2-13	0.707097	± 0.0044
P5-2-9	0.707953	± 0.0041
P5-2-15	0.706374	± 0.0056
P6-1-3	0.707640	± 0.0052
P6-1-5	0.707843	± 0.0054
P9-1-2	0.706207	± 0.0049

Party, 1988 for references). It explains the greater CaO variability when compared with the other elements. Comparatively, Al₂O₃ displays lower variability, showing that it is perhaps also mobilized during the process, but with less efficiency. The relative behaviour of these elements can explain the anomalously

high Al₂O₃/CaO ratios of some rocks, such as 5-2-15

Part of the MgO enrichment exhibited by these rocks relative to the residual mantle peridotite arrays in the fig.1, can also logically be assigned to this serpentinization effect. A MgO increase from 43.5 or 44% to the present 45% can logically be expected following a CaO and Al₂O₃ mobilization.

Surprisingly, the CaO removal through serpentinization appears to be correlated with decreasing ⁸⁷Sr/⁸⁶Sr isotopic ratios (from 0.708 to 0.7064) (Fig.5a) and with an increase in Sr content (fig.5b).

This represents important constraints relative to the way the serpentinization proceeded. It indicates that most of the Sr

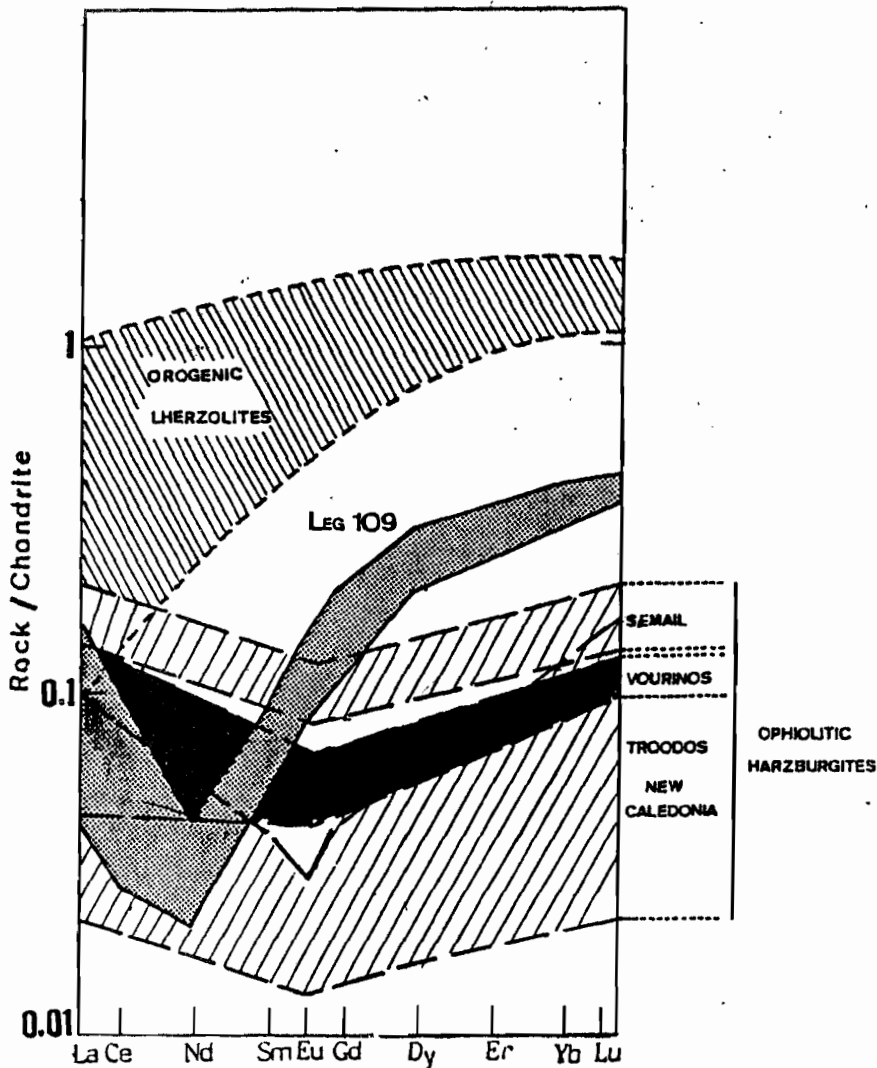


Fig.4: REE content of Leg 109 peridotite samples compared with the fields of composition of the orogenic lherzolites and of the ophiolitic harzburgites (the fields of some specific ophiolite bodies have been mentioned). Origin of the data: Orogenic Lherzolites (Loubet et al., 1975; Frey, 1969; Frey et al., 1975; Ottonello et al., 1984 a, b; Ottonello, 1980; Pallister and Knight, 1981; Menzies, 1984.

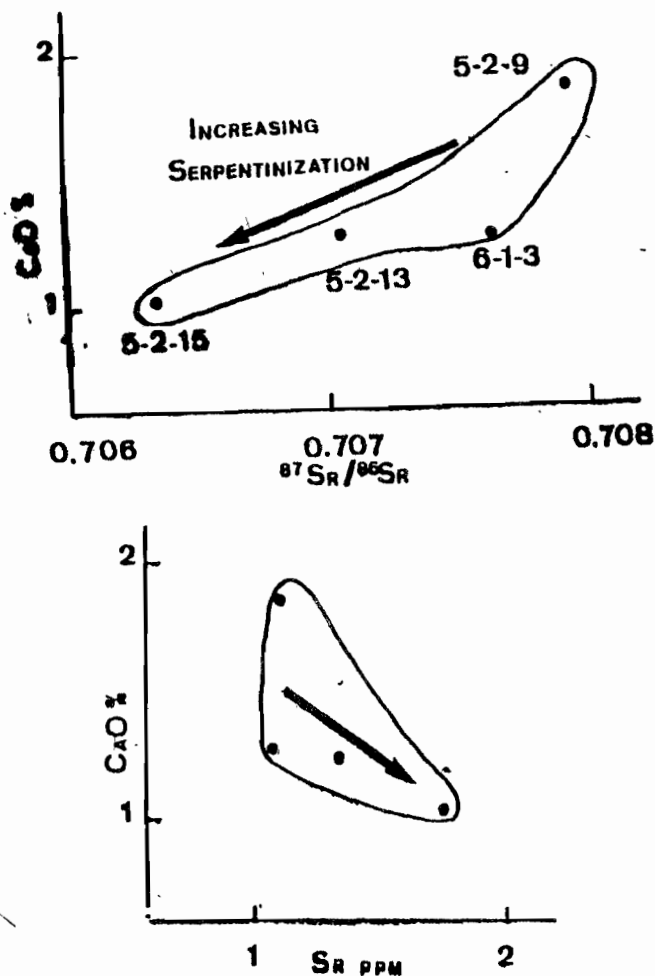


Fig. 5 ($^{87}\text{Sr}/^{86}\text{Sr}$, CaO), (Sr, CaO) Respective compositions of Leg 109 (site 670) peridotites. The evolutions of composition of the peridotites with increasing serpentinization are indicated by the arrows.

present in these rocks was brought in by the fluids. It suggests that the serpentinization developed in at least two stages.

During the first stage, the rocks were affected by a $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic enriched fluid which modified the peridotite isotopic compositions from typically low mantle isotopic ratios to high ratios close to sea water compositions. This first stage can be interpreted as induced by an interaction of the peridotites with unevolved sea water at rather low temperature. The fluids which interacted during the second stage lowered the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic composition of the rocks. This effect is indicative of a modification of the composition of the solutions during the process. This change in solutions with accentuated serpentinization apparently corresponds to the arrival of solutions which have interacted more and more strongly with

the adjacent rocks most certainly at higher temperatures.

This interpretation is supported by the following observations: (a) The REE extended chondrite normalized representation of the leg 109 peridotites indicates that the Sr content of the original magmatic rocks was certainly very low (0.01 to 0.02 times the chondrite composition, i.e. 0.10 to 0.25 ppm if we assume a relatively close behaviour of Ce and Sr during magmatic processes). Thus, it is quite plausible that the relatively high Sr content of these rocks is of foreign origin; (b) Multiple stages of serpentinization (four stages) have been recognized in these rocks from thin-section analysis with indications of a temperature rise throughout the process (Shipboard Scientific Party, 1988, site 670; Hebert et al., 1990). This is compatible with the late arrival of fluids more evolved, through effects of rock/fluid interactions, and characterized by lower $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios.

REE distribution

The effects of serpentinization on the REE distribution have been questioned by many authors (See Frey, 1982, for a review of this problem). The mobility of light REE is the most often put forward (Frey 1969; Suen et al., 1979; Ottonello et al., 1979 for example) but this is contested by other specific studies relevant to peridotites (Loubet et al., 1975; Frey et al., 1985, for example). The question of REE transport in hydrothermal solutions is also still not clear. The few studies which do exist have shown the low mobility of this group of elements with solutions either relatively light REE or heavy REE enriched depending mainly on their alkalinity (Michael et al., 1983; 1987). Clearly therefore, experimental studies at high T-P conditions are necessary for a better understanding of this problem.

Based on a number of indications, it would be reasonable to propose that in the case of the MAR peridotites from leg 109, serpentinization has had little effect on the Nd to Lu part of the spectrum. If some REE were mobilized during the process, then this occurred without noticeable fractionation of the REE with respect to each other in this part of the spectrum. The main points in support of this proposition are as follows:

(1) The degree of serpentinization of the samples analysed is very variable (Table 1). The REE spectra, however, are remarkably similar (fig.3) for all samples, (with the exception of the second piece of sample P9-1-2, which shows significantly low REE

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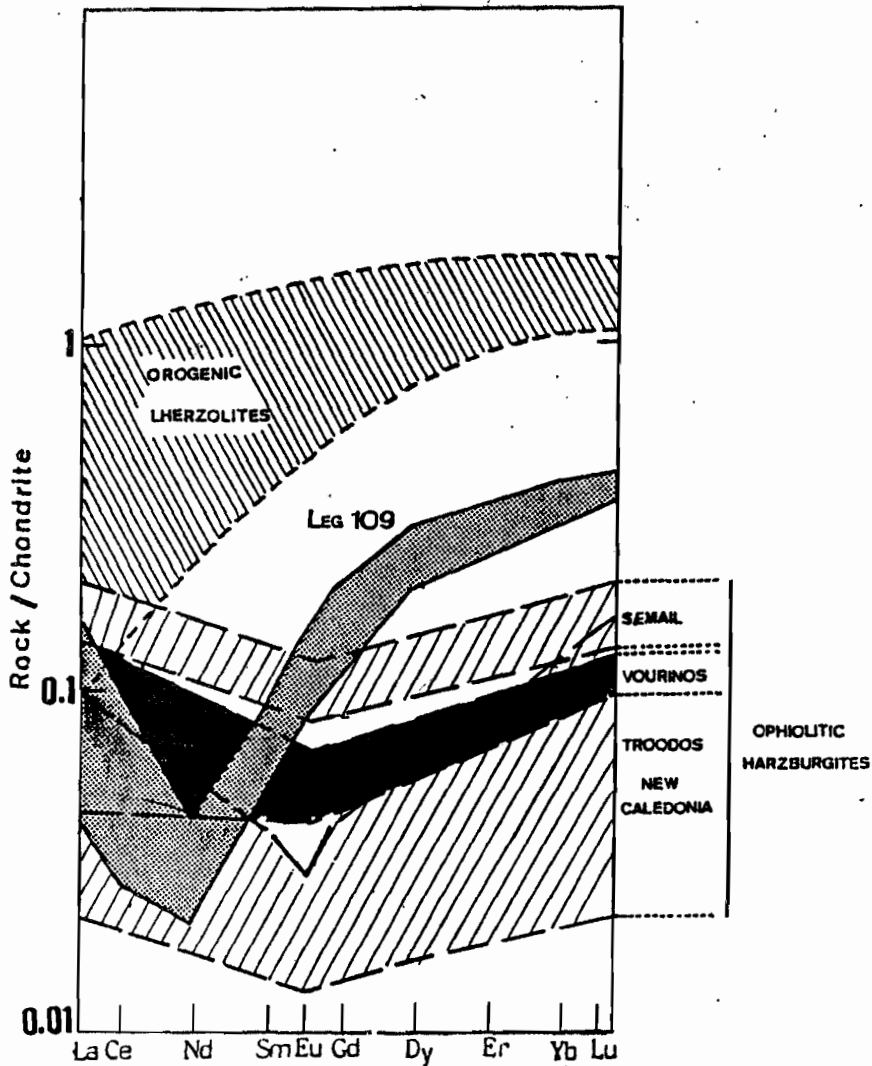


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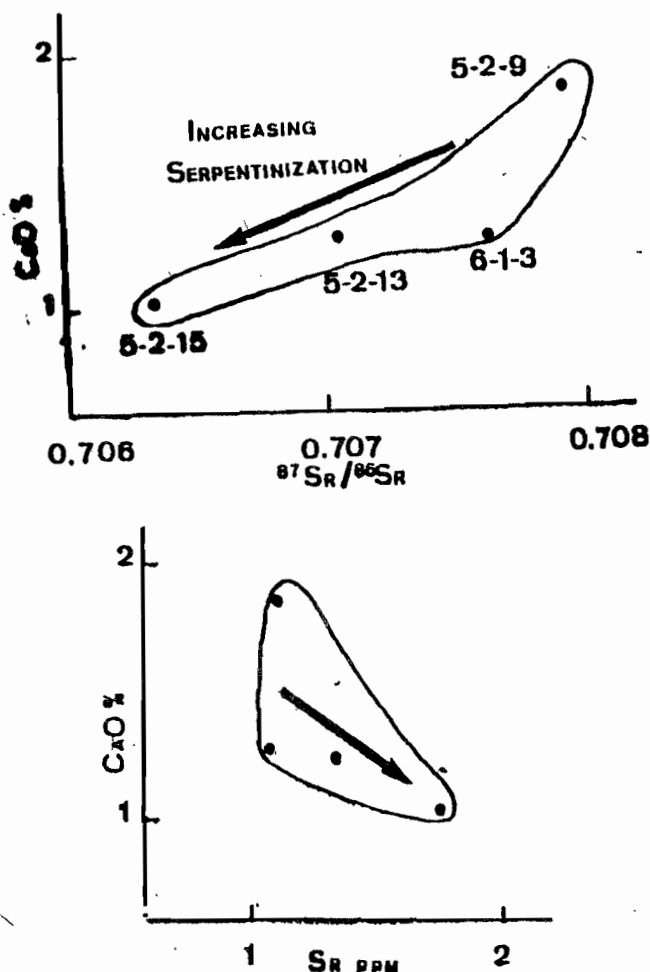


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During the first stage, the rocks were affected by a $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic enriched fluid which modified the peridotite isotopic compositions from typically low mantle isotopic ratios to high ratios close to sea water compositions. This first stage can be interpreted as induced by an interaction of the peridotites with unevolved sea water at rather low temperature. The fluids which interacted during the second stage lowered the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic composition of the rocks. This effect is indicative of a modification of the composition of the solutions during the process. This change in solutions with accentuated serpentinization apparently corresponds to the arrival of solutions which have interacted more and more strongly with

the adjacent rocks most certainly at higher temperatures.

This interpretation is supported by the following observations: (a) The REE extended chondrite normalized representation of the leg 109 peridotites indicates that the Sr content of the original magmatic rocks was certainly very low (0.01 to 0.02 times the chondrite composition, i.e. 0.10 to 0.25 ppm if we assume a relatively close behaviour of Ce and Sr during magmatic processes). Thus, it is quite plausible that the relatively high Sr content of these rocks is of foreign origin; (b) Multiple stages of serpentinization (four stages) have been recognized in these rocks from thin-section analysis with indications of a temperature rise throughout the process (Shipboard Scientific Party, 1988, site 670; Hebert et al., 1990). This is compatible with the late arrival of fluids more evolved, through effects of rock/fluid interactions, and characterized by lower $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios.

REE distribution

The effects of serpentinization on the REE distribution have been questioned by many authors (See Frey, 1982, for a review of this problem). The mobility of light REE is the most often put forward (Frey 1969; Suen et al., 1979; Ottonello et al., 1979 for example) but this is contested by other specific studies relevant to peridotites (Loubet et al., 1975; Frey et al., 1985, for example). The question of REE transport in hydrothermal solutions is also still not clear. The few studies which do exist have shown the low mobility of this group of elements with solutions either relatively light REE or heavy REE enriched depending mainly on their alkalinity (Michael et al., 1983; 1987). Clearly therefore, experimental studies at high T-P conditions are necessary for a better understanding of this problem.

Based on a number of indications, it would be reasonable to propose that in the case of the MAR peridotites from leg 109, serpentinization has had little effect on the Nd to Lu part of the spectrum. If some REE were mobilized during the process, then this occurred without noticeable fractionation of the REE with respect to each other in this part of the spectrum. The main points in support of this proposition are as follows:

(1) The degree of serpentinization of the samples analysed is very variable (Table 1). The REE spectra, however, are remarkably similar (fig.3) for all samples, (with the exception of the second piece of sample P9-1-2, which shows significantly low REE

contents), and appears not to have been affected by serpentinization.

A rough correlation is noticed between the CaO and Yb contents in all of these samples, showing the consistency of these compositions. The very similar distributions indicate that if some mobilization of the REE was induced by the serpentinization process, this mobilization proceeded without significant internal REE fractionation. As observed, even in the p9-1-2 sample which displays REE contents significantly lower than the other rocks, the Nd to Lu fractionation was also roughly maintained. This behavior can correspond to a significant decrease of the percentage of a REE bearing phase in this rock following serpentinization.

(2) Such behaviour of the REE during serpentinization of these peridotitic rocks can be understood in respect of the following:-

(a) Microprobe analysis of the phases has shown (Juteau et al., 1990b, Komor et al 1990) that the composition of a significant percentage of pyroxenes, and particularly clinopyroxenes, has been preserved in some samples, in spite of serpentinization. Moreover, clinopyroxene is the phase which, in peridotites, determines the distribution of REE. As this phase has been relatively well-preserved, it is reasonable to assume that the primary REE distribution was not much affected by serpentinization. In addition, a preferential leaching of light REE without destruction of the phases (explaining the middle to heavy REE depletion) is highly unlikely. Experimental studies carried out on volcanic glasses show that this kind of leaching only occurs through a very thin layer and only for certain elements (alkaline) (Berger et al., 1987). Considering an overall geochemical balance of alteration, this leaching can be neglected, and thus, the main factor is the later fractionation of REE by secondary phases.

(b) Serpentinization primarily affects olivine and then orthopyroxene, destroying their structures (Shipboard Scientific Party, 1988). This continues until high percentages of serpentinization are attained. Since olivine only contains negligible quantities of REE it is logical to believe that at this stage the process should have little effect on REE distribution.

(3) REE spectra similar to those in Fig. 3, with highly depleted light REE and with heavy REE contents of approximately 0.4 to 0.5 times the chondrite compositions, or even lower, have already been observed in certain ophiolitic massifs (Tiebaghi massif in the New Caledonian ophiolite (Prinzoffer and Allegre,

1985), Bay of Islands ophiolite (Suen et al., 1979), as well as in abyssal peridotites (Indian Ocean peridotites (Shih, 1972)). In these examples the degree of serpentinization is moderate. This shows that such spectra exist in practically unserpentinized rocks and coincide with the REE patterns of residual rocks.

From La to Nd, the REE patterns do not appear to be uniform anymore. A break is noticed with a variable enrichment from one sample to another; high enrichment in one piece of the p9-1-2 sample, slight enrichment in the p5-1-6 and p6-1-5 samples, and depletion from Nd to Ce in the other piece of the p9-1-2 sample, and then enrichment from Ce to La. This piece shows significant Eu depletion. These variations in contents of the light REE could be as a result of either as contamination by a magmas, mantle metasomatism, and/or serpentinization effects. Hydrothermal solutions at oceanic ridges display characteristics sufficient to reproduce some features of these serpentinized peridotites; light REE enriched patterns, displaying Eu positive anomalies, high temperature fluids with low $87\text{Sr}/86\text{Sr}$ isotopic ratios (Michard et al., 1983).

CONCLUSION

In summary the study of these Leg 109 peridotites from the MAR:

- (1) shows that these rocks have compositional characteristics intermediate between herzolites and ophiolitic harzburgites;
- (2) supports their residual nature;
- (3) shows different stages in the serpentinization process of the peridotites

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