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

M. LOUBET and U. A. LAR

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ABSTRACT

A geochemical study (major and trace elements ⁸⁷Sr/⁸⁶Sr isotopic composition) of peridotites collected during ODP Leg 109 drilling on the flanks of the Mid Atlantic Ridge (M.A.R.) (23° 10' 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 ⁸⁷Sr/⁸⁶Sr isotopically enriched fluid interpreted as low temperature unevolved sea water. The fluid corresponding to the second stage was less ⁸⁷Sr/⁸⁶Sr 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°10'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 occurrence of peridotite outcrops in the Atlantic have been advanced (Karson et al., 1987; Dick et 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 peridotites are classically interpreted as the result of 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 deformed harzburgites gives rise to various interpretations (melt contamination, metasomatism, serpentinization). Prinzoff 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 (Prinzoffe 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 modelling. 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 isotopic 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 87Sr/86Sr ratio of 0.71020 ± 0.00002 (2σ/νN). Mass discrimination effect was corrected by normalizing the 88Sr/86Sr ratio
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 87Sr/86Sr isotopic ratios are shown in Tables 2,3 and 4 respectively.

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 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 poissened with CeO₂ powder and as a

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

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Estimated Serpentinization (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 - 1 - 6 (37 - 39)</td>
<td>30</td>
</tr>
<tr>
<td>5 - 2 - 9 (73 - 75)</td>
<td>40</td>
</tr>
<tr>
<td>5 - 2 - 16 (100 - 103)</td>
<td>50</td>
</tr>
<tr>
<td>5 - 2 - 18 (116 - 118)</td>
<td>90</td>
</tr>
<tr>
<td>6 - 1 - 3 (16 - 19)</td>
<td>50</td>
</tr>
<tr>
<td>6 - 1 - 6 (30 - 34)</td>
<td>100</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Leg 109</th>
<th>PS-2-9 73 - 75</th>
<th>PS - 2 - 13 100 - 103</th>
<th>PS - 2-15 116 - 118</th>
<th>Po - 1-3 16 - 19</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>36.79</td>
<td>36.77</td>
<td>36.96</td>
<td>37.66</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.56</td>
<td>1.30</td>
<td>1.64</td>
<td>1.76</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>8.23</td>
<td>8.47</td>
<td>7.94</td>
<td>8.12</td>
</tr>
<tr>
<td>MnO</td>
<td>0.10</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>MgO</td>
<td>39.43</td>
<td>39.95</td>
<td>39.34</td>
<td>39.40</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>CaO</td>
<td>1.62</td>
<td>1.12</td>
<td>0.89</td>
<td>1.20</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
<td>0.09</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.13</td>
<td>0.19</td>
<td>0.15</td>
<td>0.17</td>
</tr>
<tr>
<td>H₂O</td>
<td>12.93</td>
<td>13.32</td>
<td>13.52</td>
<td>12.62</td>
</tr>
<tr>
<td>Total</td>
<td>100.87</td>
<td>101.32</td>
<td>100.59</td>
<td>101.09</td>
</tr>
</tbody>
</table>

*Total Fe as Fe₂O₃
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 has 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 lherzolites 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.

$^{87}\text{Sr}/^{86}\text{Sr}$ ratio

$^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios are well above
two poles of composition of the mantle peridotites (for example, the Al2O3 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 characteristic of the abyssal peridotites which might result from (a) a distinctive nature of these rocks (cumulates) or (b) a CaO mobilization following

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. Serpentinitized 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

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti XRF</th>
<th>V XRF</th>
<th>Cr XRF</th>
<th>Co XRF</th>
<th>Ni XRF</th>
<th>Zn XRF</th>
<th>Ba ID</th>
<th>Rb XRF</th>
<th>Rb ID</th>
<th>Nb XRF</th>
<th>La ID</th>
<th>Ce ID</th>
<th>Sr ID</th>
<th>Y XRF</th>
<th>Zr XRF</th>
<th>Sm ID</th>
<th>Eu ID</th>
<th>Gd ID</th>
<th>Dy ID</th>
<th>Yb ID</th>
<th>Lu ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>P5-1-4</td>
<td>0.00</td>
<td>0</td>
<td>0.01</td>
<td>0.07</td>
<td>0.00</td>
<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>P5-2-9</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
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<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>P5-2-13</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>

For the few rocks analyzed, significant increase of calcium through this process has been advocated (see Shipboard Scientific Log).
TABLE 4: {superscript}87/Sr/{superscript}86Sr composition of 23° 10'N MAR, Leg 109 peridotites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>{superscript}87/Sr/{superscript}86Sr</th>
<th>2 Sigma %</th>
</tr>
</thead>
<tbody>
<tr>
<td>P5-1-6</td>
<td>0.706581</td>
<td>± 0.0011</td>
</tr>
<tr>
<td>P5-2-13</td>
<td>0.707097</td>
<td>± 0.0014</td>
</tr>
<tr>
<td>P5-2-9</td>
<td>0.707953</td>
<td>± 0.0041</td>
</tr>
<tr>
<td>P5-2-15</td>
<td>0.706374</td>
<td>± 0.0035</td>
</tr>
<tr>
<td>P6-1-3</td>
<td>0.707660</td>
<td>± 0.0052</td>
</tr>
<tr>
<td>P6-1-5</td>
<td>0.707843</td>
<td>± 0.0034</td>
</tr>
<tr>
<td>P9-1-2</td>
<td>0.706227</td>
<td>± 0.0049</td>
</tr>
</tbody>
</table>

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

During the first stage, the rocks were affected by a $^{87}$Sr/$^{86}$Sr isotopically 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 $^{87}$Sr/$^{86}$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 serpenitization 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 Ca 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 serpenitization (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 $^{87}$Sr/$^{86}$Sr isotopic ratios.

**REE distribution**

The effects of serpenitization 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 1989; 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, serpenitization 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 serpenitization of the samples analyzed is very variable (Table 1).
2. 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 lower REE.
MAJOR AND TRACE ELEMENTS GEOCHEMICAL CHARACTERISTICS OF THE MID- ATLANTIC RIDGE PERIDOTITES AND THE UPPER MANTLE

TABLE 4:  \(^{87}Sr/^{86}Sr\) composition of 23* 10°N MAR Leg 109 peridotites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(^{87}Sr/^{86}Sr)</th>
<th>2 Sigma %</th>
</tr>
</thead>
<tbody>
<tr>
<td>P5 - 1</td>
<td>0.708561</td>
<td>± 0.0051</td>
</tr>
<tr>
<td>P5 - 2</td>
<td>0.707097</td>
<td>± 0.0044</td>
</tr>
<tr>
<td>P5 - 2 - 9</td>
<td>0.707952</td>
<td>± 0.0041</td>
</tr>
<tr>
<td>P5 - 2 - 15</td>
<td>0.706974</td>
<td>± 0.0026</td>
</tr>
<tr>
<td>P6 - 1</td>
<td>0.707346</td>
<td>± 0.0032</td>
</tr>
<tr>
<td>P6 - 1 - 5</td>
<td>0.707943</td>
<td>± 0.0054</td>
</tr>
<tr>
<td>P9 - 1</td>
<td>0.708207</td>
<td>± 0.0045</td>
</tr>
</tbody>
</table>

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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 (Louat et al., 1975; Frey, 1969; Frey et al., 1975; Ottosello et al., 1984 a, b; Ottosello, 1980; Pallister and Knight, 1981; Menzies, 1984)
present in these rocks was brought in by the fluids. It suggests that the serpentinization developed in at least two stages.

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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 87Sr/86Sr 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; Ottolino 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: 1997). 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 lower REE.
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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 behavior 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 primary 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 (Prinzoff 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 contamination by a magma, 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 87Sr/86Sr 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 lherzolites and ophiolitic harzburgites;
(2) supports their residual nature;
(3) shows different stages in the serpentinitization process of the peridotites.

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REFERENCES


