CHARACTERISTICS OF THE LITHOSPHERIC MANTLE BENEATH NORTHERN MADAGASCAR INFERRED FROM ULTRAMAFIC XENOLITHS IN ALKALINE LAVAS

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INTRODUCTION

The mineralogy and the composition of the mantle can be easily constrained from the petrology of ultramafic xenoliths collected during the ascent of alkali magmas to the surface. Because this kind of lavas is erupted rapidly, xenoliths preserve the mineralogical and chemical features of the mantle at the moment of the eruption.

This thesis reports the first occurrence of mantle xenoliths from Northern Madagascar. The mantle xenoliths of this thesis are associated to Miocene-Quaternary alkali basalts and basanites of three volcanic districts: Massif d'Ambre, Bobaomby and Nosy Be Archipelago (Melluso & Morra, 2000; Melluso *et al.*, 2007). The aim of this thesis is to assess the petrographic, geochemical and isotopic features of a still poorly-known portion of subcontinental lithospheric mantle, obtained by major and trace elements analysis, as well as Sr-Nd isotopic ratios. Over 100 xenoliths were collected, of which 51 among the largest and the less altered, were selected for this study. Major elements analyses were performed on thin sections with EDS and WDS microprobes (Universities of Naples and Rome). Trace elements concentration was determined by LAM-ICPMS and SIMS at CNR-Institute of Geosciences and Earth Resources of Pavia on clinopyroxene, orthopyroxene and amphibole. $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios have been measured on hand-picked clinopyroxenes at SOEST (School of Ocean and Earth Science and Technology, University of Hawaii at Manoa).

PETROGRAPHY AND MODAL COMPOSITION

Xenoliths have rounded to elliptical shape, with a diameter ranging from about 3 to 15 cm. The texture of these xenoliths is mostly protogranular (Pike & Schwarzman, 1977), characterized by large grains of olivine and orthopyroxene (up to 1 cm), with smaller clinopyroxene and spinel crystals. Just one sample (a wehrlite) shows porphyroclastic texture, with a single large crystal of clinopyroxene set in a fine-grained matrix of olivine and clinopyroxene.

The xenoliths show the typical four-phase mantle assemblage (olivine, orthopyroxene, clinopyroxene and spinel) and can be classified as lherzolites, harzburgites, wehrlites and one websterite. Olivine content increases from lherzolites to harzburgites (from 54.9 to 76.1% and from 70.8 to 85.3% respectively), and ranges from 61.6 to 93.3% in the wehrlites. Orthopyroxene ranges from 8.5 to 28.2% in the lherzolites and from 9.5 to 30.4% in harzburgites. Clinopyroxene ranges from 5.5 to 15.5% in the lherzolites and from 0 to 4.7% in harzburgites, whereas ranges from 9.6 to 36.3% in the wehrlites. Spinel content ranges from 0 to 6.4% in the lherzolites, from 0.3 to 9% in harzburgites and from 0 to 3.7% in the wehrlites. The websterite is characterized by the following modal percentages: 78.8% of orthopyroxene, 17.5% of clinopyroxene and 3.7 % of spinel.

MINERAL CHEMISTRY

Olivine is forsterite, with Mg# (Mg#: Mg/[Mg+Fe]·100) ranging from 87.9 to 90.4 in the lherzolites, from 89.2 to 91.4 in the harzburgites and from 80.7 to 89.5 in the wehrlites. Orthopyroxene is enstatite, with Mg# ranging from 88.1 to 91.2 in the lherzolites, from 89.3 to 91.7 in the harzburgites and from 85.4 to 86.7 in the websterite. Clinopyroxene is diopside-Mg augite, with Mg# ranging from 88.3 to 92.6 in the lherzolites, from 88.5 to 93.7 in the harzburgites, from 79.6 to 92.3 in the wehrlites and 87.4 to 91.8 in the websterite. Spinel is aluminous, Al_2O_3 ranges from 28.72 to 55.39% in the spinel from lherzolites and from 24.74 to 44.78% in the spinel from harzburgites. Cr_2O_3 ranges from 9.40 to 39.63% in the spinel from lherzolites and from 23.18 to 43.43% in the spinel from harzburgites. Concerning wehrlites, Al_2O_3 is homogeneous in the wehrlites-I and -II, ranging from 50.81 to 52.50% and from 53.19 to 54.80% respectively, whereas Cr_2O_3 is higher in spinel of wehrlites-I (from 13.14 to 14.75%) than in spinel of wehrlites-II (from 6.06 to 6.82%). Amphibole was found in just one sample and is pargasite with TiO_2 and CaO ranging from 1.76 to 1.91% and from 11.77 to 12.22% respectively.

GEOTHERMOBAROMETRY

Temperatures and pressures of the xenoliths at the time of their capture by the host lavas were calculated in each sample with the T_{BKN} geothermometer of Brey & Kohler (1990) that revealed some differences of temperature on the basis of the provenance of the samples rather than of the rock type. In fact, the temperatures range from 826 to 1160ºC in lherzolites and from 812 to 1171°C for harzburgites. Among lherzolites, some samples show very low temperatures (727, 740 and 768°C respectively). Temperature estimated for the websterite is 880ºC.

The temperatures in the different xenolith suites range in the following way: from 727 to 1000ºC for the samples from Massif d'Ambre, from 812 to 908°C for the samples from Bobaomby and from 957 to 1171ºC for the samples from Nosy Be Archipelago.

Temperatures of wehrlites from Nosy Be Archipelago were determined only by olivine-spinel geothermometers, that gave a temperature ranging from 1054 to 1068ºC for the wehrlites-I and from 1028 to 1096ºC for wehrlites-II.

The geobarometer of Mercier gave a range of pressure from 10 to 11 kbar, corresponding to a depth of 35-40 km, much shallower than that estimated for the source of host lavas (60-80 km, see Melluso & Morra, 2000).

TRACE ELEMENTS COMPOSITION

On the basis of the incompatible trace elements content and Primitive Mantle- (values from Sun & McDonough, 1989) and Chondrite-I– (values from Anders & Grevesse, 1989) normalized patterns, primary clinopyroxenes from lherzolites and harzburgites of Massif d'Ambre and Bobaomby districts can be divided into three groups:

1) Group 1 (Fig 1), showing a low ΣLREE (Light Rare Earth Element, from 3.23 to 8.00 ppm) coupled with higher ΣHREE (Heavy Rare Earth Element, from 7.58 to 12.10 ppm) and, as consequence, low La_N/Yb_N (from 0.17 to 0.48). Primitive Mantle- (hereafter PM) normalized diagram shows a strong trough at Ba, Nb and a smaller trough at Ti, whereas U shows a positive peak. Chondrite-I (hereafter C-I)-normalized diagram shows a downward concave pattern and strong fractionation of LREE respect to HREE.

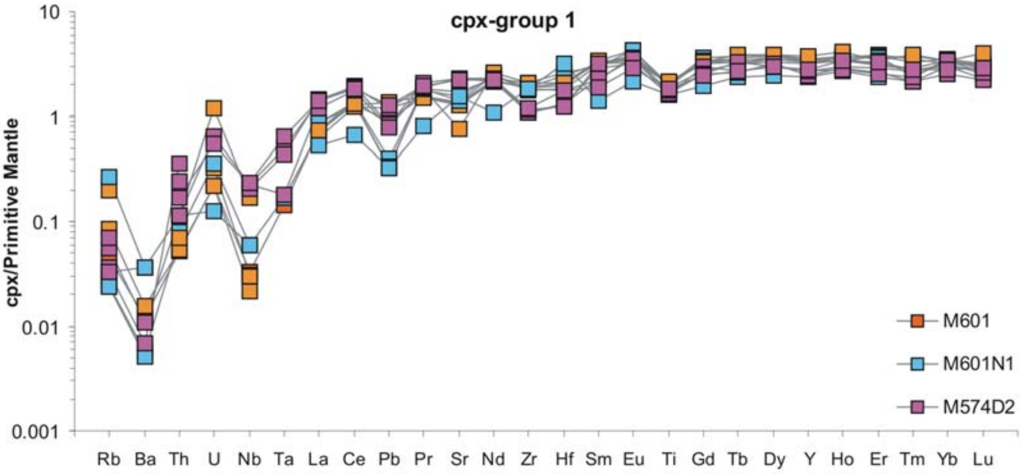

Fig 1 - Primitive mantle-normalized diagram of trace elements of clinopyroxenes (group 1) of xenoliths from Bobaomby-Massif d'Ambre.

2) Group 2 (Fig 2), showing higher ΣLREE (from 7.69 to 12.17 ppm) and ΣHREE (from 17.83 to 23.21 ppm) than clinopyroxene from group 1, with low La_N/Yb_N (from 0.45 to 1.05). PM-normalized diagram shows a strong trough at Nb and Ta and a smaller one at Zr and Hf, whereas U a strong positive peak. Most of clinopyroxene has a trough at Ba. C-I-normalized diagram show a nearly-flat pattern of REE, except for a small positive anomaly at Eu.

3) Group 3 (Fig 3), showing the highest ΣLREE (from 14.91 to 35.99 ppm) and the lowest ΣHREE (from 5.31 to 13.66 ppm) of the three groups, and have high La_N/Yb_N (from 0.85 to 4.76). PM-normalized diagram shows a negative peak at Ta and a stronger one at Nb, and two small negative anomalies at Zr, Hf, Ti. C-I-normalized diagram shows a strong fractionation of HREE respect to LREE.

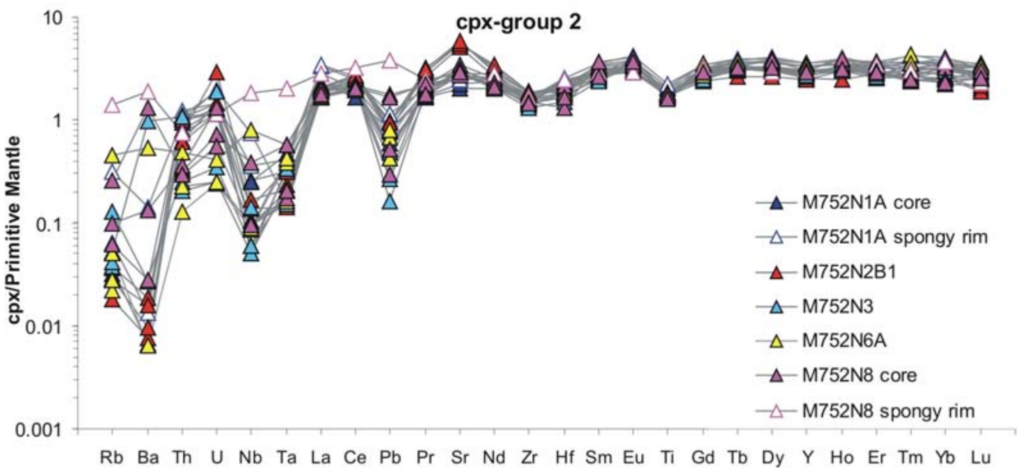

Fig 2 - Primitive mantle-normalized diagram of trace elements of clinopyroxenes (group 2) of xenoliths from Bobaomby-Massif d'Ambre.

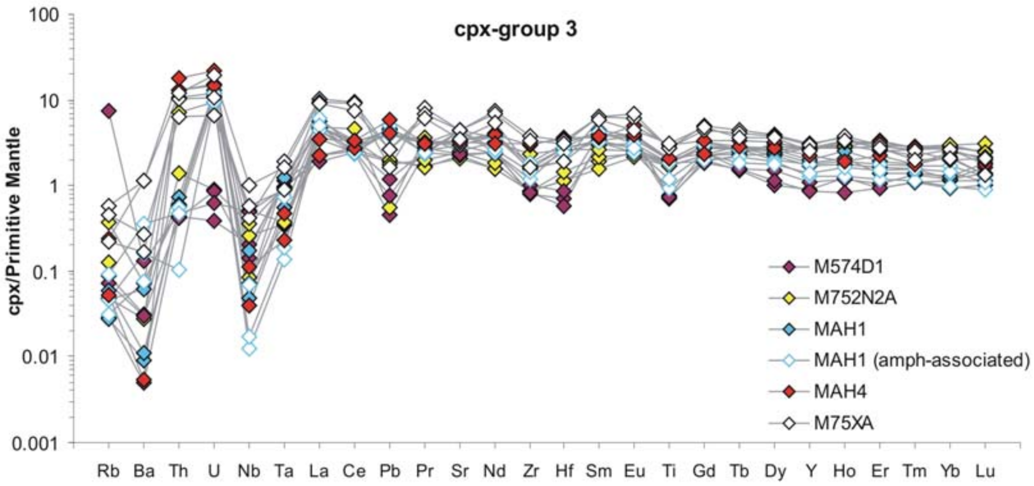

Fig 3 - Primitive mantle-normalized diagram of trace elements of clinopyroxenes (group 3) of xenoliths from Bobaomby-Massif d'Ambre.

Clinopyroxene from websterite is characterized by high ΣLREE (from 19.56 to 21.49 ppm) coupled with lower ΣHREE (from 10.62 to 10.88 ppm) and a low La_N/Yb_N (from 2.22 to 2.40). In the PM-normalized diagram, the incompatible elements show a nearly-flat pattern, except for the important trough at Ba and, with lower amount, at Nb, Ta, Zr and Hf, whereas Th and U display a positive peak. The pattern of C-I-normalized REE is very flat for HREE (except for the positive anomaly at Eu), and steeper for LREE.

Trace elements content of amphibole is very similar to the coexisting clinopyroxene, except for those elements which are better partioned into amphibole, like Rb (from 4.98 to 6.59 ppm), Nb (from 2.99 to 4.69 ppm), Ta (from 2.99 to 4.69 ppm), Sr (from 381 to 487 ppm) and Pb (from 16.97 to 22.93 ppm).

Clinopyroxene of lherzolites and harzburgites from Nosy Be Archipelago has been divided into two groups, on the basis of the trace elements content and pattern in the normalized diagrams (Fig. 4):

1) Group 1, characterized by low ΣLREE (7.3 ppm) and high ΣHREE (9.9 ppm), with very low La_N/Yb_N (0.11) and its PM- and C-I-normalized diagram is downward-concave, with the first showing negative peaks at Zr and Ti.

2) Group 2, including clinopyroxenes from and harzburgites. Lherzolites and harzburgites have a similar pattern in the PM-normalized diagram, with troughs at Zr and Ti but they differ for the trace elements content. In fact, clinopyroxene from lherzolites has lower ΣLREE (from 10.6 to 24.4 ppm) and higher ΣHREE (from 4.4 to 8.5 ppm) than those from harzburgites (from 11.4 to 31.2 and from 2.6 to 6.4 ppm respectively). As a consequence, clinopyroxene from lherzolites has lower La_N/Yb_N (from 1.80 to 1.85) than clinopyroxene from harzburgites (from 1.48 to 9.02). C-I-normalized diagram of REE shows a downward concave diagram for each sample.

Clinopyroxene from wehrlites-I displays lower ΣLREE (from 25.5 to 26.4 ppm) and ΣHREE (from 8.9 to 9.2 ppm) than clinopyroxene from wehrlites-II (from 37.3 to 38.3 and from 11.1 to 11.8 ppm, respectively). For this reason, La_N/Yb_N ratio for clinopyroxene from wehrlites-I is slightly lower (from 1.64 to 2.13) than clinopyroxene from wehrlites-II (from 3.08 to 3.51). PM-normalized diagram of clinopyroxene from wehrlites shows similar patterns for the two wehrlite types, characterized by small

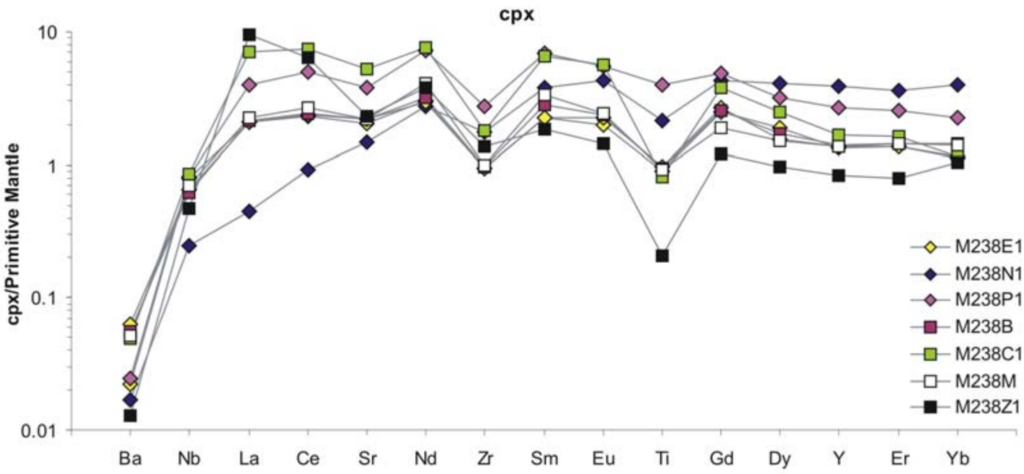

Fig. 4 - Primitive mantle-normalized diagram of trace elements of clinopyroxenes of xenoliths from Nosy Be Archipelago.

troughs at Sr and Zr and by the lack of troughs at Ti, whereas the C-I-normalized diagram shows concave-downward patterns.

ISOTOPE GEOCHEMISTRY

$^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios were determined on clinopyroxenes separates from 11 samples from Bobaomby and Massif d'Ambre districts. These clinopyroxenes displays a wide range of isotopic composition, with $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ranging from 0.70195 to 0.70427 and from 0.51276 to 0.51359 (corresponding to an εNd ranging from 2.3 to 18.6), respectively. In the diagram $^{87}Sr/^{86}Sr$ *vs.* $^{143}Nd/^{144}Nd$ (Fig. 5) the data plot within the depleted quadrant, defining an array trending from the field of depleted mantle towards bulk Earth (BE) values. In some respects, the Sr-Nd isotope ratios partially mirror the trace element contents of clinopyroxenes. In fact, the most LREE-depleted samples show the highest $^{143}Nd/^{144}Nd$ (0.51359, corresponding to an εNd: 18.6) and the lowest $^{87}Sr/^{86}Sr$ (from 0.70195 to 0.70199), approaching to the DMM end member (Depleted MORB Mantle; Zindler & Hart, 1986) and plotting very far from the other samples in the $^{87}Sr/^{86}Sr$ *vs.* $^{143}Nd/^{144}Nd$ diagram, that mostly fall in the OIB (Oceanic Island Basalt) field. The most LREE-enriched samples instead, display the lowest $^{143}Nd/^{144}Nd$ (from 0.51276 to 0.51284, corresponding to a εNd ranging from 2.3 to 3.9). Moreover, three samples of clinopyroxenes from group 2 show a very narrow range of isotopic composition ($^{87}Sr/^{86}Sr$ from 0.70410 to 0.70417, and $^{143}Nd/^{144}Nd$ from 0.51308 to 0.51311).

DISCUSSION

On the basis of their petrological features, lherzolites and harzburgites represent mantle residues that underwent partial melting by extraction of basaltic melts. Several facts argue for this hypothesis. Concerning the modal composition, the continuous modal variations from fertile lherzolites to strongly refractory harzburgites can be a well-known feature of partial melting of the mantle by melt extraction

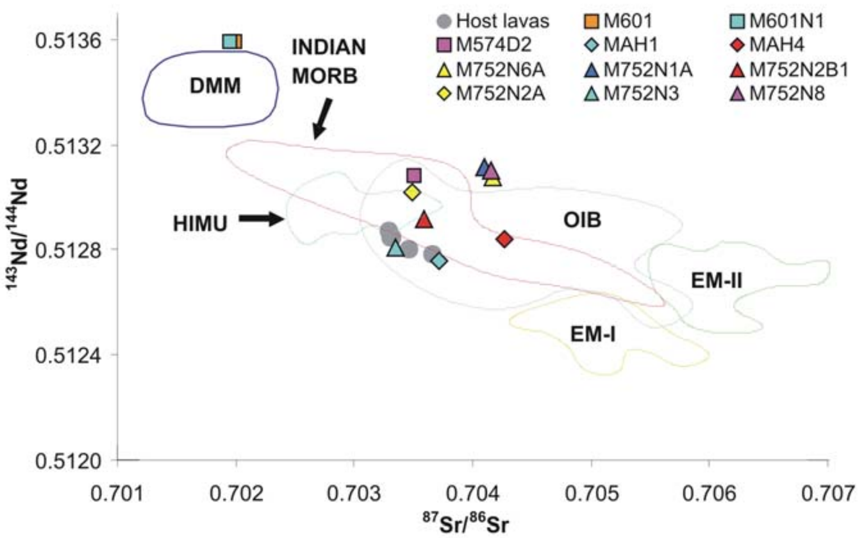

Fig. 5 - $^{87}Sr/^{86}Sr$ *vs.* $^{143}Nd/^{144}Nd$ diagram of clinopyroxene in xenoliths from Massif d'Ambre and Bobaomby. Values for host lavas and fields of Indian MORB, DMM, EM-I, EM-II, HIMU end-members (fields from Zindler & Hart, 1986) and BE (Bulk Earth) are shown for comparison.

(Yoder, 1976). Concerning the chemical composition of the mineralogical phases and the whole rocks, several characteristics suggest the same hypothesis:

- the increasing of olivine content and the decreasing of clinopyroxene content from lherzolites to harzburgites, since clinopyroxene is the main (and the first) mineral consumed during partial melting of mantle peridotites;
- the general increasing of Mg# of olivine, orthopyroxene and clinopyroxene from lherzolites to harzburgites;
- the increasing of Cr_2O_3 of spinel from lherzolites to harzburgites
- the LREE depletion in some of lherzolites and harzburgites;
- the high εNd of some samples.

The degree of melting of the xenolith was determined using the equations of Johnson *et al.* (1990) for fractional and batch melting. Clinopyroxene from group 1 from Bobaomby and Massif d'Ambre district seems to be the residual product of 1-3% of fractional partial melting or of 1-7% of batch partial melting, starting from a primitive mantle source. The melting event (or multiple melting events) undergone by these samples should be very ancient (*e.g.*, Faure, 1986), as indicated by the very high εNd value coupled with low $^{87}Sr/^{86}Sr$ ratio of the clinopyroxene. Concerning clinopyroxene from group 2, the best fit is obtained for a 1% of fractional partial melting or for a 1-3% of batch melting. LREE-enriched samples of group 3 show a degree of partial melting ranging from 1 to 15% following the fractional model and a less realistic 1-25% for the batch model.

Concerning the clinopyroxene from Nosy Be Archipelago, sample of group 1 seems to be the residual product of small degree of fractional partial melting (1%) or batch melting (5%), whereas samples from group 2 are the result of a degree of fractional melting ranging from 3 to 10% and of a less realistic 5- 25% of batch melting.

The geochemical characteristics of lherzolites and harzburgites of this study indicate that several xenoliths experienced a complex modal and/or cryptic metasomatic history, which modified major oxides, trace elements and isotopic compositions of residual lithospheric mantle after various degree of partial melting. Clinopyroxene belonging to group 3 of Massif d'Ambre and Bobaomby and to group 2 of Nosy Be show clear evidence of cryptic metasomatism. In fact, although the most of the HREE concentrations of these samples can be explained by low degree of partial melting of a primitive mantle source, the LREE concentrations are higher than those expected for a residue of partial melting or the primitive mantle, and require the involvement of incompatible components to clinopyroxenes previously depleted by partial melting. This enrichment in LREE is similar to that expected for metasomatism by mafic-silicate melts (Menzies & Hawkesworth, 1987). Other samples show clear evidence of cryptic and modal metasomatism, for the occurrence of amphibole and secondary veins.

Several facts argue for a cumulitic origin for the wehrlites. The high TiO_2 content of clinopyroxene (usually up to 1%) is consistent with a cumulate origin. The crystallization process produces a series of rocks with comparatively large variations in compatible elements concentrations compared with those of incompatible elements. Wehrlites of Nosy Be show a great variability concerning the compatible elements and small variations concerning the incompatible elements. For example, Cr_2O_3 in clinopyroxene ranges from 0.14 to 1.57%, whereas a moderately-incompatible element like Yb shows a narrow range (from 2.05 to 2.78 ppm). Comparing the liquids in equilibrium with clinopyroxene of wehrlites with host basanites, their geochemical similarity is evident. This fact can suggest that wehrlites represent high pressure cumulate at mantle depths of the host basanites (see Beard *et al.*, 2007, and references therein) or of similar melts.

CONCLUSIONS

Ultramafic xenoliths found in Miocene-Quaternary lavas of Northern Madagascar reflect a heterogeneous lithospheric spinel facies- upper mantle, being formed by several lithologies such as lherzolites, harzburgites, wehrlites and websterites. On the basis of geobarometric calculations, these xenoliths were located at a depth of 35-40 km (corresponding to a pressure of 10-11 kbar) before being entrained by the ascending magma. The composition of these lithologies, both from a chemical and from an isotopic point of view, revealed a very complex history for the lithospheric mantle beneath Northern Madagascar.

Lherzolites and harzburgites are portions of upper mantle that underwent variable degrees of partial melting by melt extraction. These melting events are responsible for the "refractory" composition of both major and trace elements and for the depleted isotopic composition of some samples. Among these samples, some represent portions of cold and old lithosphere, as testified by low equilibrium temperatures and the very high εNd values.

Some of lherzolites and harzburgites underwent metasomatic processes after partial melting. Metasomatism changed the composition of the mantle, increasing the content of incompatible elements (like LREE) in clinopyroxene. The metasomatizing agent is mostly a SiO_2-undersaturated alkaline melt, with a trace element composition similar to host lavas. In few cases, metasomatic processes introduced in the mantle new phases like amphibole and secondary olivine, clinopyroxene and orthopyroxene. In other cases, the action of a SiO_2-oversaturated melt (a tholeiitic or an evolved alkaline melt) is responsible for the formation of secondary veins and for the formation of websterite.

Wehrlites represent veins or pockets of high pressure cumulates within the mantle peridotite. Probably these cumulates are genetically related to the host basanites, on the basis of their geochemical similarity.

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