

A TWO-COMPONENT MANTLE EXTENDING FROM MT. ETNA TO HYBLEAN PLATEAU (EASTERN SICILY) AS INFERRED BY AN INTEGRATED APPROACH WITH NOBLE GASES, TRACE ELEMENTS AND ISOTOPE GEOCHEMISTRY

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INTRODUCTION

The eastern sector of Sicily was characterized since Trias by a mafic volcanism that occurred mainly in two areas: the Hyblean Plateau and the Mount Etna, this latter located 50 km northward of Hyblean Plateau.

The spatial and temporal vicinity of the two volcanic provinces led many authors to compare the two areas: petrological, geochemical and isotopic investigations of the products erupted in the two volcanic provinces indicated that their sources have similar characteristics (Carter & Civetta, 1977; Carter *et al.*, 1978; Cadoux *et al.*, 2007; Trua *et al.*, 1998).

The aim of this study was to investigate and compare the features of the Hyblean and Etnean mantle sources, in order to highlight possible similarity in their geochemical signatures and/or processes that have acted in both the mantle sectors. We focused on the geochemical and petrological characteristics of selected primitive products of Etna and some mantle-derived xenoliths from alkaline lavas of Hyblean region and we performed on these products a multi-isotopic study of noble gases (He, Ar, Ne) released from olivine/pyroxene-hosted fluid inclusions (FI) integrated by geochemistry of whole rocks and/or phenocrysts (major and trace elements, Sr-Nd isotopic systematics).

HYBLEAN PLATEAU

The studied samples consist of three peridotites (both lherzolites and harzburgites), four pyroxenites (both websterites and clinopyroxenites) and finally one composite peridotite-pyroxenite. All the rocks were found into some Miocene diatremes of the Hyblean area, in particular the Valle Guffari diatreme and Cozzo Molino pipe.

Trace elements and Sr-Nd isotopes

The chondrite-normalized REE distribution in peridotites showed consistent patterns among the different samples, suggesting a homogeneous source composition. Compared to chondrite, all samples displayed evident LREE enrichment ($La_n/Yb_n \approx 20$) whereas HREE were similar or slightly depleted. In previously published data of Hyblean peridotites such LREE enrichments were attributed to a pervasive or, more likely, cryptic metasomatism of a moderately depleted mantle (Perinelli *et al.*, 2008; Sapienza & Scribano, 2000; Sapienza *et al.*, 2005). The residual nature of the peridotites was also confirmed by the depletion observed in HFS elements relative to primordial mantle abundances. The pyroxenitic samples showed a REE upward-convex pattern, characterized by a less-pronounced enrichment of LREE and of HREE compared to MREE. The enrichment of LREE in pyroxenites relatively to chondrites varied among the studied samples ($La_n/Yb_n = 2.4-11.3$). As pyroxenites were recovered as veins in peridotite matrix, they would represent the crystallization product of deep magmatic liquids that intruded the peridotites at different levels of the lithospheric mantle (Sapienza & Scribano, 2000). In this framework, the differences in LREE enrichments among pyroxenite samples could reflect varying degrees of metasomatism, depending on the extent to which the metasomatizing melts interacted with the surrounding peridotite.

The relationship between Zr and the Zr/Nb ratios defined two clearly distinguishable compositional fields for pyroxenites and peridotites: pyroxenites were characterized by Zr concentrations of 26-40 ppm and a Zr/Nb ratio of ~ 20 , similar to that typical of a DM, whereas peridotites exhibited a much lower Zr content of ~ 8 ppm and a Zr/Nb ratio of ~ 4 , approaching the HIMU range.

The peridotites showed almost homogeneous $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ values of ~ 0.7029 and ~ 0.5129 , respectively, whereas the pyroxenites exhibited $^{143}\text{Nd}/^{144}\text{Nd} \approx 0.5130$ and a more variable $^{87}\text{Sr}/^{86}\text{Sr}$ ratio between 0.7028 and 0.7031. Consideration of the complete data set indicated the absence of any appreciable differences in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios among peridotites and pyroxenites, whereas their $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were slightly but significantly more variable. The more radiogenic Nd isotopic value of pyroxenites, with respect to peridotites, confirmed the presence of two distinct compositional groups, as already noticed from trace element geochemistry, and evidenced once again a slight tendency of pyroxenitic and peridotitic nodules respectively toward a depleted mantle and an HIMU-type source.

Noble gases

The $^3\text{He}/^4\text{He}$ values from fluid inclusions varied between 7.0 and 7.4 Ra in the peridotites whereas they were in the range 7.2-7.6 Ra in the pyroxenites. The $^4\text{He}/^{40}\text{Ar}$ ratios varied between 0.4 and 8 in the peridotites and between 0.6 and 15 in the pyroxenites (Fig. 1). In order to account for the observed range of R/Ra and $^4\text{He}/^{40}\text{Ar}$ ratios, we considered some processes that could affect the noble-gas signature. A magma ascending from the mantle increases its $^4\text{He}/^{40}\text{Ar}$ ratio as a consequence of degassing fractionation due to the higher solubility of He with respect to Ar (e.g., Iacono-Marziano *et al.*, 2010). Based on the equilibrium degassing calculations of Paonita & Martelli (2007) for a typical basalt raising from upper mantle and assuming an open-system degassing, a hypothetical pressure decrease from ~ 0.9 to 0.7 GPa is readily able to explain the observed $^4\text{He}/^{40}\text{Ar}$ variations. A further process must occur in conjunction with degassing to explain the measured $^3\text{He}/^4\text{He}$ variations as a kinetic fractionation of ^3He and ^4He during magma degassing has to be excluded (Paonita & Martelli, 2007). We propose that the He-isotope variability resulted from mantle heterogeneous characteristics, where two local end-members having different R/Ra values can be identified: (1) the peridotitic domain having R/Ra ≈ 7 , similar to those of a HIMU-type mantle source (R/Ra = 5-7; Hanyu & Kaneoka, 1998) and (2) the pyroxenitic domain with R/Ra ~ 7.6 , approaching those of a DM-type source (R/Ra = 8 ± 1). If we assume a mixing processes between a high-R/Ra pyroxenite having variable $^4\text{He}/^{40}\text{Ar}$ ratios as a consequence of the above described degassing process, and a low-R/Ra peridotitic mantle with $^4\text{He}/^{40}\text{Ar} = 0.4$ -1.0, then the complete data set can be explained (see Fig. 1).

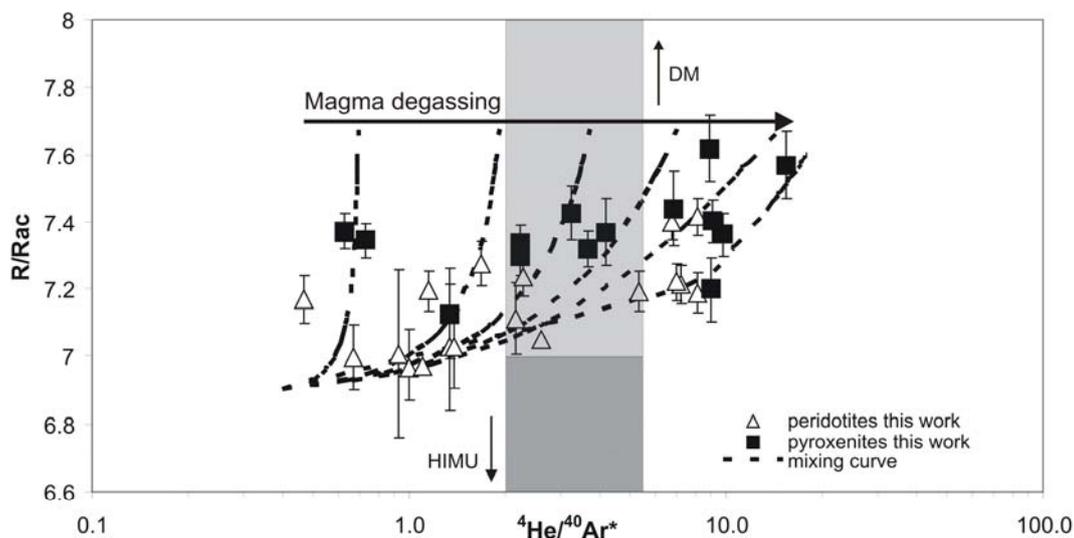


Fig. 1 - Plot of $^3\text{He}/^4\text{He}$ (R/Ra) vs. $^4\text{He}/^{40}\text{Ar}^*$ ratios of peridotites and pyroxenites. The dashed curves result from a mixing, which is a consequence of metasomatic processes, between a DM and a HIMU end-member. The dark thick arrow indicates the variations of $^4\text{He}/^{40}\text{Ar}^*$ ratio during degassing processes. HIMU and DM fields are from Hanyu & Kaneoka, 1998; Moreira & Kurz, 2001; Allègre *et al.*, 1995.

Evidences of mantle metasomatism by coupling noble gases and trace elements data

We investigated the quantitative relationships existing between trace elements and $^3\text{He}/^4\text{He}$ data. Pyroxenites and peridotites defined two distinct end-members of Hyblean mantle, where the highest R/Ra ($R/Ra \approx 7.4$) values were found in the pyroxenites that also showed the highest Sm and Nd concentrations ($\text{Sm} \approx 3.5$ ppm, and $\text{Nd} \approx 13$ ppm), whereas the same correspondence at the lowest values was observed in the peridotites ($R/Ra \approx 7$; $\text{Sm} \approx 0.25$ ppm; $\text{Nd} \approx 0.1$ ppm). Different degrees of metasomatism were modelled assuming a mixing process between the two end-members, as already observed for the noble gases and the REE data independently. The strongly convex shape of the resulting mixing curves (Fig. 2) is in a good agreement with our data, suggesting that the cryptic metasomatic process could potentially control both trace-element and noble-gas signatures. Whereas Sm and Nd mix linearly, the large amount of He in pyroxenites makes the isotopic ratio of this volatile extremely sensitive to put into evidence even very small extents of metasomatism. In fact, a very low metasomatic contribution from pyroxenite ($< 10\%$) dramatically changes the isotope ratio of peridotite mantle although it does not practically modify the trace elements.

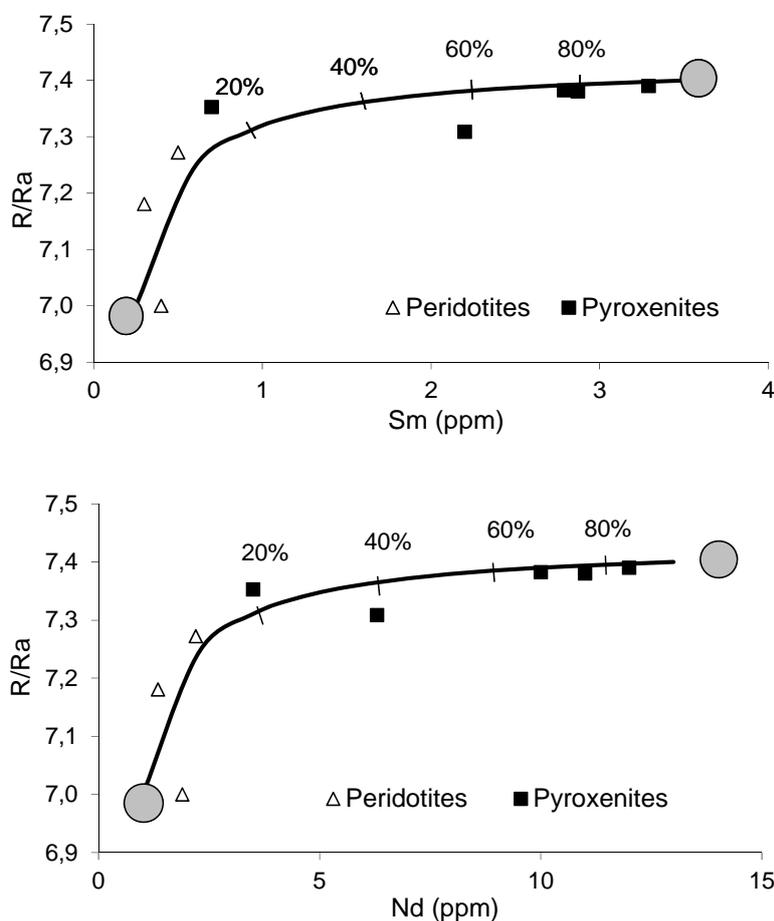


Fig. 2 - Plot of the whole rock concentrations of $^3\text{He}/^4\text{He}$ (R/Ra) vs. Sm (a) and Nd (b) from Hyblean peridotites and pyroxenites. The curves describe a mixing trend between two hypothetical end-members associated respectively with peridotitic and pyroxenitic sources. Ticks indicate percentages of the pyroxenitic end-member. The He concentrations of the two end-members, used to calculate the mixing path, were the highest measured in pyroxenites and the lowest in peridotites.

MOUNT ETNA

The studied samples on Mt. Etna consisted in basaltic lavas (Mt. Spagnolo, Mt. Maletto, Mt. De Fiore, Mt. Montagnola) collected from subaphiric eccentric edifices, erupted during the last 15 ka, and Mg-rich tephra (the fall stratified basalt FS and the tephra layer S11), erupted 3-4 ka BP. On the TAS diagram Mt. Maletto, S11, and FS plot in the field of basalts, Mt. De Fiore in that of trakybasalt and finally Mt. Montagnola and Mt. Spagnolo in an intermediate zone between the previous.

Trace elements and Sr-Nd isotopes

Compared to chondrite, all the samples showed a similar pattern characterized by a general stronger LREE enrichment with respect to HREE ($La_n/Yb_n = 11-26$) (Armienti *et al.*, 1988; Tanguy *et al.*, 1997; Coltelli *et al.*, 2005; Corsaro *et al.*, 2009) and comparable to that of Hyblean peridotites. The differences in LREE concentrations among the samples, increasing from FS picritic basalt to Mt. Spagnolo basalt could be ascribed to a different degree of melting of a common mantle source, being the first melt more enriched in incompatible elements respect to the following ones.

Concentration ratios among some incompatible trace elements (Zr/Nb vs. Ce/Yb and Th/Y vs. La/Yb) for the studied Etnean lavas are characterized by positive or negative trends that partially or totally plot in the field of Hyblean peridotites, thus suggesting a close similarity of their mantle source with those of the Hyblean mantle. Since these observed variations trends could be produced by variable degrees of melting of the same mantle together with crystallization processes, we calculated by MELTS code the effects of these processes on major and trace element geochemistry. Given the similarity found in the trace elements between the Etnean lavas and Hyblean peridotitic mantle, we assumed a Hyblean lherzolite (major elements composition) as a starting mantle source and we simulated an isobaric batch melting at 1 GPa, increasing the temperatures from the anhydrous solidus ($T \sim 1300$ °C) up to 1400 °C (corresponding to 13% of melting) and considering the system buffered for fO_2 at QFM. Then, starting from the resulting major element compositions from the different melting percentages of the same mantle source, we simulated an isobaric crystallization processes at 0.4 GPa decreasing gradually the temperatures from ~ 1200 to 1050 °C in a melt characterized by $\sim 3\%$ of H_2O . Comparison of the computed results with the measured compositions of Etnean lavas shows that degrees of melting growing from Mt. Spagnolo ($\sim 1\%$) to FS ($\sim 9\%$), together with variable percentages of crystallization ($\sim 0-5\%$ for FS, $\sim 12-14\%$ for Mt. Maletto, $\sim 13-17\%$ for Mt. Montagnola, and Mt. De Fiore and finally $\sim 4-16\%$ for Mt. Spagnolo) were able to fully explain the whole compositional range exhibited by Etnean lavas. Finally, through the fractions of batch melting and crystallization obtained for each lavas, we went back to initial trace elements composition (Zr/Nb vs. Ce/Yb and Th/Y vs. La/Yb ratios) of the mantle source characterizing each investigated lavas. As a main result, the calculations bring back to a primordial source testifying a common origin for all the investigated lavas. This source falls along a hypothetical mixing curve between a peridotitic and pyroxenitic end-member, highlighting a significant contribution of pyroxenitic term (about 10-20%).

The $^{143}Nd/^{144}Nd$ of Etnean samples was in the range of 0.51286-0.51289 whereas $^{87}Sr/^{86}Sr$ varied in the range 0.7033-0.7037 (Kamenetsky & Clocchiatti, 1996; Armienti *et al.*, 2004; Viccaro & Cristofolini, 2008). Between all the lavas, Mt. Spagnolo showed the most primitive composition (*i.e.*, the least radiogenic Sr and the highest radiogenic Nd), and reflected both a peridotitic and pyroxenitic contribution. Assuming the isotopic composition of Mt. Spagnolo next to that of the primordial Etnean mantle, then a fluids contamination in the magmatic reservoir by a magma enriched in a crustal component could move the primordial isotopic marker of this lava toward more radiogenic values, so explaining the more evolved isotopic ratios measured in the other lavas.

Noble gases

The $^3He/^4He$ measured in olivine phenocrysts ranged from 7.62 to 6.69 Ra, decreasing from the oldest Mt. Spagnolo and Mt. Maletto products to the most recent FS, to Mt. De Fiore, and, finally, to Mt. Montagnola. In order to understand the significance of this range of helium isotopic values in lavas we compared them to

helium isotopes measured in gas emissions during the 2001 eruption (Caracausi *et al.*, 2003). The gaseous manifestations sampled during the 2001 eruption highlighted for the Etnean mantle source a He isotopic marker at least of 7.6 Ra. Therefore, while helium isotopes of Mt. Spagnolo are coherent with the most uncontaminated mantle source, $^3\text{He}/^4\text{He}$ values lower than 7.6 measured in several Etnean lavas investigated in this work probably enlighten a partial contamination of the magma by crustal material, characterised by more radiogenic helium.

Influence of a metasomatic component in the Etnean lava genesis highlighted from noble gases and trace elements geochemistry

In order to confirm 1) the relationship among the Hyblean and Etnean mantle in the case of He isotopes and 2) if, and eventually, how much a metasomatic pyroxenitic component is involved in the melting of the Etnean peridotitic mantle, we reported the values of the estimated primordial mantle source for the Etnean lavas in a $^3\text{He}/^4\text{He}$ vs. Nd plot (Fig. 3). The Nd elemental concentration for the original source was calculated with the same procedure used for the others investigated trace elements (see previous section), while the $^3\text{He}/^4\text{He}$ value considered representative of the Etnean mantle source is that from Mt. Spagnolo. It was remarkable that, due to the strong convexity of this curve, the Etna source was nearly compatible with the mixing process. In fact, the low Nd abundance (~ 2 ppm), typical of a peridotitic source, associated to the high R/Ra values ($R/Ra = 7.6$), typical of a pyroxenitic mantle, highlights the contribution of pyroxenitic veins in the genesis of Etnean lavas from a mainly peridotitic mantle. Also, the mixing curve between the peridotitic and the pyroxenitic end-member allows to evaluate the amount of pyroxenitic melt involved in the genesis of Etnean lava, that resulted to be $\sim 10\%$.

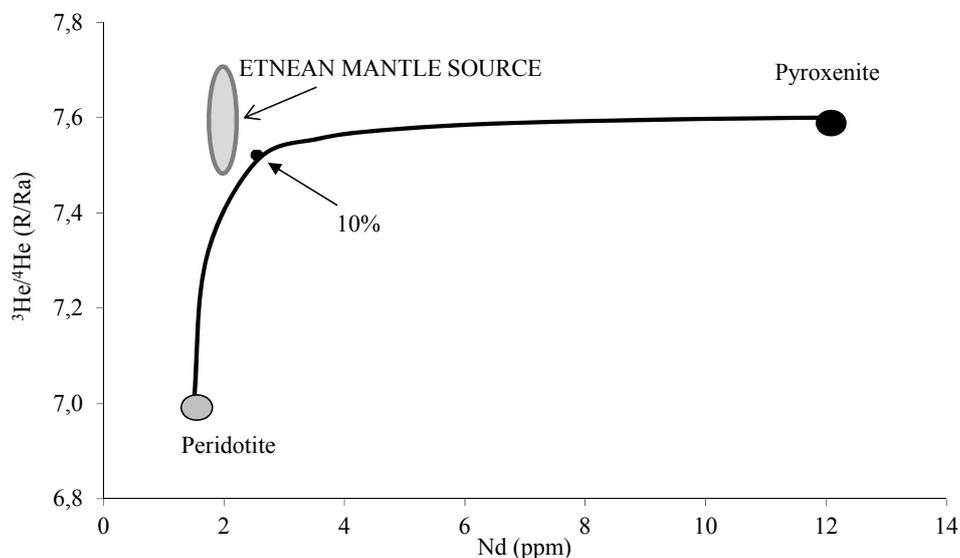


Fig. 3 - Plot of $^3\text{He}/^4\text{He}$ (R/Ra) vs. Nd abundances from calculated Etnean mantle source. The curve describes a mixing trend between two hypothetical end-members associated respectively with a peridotitic ($R/Ra = 7$; $Nd = 1.5$ ppm) and a pyroxenitic ($R/Ra = 7.6$; $Nd = 12$ ppm) source. The point marked on the mixing curve indicates the percentage of pyroxenitic end-member. The He concentrations of the two end-members, used to calculate the mixing path, are the highest measured in pyroxenites and the lowest in peridotites.

CONCLUSIONS

This study led us to the following conclusions:

1) The mantle below the Hyblean area is heterogeneous, featured by a shallower peridotitic layer with more enriched geochemical fingerprint (R/Ra of ~ 7, $^{143}\text{Nd}/^{144}\text{Nd}$ of ~ 0.5129 and Zr/Nb of ~ 4) with respect to a deeper pyroxenitic layer characterized by a more primitive character (R/Ra up to 7.6, $^{143}\text{Nd}/^{144}\text{Nd}$ of ~ 0.5130 and Zr/Nb of ~ 30). Our interpretation is that metasomatic processes interested the Hyblean lithosphere, and the deep-seated pyroxenites (former primitive mantle melts) were the metasomatizing agent. During their ascent, these primitive melts permeated the peridotitic mantle at different levels, producing a variable degree of refertilization.

2) The metasomatic processes affected distributions of both trace elements and noble gases but two different geochemical tracers displayed very different sensitivity to the effects of metasomatic mixing between two end-members.

3) Primitive magmas from Etna originated from different melting degree of a mantle source very similar to the Hyblean one in terms of both trace elements and noble gases. The geochemical characteristics of the Etnean mantle source suggest a strict relation with the Hyblean mantle, supporting the hypothesis of a heterogeneous and metasomatized lithosphere common to both areas. Indeed, the geochemistry of trace elements locates this source on the mixing zone between the peridotite and pyroxenite groups, thus testifying a simultaneous contribution of two components in the genesis of the investigated lavas. Also the Nd isotopes underline a certain relation with both the mantle levels while the helium isotopes, showing a higher sensitivity to effect of metasomatic mixing, exhibit typical pyroxenitic values.

4) During their storage in the magmatic reservoir and their rise to surface, the studied Etnean magmas were interested by a variable level of crystallization and were possibly contaminated varyingly by fluids from a crustal component. This explains the more evolved He and Sr-Nd isotopic composition of particular samples with respect to more primitive lavas

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