EVIDENCE OF ENRICHED MANTLE (EM-2) SOURCE CONTRIBUTION TO ETNEAN MAGMAS: A COMPREHENSIVE STUDY ON FLUID AND MELT INCLUSIONS OF 2001-2006 ERUPTIONS

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INTRODUCTION

Mt. Etna (Sicily, Italy) is one of the most active volcano in the world and the greatest one in Europe. Its activity probably started in the late-Pleistocene, ~ 0.5 Ma ago (Condomines *et al.*, 1982) and from then it was characterised by several changes in its eruptive style. Mt. Etna has the longest period of documented eruptions in the world and is noted for the wide variety of eruption styles.

Present-day Mt. Etna activity consists in summit and flank eruptions, prevailingly effusive accompanied by strombolian ejections of tephra (bombs and scoriaceous lapilli).

During the last ten years Mt. Etna activity has been characterised by frequent and sudden eruptions with many new and unusual geochemical and petrological features. In particular, the flank eruption of July-August 2001 and the dramatic flank eruption that lasted from October 2002 until late January 2003 are considered as two of the most unusual and complex eruptions recorded during the past 300 years.

These two eruptions had several similarities. Both were characterised by an extraordinary explosive activity and both affected two portions of the Etnean plumbing system. But the most striking feature of these two energetic eruptive events was the occurrence of textural and compositional differences in products contemporaneously erupted from distinct vents during a same eruption (Métrich *et al.*, 2004; Clocchiatti *et al.*, 2004; Spilliaert *et al.*, 2006; Corsaro *et al.*, 2007). In particular, lavas from the 2001 upper vents (≈ 2700 m; hereafter 2001 UV) and from the 2002-2003 northern fracture (hereafter 2002 N) are trachybasalts mineralogically similar to those that erupted in previous decades, while lavas from the 2001 lower vents (≈ 2100 and 2600 m; hereafter 2001 LV) and from the 2002-2003 southern fracture (thereafter 2002 S) are slightly more basic, primitive, and volatile-rich (Clocchiatti *et al.*, 2004; Corsaro *et al.*, 2007). After these two unusual events, at Mt. Etna occurred other two minor eruptions in 2004 and 2006.

Among the geochemical features that can be studied in the erupted products, fluid and melt inclusions hosted in olivine and clinopyroxene phenocrysts of the volcanic products (tephra and lavas) emitted during 2001-2006 eruptions, were selected for this study. It is well known in fact that melt and fluid inclusions could preserve more pristine characters of the related magmas providing useful constraints on the mantle source(s) and its evolution over space and time.

The aim of this study is to provide a contribution in acquiring further information on both the genesis and evolution of the recent erupted magmas, by better defining the characters of the magma source(s) and the dynamics of melts in the plumbing system. We are confident it will improve our knowledge on *how Mt. Etna works*, considering also the possible relations linking new data on the sampled volcanic rocks with those acquired during the geochemical monitoring. This work of thesis is basically divided into two main sections which regards respectively i) Fluid inclusions, and ii) Melt inclusions.

FLUID INCLUSIONS

In this section, are presented new data on noble gases obtained by *in-vacuo* crushing of olivines and pyroxenes extracted from the products erupted from Mt. Etna during 2001-2005.

Fluid inclusions are a common feature of minerals. During magma crystallization, when a crystal grows in the presence of a vapor phase, some of the gas may be trapped as imperfections in the growing crystal to form fluid inclusions (thereafter FIs). Their presence suggests oversaturation of magma with a fluid phase and partial degassing at the stage of host mineral crystallization. When properly interpreted, FIs provide information, which cannot be obtained otherwise: they are the only direct evidence for the role of the fluid during intratelluric processes.

Among the noble gases, the helium-isotope signature can be used to determine the source and processes ongoing during magma crystallization. In particular, during their growth within magma, olivines and pyroxenes trap FIs containing helium isotopes that are representative of the magmatic conditions, and can be investigated a long time after the eruption (Scarsi, 2000; Hilton *et al.*, 2002). The noble gases in FIs from etnean lavas have been investigated only by Marty *et al.* (1994) in selected historical lavas in order to constrain the origin and evolution of Mt. Etna magmatism.

In this work, He and Ar have been investigated in olivine and clinopyroxene FIs from lavas and pyroclastic deposits erupted at Mt. Etna during the 2001 (UV and LV), 2002-2003 (N and S), and 2004-2005 eruptions.

Analytical techniques

Rock samples were crushed to a grain size below 2 mm, taking into account that most of the minerals have a grain size below 1 mm. Then 0.5 mm crystals (olivine and clinopyroxene) were selected by hand under a binocular microscope. Separated minerals were ultrasonically cleaned in 5% HNO_3, and then in distilled water and high-purity acetone. During each analytical session, about 1 g of olivines or 2 g of pyroxenes were loaded in the crusher. Gases were extracted by *in-vacuo* crushing at about 200 bar pressure. Helium, neon, and argon were cleaned up in a stainless steel ultrahigh-vacuum line, by adsorbing reactive species in Zr-Al getter pumps, separating Ar from He and Ne by charcoal trap cooled at 77 K by liquid nitrogen. He and Ne were then adsorbed and concentrated in another charcoal trap (cryogenic pump), cooled down at 12 K by a cold-head. A temperature controller allowed to separate the two species by releasing He at 40 K and Ne at 85 K, that were then separately admitted in a split flight tube mass spectrometer (Helix SFT) for isotope analysis. Ar previously adsorbed was finally released from the charcoal by heating the trap at room temperature and then admitted in a multi-collector mass spectrometer (Argus). Analytical error in air standard He isotope analysis was generally below 1%, while in Ar analysis was generally below 0.1% (Nuccio *et al.*, 2008).

Results and discussion

The He and Ar abundances and relative isotope ratios are in agreement with the values reported by Marty *et al.* (1994) for olivine and pyroxene FIs from etnean historical lavas.

The measured helium isotope ratios (expressed as R/Ra, where R is ^{3}He/^{4}He of the sample and Ra is the same ratio in atmosphere) of olivine and pyroxene FIs vary widely, from 5.2 to 7.0 Ra, and ^{40}Ar/^{36}Ar ratios are between 300 and 310, which is near to the atmospheric value of 295.5.

By crushing co-genetic olivines and pyroxenes, they revealed that both helium abundance and ^{3}He/^{4}He ratio tends to be lower in pyroxenes (Fig. 1). This effect has been attributed to the closure temperature being lower for pyroxene than for olivines, that caused higher loss of magmatic volatiles and

fractionation in the formers, coupled to more evident effects of air contamination. Atmospheric contamination was also identified on the basis of argon isotopes, which were not used as a tracer of the magmatic source. We believe that the differences of air-corrected isotope ratios between olivines and pyroxenes mainly depend on the capability on the two minerals to provide a true barrier for He diffusion. Indeed, olivine has a crystal structure that reduce any secondary exchange, after crystallization, thus preserving the original magma signature (Craig & Lupton, 1976; Ozima & Podosek, 1983; Martelli *et al.*, 2004).
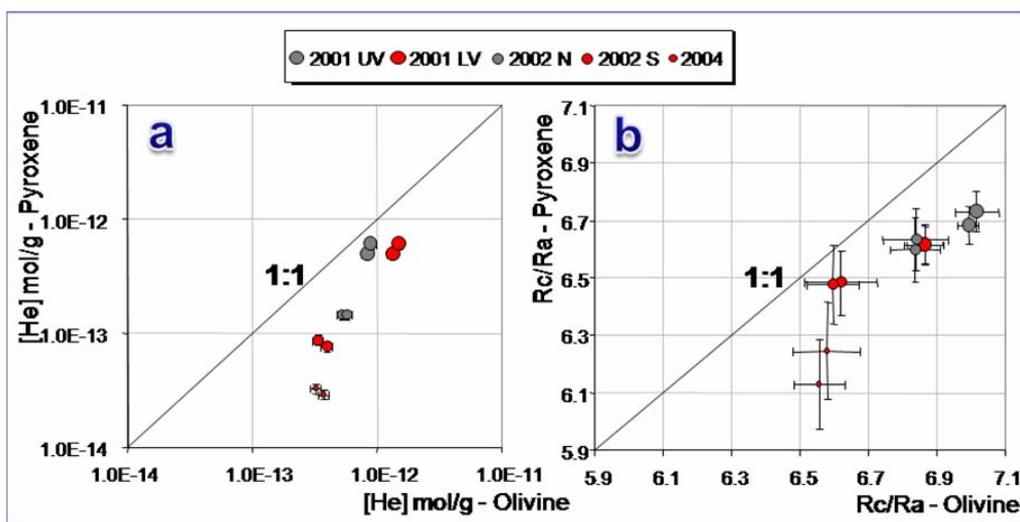

Fig. 1 - a) Comparison of He abundance between investigated olivines and pyroxenes. Grey and red colours indicate the two parental magma series. Circles progressively decrease in size from 2001 products to 2004-2005 products. Each point represents an individual mineral sample. b) ^{3}He/^{4}He ratios (expressed as Rc/Ra) of the investigated olivines and pyroxenes.

Another finding in our investigation was that the He and Ar contents as well as the helium isotope ratio generally decrease in both olivines and pyroxenes from the 2001 to the 2004-2005 products (Fig. 1 and Fig. 2). The decreasing trend of the helium isotope ratios from 2001 toward 2004-2005 lavas results in a difference of 0.5 Ra between 2001 UV and 2004-2005 olivines and up to 0.6 Ra in the cogenetic pyroxenes (Fig. 1). In accordance with the petrological evidence, we attributed the observed decreasing trend in He abundances to a progressive loss of volatiles due to magma degassing between the 2001 eruption and those of 2002-2003 and 2004-2005 and we suggest that this process could also induce a preferential ^{3}He loss in the residual magma. In agreement with the process described by Caracausi *et al.* (2003), the exsolving bubbles in etnean magmas could in fact grow far from equilibrium, and thus become kinetically enriched in ^{3}He. Accordingly, the progressive outgassing of ^{3}He-enriched bubbles can explain the decrease of the ^{3}He/^{4}He ratios measured in the FI of 2002-2003 and 2004-2005 phenocrysts with respect to the ones erupted in 2001.

The decrease in He-isotope ratios from 2001 to 2004-2005, recorded in olivine-hosted FI, was also found in the helium-isotope data obtained during the same period through the long-term monitoring of

volcanic gases at the surface (Rizzo *et al.*, 2006). To our knowledge, this is the first time that temporal trends from FIs and emitted gases have been compared. The results provide strong evidence of a direct link between gases discharged at the surface and the volatiles released from magma, and highlight the power of using Etnean peripheral gases as real-time indicators of magma dynamics at depth.
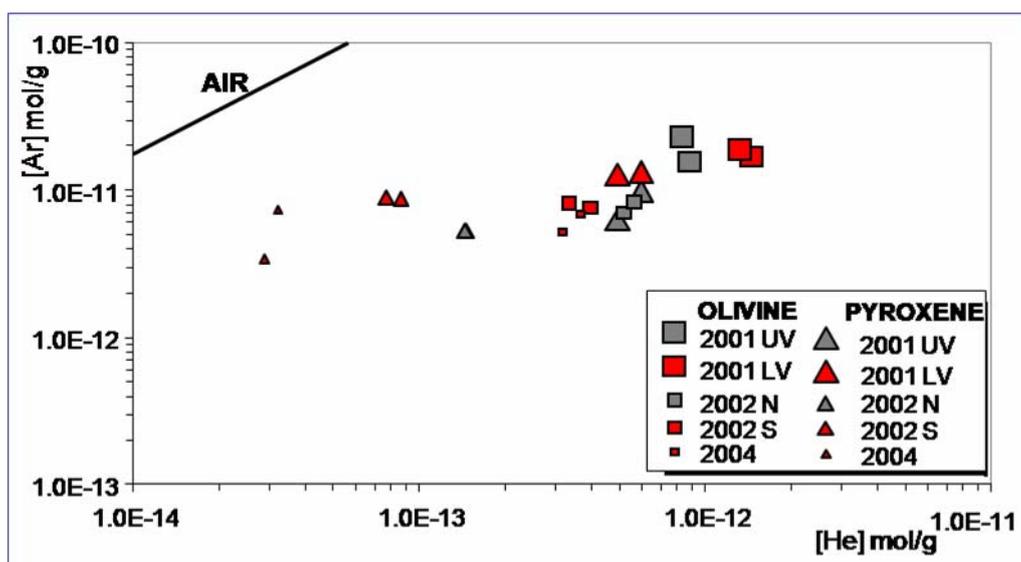

Fig. 2 - He *versus* Ar abundance in FIs of investigated olivines and pyroxenes. Squares and triangles have dimensions progressively smaller in size from 2001 products to 2004-2005 products. The line representing the He/Ar ratio in the atmosphere is also shown.

MELT INCLUSIONS

In this section were discussed data about the major, volatiles and trace elements compositions of olivine-hosted melt inclusions. Melt inclusions (thereafter MIs) trap small amounts of the unaltered and non-degassed silicate melt from which phenocrysts grow. Analyses of MIs can provide important geochemical information on the melt and help to better understand igneous petrogenesis. The use of MIs to study magmatic processes is based on the assumption that the inclusions represent the melt present at the time of trapping, and that nothing has been added to or lost from the inclusion since trapping (Bodnar & Student, 2006).

In this study, MIs occur as isolated inclusions or in assemblages defining crystal growth zones. Their size vary from < 10 μm to > 100 μm, however most inclusions are typically 5-50 μm. Typically, isolated inclusions are larger than those in well-defined crystal growth assemblages. MIs are composed of homogeneous glass with or without a small bubble, but without any trapped or daughter minerals and their shape is rounded to elongate. The MIs are assumed to be primary because they are trapped along crystal growth faces or between growth zones with no visible fractures.

Analytical techniques

Phenocrysts containing MIs were mounted in epoxy resin, and the MIs were brought closer to the surface of the crystal by continued grinding and polishing by hand on glass plates for better visual inspection. MIs located along fractures or near the edges of crystals were ignored as were those containing a shrinkage or vapor bubble.

The major and minor element compositions of exposed MI were determined using an Cameca SX-50 electron microprobe (EMPA) at CNR-IGG of Padova. Measured values were corrected for post-entrapment crystallization (PEC). The trace elements and H_2O analysis in the MIs were done with a Cameca IMS 4f ion microprobe (SIMS) installed at CNR-IGG of Pavia.

Results and discussions

One of the most important results of this study is a documentation of large chemical variability, among melt inclusions found in samples belonging to the different magmas, simultaneously emitted during 2001 and 2002-2003 eruptions, already recognised on the basis of petrographic investigations (Clocchiatti *et al.*, 2004). It is worth noticing that primitive melt inclusions within a single phenocryst or a single lava sample have relatively uniform major element compositions but their trace elements signature may be highly variable. On the basis of trace elements compositions, MIs can be clustered into two groups (Fig. 3) named "type 1" and "type 2".
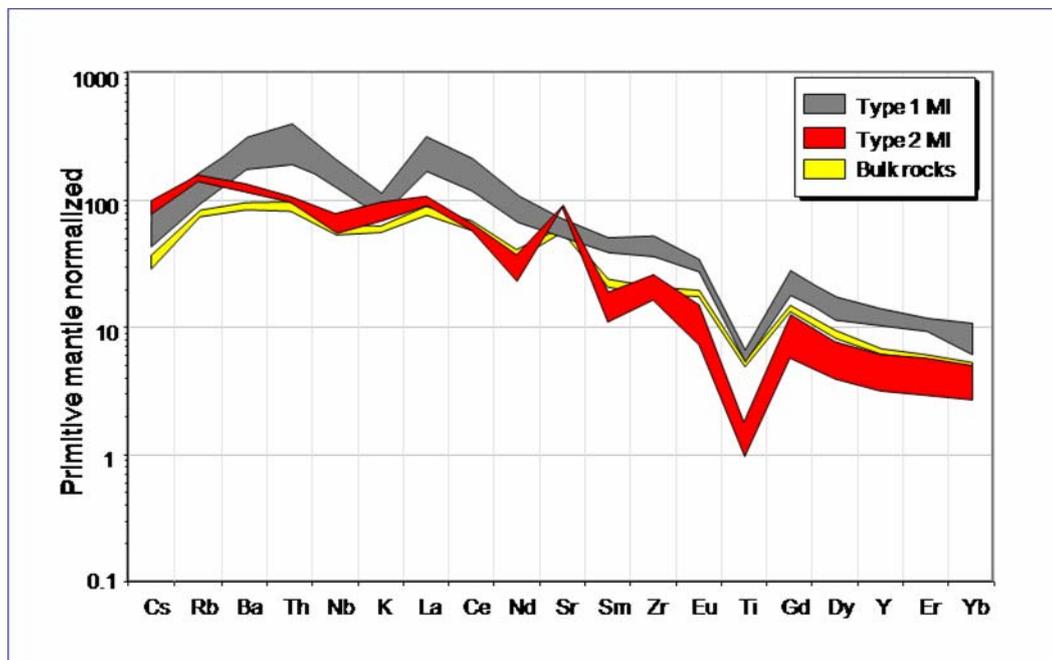

Fig. 3 - Trace element abundance normalised to the composition of the primitive mantle and plotted from left to right in order of increasing compatibility. Olivine-hosted MIs in etnean trachybasalts and alkali basalts belonging to the suites of different eruptions (2001, 2002 and 2006). Bulk rocks from Corsaro *et al.* (2007) were also plotted for comparison.

The different chemical composition of the two MI suites can be related to either source or en-route processes, such as fractional crystallisation or assimilation that modified the primitive melt chemistry. Simple arguments allow us to reject the latter possibility. Indeed, geochemical modelling shows that the two MI suites do not represent batches of the same parental magma that variously evolved by fractional crystallisation. On the other hand, the role of crust contamination cannot account for the different geochemical signatures of the two MI suites. Therefore, the different chemical composition of the two MI suites have been generated by either varying degrees of partial melting of the same mantle source or distinct magma sources. We first evaluate the former hypothesis and verified that the two recognised melts must derive from different mantle sources located at different mantle depths. The deeper source is probably asthenospheric and produces parental melts of type 1 MI; it has FOZO/C to HIMU isotopic signatures (Cadoux *et al.*, 2007) and is similar in composition to the mantle sectors that gave rise also to the older Hyblean lavas. The second source feeds parental melts of type 2 MIs and seems to be lithospheric and located at shallower depth relative to the source of type 1 MIs, possibly near the mantle-crust interface. With the aim of identifying the mantle sources involved in the melts production, ratios involving highly incompatible elements with nearly identical D (solid/melt) plotted against each other were used.

Because they remain uniform irrespective of their absolute concentrations and, therefore, do not vary with increasing concentrations in the magma during partial melting process, concentration ratios of these incompatible elements, namely Ce/Nb, K/La, Be/Nb, Rb/La and Ba/La primarily reflect those in present-day mantle magma sources (Hofmann *et al.*, 1986).

Schiano *et al.* (2001) used these ratios to postulate that the Etnean mantle source has changed from a HIMU-type to an arc-type, close in trace element composition to Vulcano primitive MIs**.** Instead, the trend defined by our samples falls far from the Vulcano Island subductive component and clearly point toward the EM-2 mantle source, namely a mantle source enriched by contribution of oceanic crust plus terrigenous sediments (Willbold & Stracke, 2006, and references therein).

The highest EM-2 contribution occurs in type 2 MIs erupted from 2001 LV and 2002 South fissures, which poured out products clearly different from any other one previously erupted from Mt. Etna. Rather than a general transition towards arc-type mantle sources beneath Mount Etna (Schiano *et al.*, 2001), we propose here that modern Etnean eruptions are supplied by magmas from two coexisting sources located at different depths within an Hyblean-like mantle. The contribution of magma with EM2-like signature seems to increase over time.

REFERENCES

Bodnar, R.J. & Student, J.J. (2006): Melt inclusions in plutonic rocks: Petrography and microthermometry. *In*: "Melt inclusions in plutonic rocks", J.D. Webster, ed. Mineral. Ass. Canada, Short Course, **36**, 1-26.

Cadoux, A., Blichert-Toft, J., Pinti, D.L., Albarede, F. (2007): A unique lower mantle source for Southern Italy volcanics. *Earth Planet. Sci. Letters*, **259**, 227-238.

Caracausi, A., Favara, R., Giammanco, S., Italiano, F., Paonita, A., Pecoraino, G., Rizzo, A., Nuccio, P.M. (2003): Mount Etna: Geochemical signals of magma ascent and unusually extensive plumbing system. *Geophys. Res. Lett.* **30**, doi:10.1029/2002GL015463.

Clocchiatti, R., Condomines, M., Guènot, N., Tanguy, J.C. (2004): Magma changes at Mount Etna: the 2001 and 2002-2003 eruptions. *Earth Planet. Sci. Letters*, **226**, 397-414.

Condomines, M., Tanguy, J.C., Kieffer, G., Allegre, C.J. (1982): Magmatic evolution of a volcano studied by ^{230}Th-^{238}U disequilibrium and trace elements systematics: the Etna case. *Geochim. Cosmochim. Acta*, **46**, 1397-1416.

Corsaro, R., Miraglia, L., Pompilio, M. (2007): Petrologic evidence of a complex plumbing system feeding the July-August 2001 eruption of Mt. Etna, Sicily, Italy. *Bull. Volcanol.*, **69**, 401-421.

Craig, H. & Lupton, J.E. (1976): Primordial neon, helium and hydrogen in oceanic basalts. *Earth Planet. Sci. Letters*, **31**, 369-385.

Hilton, D.R., Fischer, T.P., Marty, B. (2002): Noble gases in subduction zones and volatile recycling. MSA Special Volume: *Noble Gases Geochem. Cosmochem.*, **47**, 319-362.

Hofmann, A.W., Jochum, K.P., Seufert, M., White, W.M. (1986): Nb and Pb in oceanic basalts: new constraints on mantle evolution. *Earth Planet. Sci. Letters*, **79**, 33-45.

Martelli, M., Nuccio, P.M., Stuart, F.M., Burgess, R., Ellam, R.M., Italiano, F. (2004): Helium strontium isotope constraints on mantle evolution beneath the Roman Comagmatic Province, Italy. *Earth Planet. Sci. Letters*, **224**, 295-308.

Marty, B., Trull, T., Lussiez, P., Basile, I., Tanguy, J.C. (1994): He, Ar, O, Sr and Nd isotope constraints on the origin and evolution of Mount Etna magmatism. *Earth Planet. Sci. Letters*, **126**, 23-29.

Métrich, N., Allard, P., Spilliaert, N., Andronico, D, Burton, M. (2004): 2001 flank eruption of the alkali- and volatile-rich primitive basalt responsible for Mount Etna's evolution in the last three decades. *Earth Planet. Sci. Letters*, **228**, 1-17.

Nuccio, P.M., Paonita, A., Rizzo, A., Rosciglione, A. (2008): Elemental and isotope covariation of noble gases in mineral phases from Etnean volcanics erupted during 2001-2005, and genetic relation with peripheral gas discharges. *Earth Planet. Sci. Letters*, **272**, 683-690.

Ozima, M. & Podosek, F.A. (1983): Noble gas geochemistry. Cambridge University Press, Cambridge, 367 p.

Rizzo, A., Caracausi, A., Favara, R., Martelli, M., Paonita, A., Paternoster, M., Nuccio, P.M., Rosciglione, A. (2006): New insights into magma dynamics during last two eruptions of Mount Etna as inferred by geochemical monitoring from 2002 to 2005. *Geochem. Geophys. Geosyst.*, **7**, Q06008.

Scarsi, P. (2000): Fractional extraction of helium by cushing of olivine and clinopyroxene phenocrysts: effects on the ^{3}He/^{4}He measured ratio. *Geochim. Cosmochim. Acta*, **64**, 3751-3762.

Schiano, P., Clocchiatti, R., Ottolini, L., Busà, L. (2001): Transition of Mount Etna lavas from a mantle-plume to an island-arc magmatic source. *Nature*, **412**, 900-904.

Spilliaert, N., Allard, P., Mètrich, N., Sobolev, A.V. (2006): Melt inclusion record of the conditions of ascent, degassing, and extrusion of volatile-rich alkali basalt during the powerful 2002 flank eruption of Mount Etna (Italy). *J. Geophys. Res.*, **111**, B04203.

Willbold, M. & Stracke, A. (2006): Trace element composition of mantle end-members: Implications for recycling of oceanic and upper and lower continental crust. *Geochem. Geophys. Geosyst.*, **7**, Q04004.