

**ELEMENTAL AND ISOTOPE COVARIATION OF NOBLE GASES IN MINERAL PHASES FROM
ETNEAN VOLCANICS ERUPTED DURING 2001–2005, AND GENETIC RELATION WITH
PERIPHERAL GAS DISCHARGES**

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Abstract

During 2001–2005, Mount Etna was characterized by intense eruptive activity involving the emission of petrologically different products from several vents, which involved at least two types of magma with different degrees of evolution. We investigated the ratios and abundances for noble-gas isotopes in fluid inclusions trapped in olivines and pyroxenes in the erupted products. We confirm that olivine has the most efficient crystalline structure for preserving the pristine composition of entrapped gases, while pyroxene can suffer diffusive He loss. Both the minerals also experience noble gas air contamination after eruption. Helium isotopes of the products genetically linked to the two different magmas fall in the isotopic range typical of the Etnean volcanism. This result is compatible with the metasomatic process that the Etnean mantle is undergoing by fluids from the Ionian slab during the last ten kyrs, as previously inferred by isotope and trace element geochemistry. Significant differences were also observed among olivines of the same parental magma that erupted throughout 2001–2005, with $^3\text{He}/^4\text{He}$ ratios moving from about 7.0 Ra in 2001 volcanites, to 6.6 Ra in 2004–2005 products. Changes in He abundances and isotope ratios were attributed to variations in protracted

degassing of the same magma bodies from the 2001 to the 2004–2005 events, with the latter lacking any contribution of undegassed magma. The decrease in $^3\text{He}/^4\text{He}$ is similar to that found from measurements carried out every fifteen days during the same period in gases discharged at the periphery of the volcano. To our knowledge this is the first time that such a comparison has been performed so in detail, and provides strong evidence of the real-time feeding of peripheral emissions by magmatic degassing.

Keywords: noble gases, helium isotopes, fluid inclusions, magma degassing

1. Introduction

Mount Etna is the most active volcano in Europe, and in the last ten years its eruptive activity has increased. Two of its most energetic eruptions occurred between 2001 and 2003, followed by a third eruption that began in September 2004. A peculiar feature of these two energetic eruptions was that two petrologically different magmas were simultaneously erupted from several vents (Clocchiatti et al., 2004; Corsaro and Miraglia, 2005; Corsaro et al., 2007). Particularly, lavas from the 2001 upper vents (≈ 2700 m; hereafter 2001 UV) and from the 2002-2003 northern fracture (hereafter 2002 N) were 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) were slightly more basic, primitive, and volatile-rich (Clocchiatti et al., 2004; Corsaro et al., 2007).

Among the geochemical features that can be studied in the erupted products, the abundances and isotopic compositions of noble gases entrapped in fluid inclusions (hereafter FIs) of igneous rocks have been widely investigated because they provide useful constraints on the mantle source and its evolution over space and time (Craig and

Lupton, 1976; Mamyrin and Tolstikhin, 1984; Ozima and Podosek, 1983; Hilton et al., 1993; Patterson et al., 1997; Martelli et al., 2004; Shaw et al., 2006). 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 Mount Etna magmatism. They found that the $^3\text{He}/^4\text{He}$ ratio in the olivines was generally constant throughout the volcano's history ($6.7 \pm 0.4 R_a$, corresponding to a $^3\text{He}/^4\text{He}$ -ratio R_a in air of 1.39×10^{-6} ; Ozima and Podosek, 1983), suggesting that a single mantle source feeds Etnean magmas. By crushing cogenetic olivines and pyroxenes, they also revealed that the $^3\text{He}/^4\text{He}$ ratio tends to be lower in pyroxenes, which was attributed to the helium trap depth being lower than that of the parental olivines, coupled to a shallower contribution of radiogenic or atmospheric helium to the phenocrysts. Atmospheric contamination was also identified on the basis of argon isotopes, which were not used as a tracer of the magmatic source.

In this paper, we present new data on noble gases obtained by *in-vacuo* crushing of olivines and pyroxenes extracted from the products that erupted from Mount Etna during 2001–2005. Our results update those of Marty et al. (1994), and are compared with them here. In particular, we evaluated the differences in He abundances and isotopic composition observed between the two erupted series, as well as the variations in each parental magma over time. The observations from the FIs were compared with those recorded – over the same time span – by the long-term monitoring of certain peripheral

gas emissions at sites located around the volcano. To our knowledge, this is the first time that such a comparison has been performed.

2. Eruptive activity and petrological features of the erupted products

In the period from 2001 to 2005, Mount Etna was characterized by frequent and sudden eruptions that exhibited many novel geochemical and petrological features. A powerful eruption started on July 17, 2001 and lasted 24 days (until August 9), during which at least eight distinct lava flows occurred on the southern and south-southwestern flanks of the volcano (Behncke and Neri, 2003). This eruption was characterized by a highly vigorous dynamic sequence of events and frequent changes in the style of eruptive activity. The largest lava flows were produced by the fissures at 2100 and 2700 m above sea level (a.s.l.). Mount Etna subsequently remained almost quiescent until March 2002, when the summit craters reactivated (Patané et al., 2003a, 2003b; Andronico et al., 2005). Strombolian activity at the summit craters, together with shallow seismicity and deformation, preceded the 2002–2003 eruption, which began on October 27, 2002 and ended on January 28, 2003 (Andronico et al., 2005; Neri et al., 2005). This eruption was characterized by the reactivation of the feeding system that had been active on the south rift during 2001, and by the development of a fissure radiating down from the summit craters, along the northeastern rift. Both the 2001 and 2002–2003 eruptions are noteworthy for the exceptional explosive activity (among the most intense in recent times) that significantly modified the morphology of the upper parts of the southern volcano slope, with the growth of two distinct cones (Patané et al., 2003; Andronico et al., 2005). Furthermore, the chance to observe different magmas feeding the same eruptive activity was extraordinary, with a similar condition having last occurred 300 years previously (Andronico et al., 2005). Petrological investigations revealed that

the magmas that erupted during 2001, 2002–2003, and 2004–2005 exhibited specific characteristic features. In particular, the trachybasalts that erupted from 2001 UV and 2002 N were mineralogically similar, and also to lavas that erupted in previous decades from the summit craters (Clocchiatti et al., 2004). In contrast, lavas from 2001 LV and 2002–2003 S were more basic, showed the occasional occurrence of amphibole and orthopyroxene, and abundant sandstone inclusions that were also found in some historical investigations on Mount Etna (Michaud, 1995). These products belong to a magma among the most primitive erupted in the past centuries, they are rich in volatiles and resided at greater depth than magma feeding 2001 UV and 2002–2003 S lavas (Corsaro et al., 2007).

The 2002–2003 eruption was followed by a period of quiescence. A new eruption began high on the E flank without any warning on September 7, 2004 and lasted until March 8, 2005. This eruption differed significantly from the previous two eruptions in its lack of both geophysical and geochemical precursors and in its slow evolution (Corsaro and Miraglia, 2005; Patané et al., 2005; Neri and Acocella, 2006; Rizzo et al., 2006). The petrography of lavas erupted during 2004–2005 suggests that magma feeding this eruption was stored in the shallow plumbing system, where it had undergone extensive loss of volatiles and crystallization (Corsaro and Miraglia, 2005). This is in agreement with the lack of explosive activity (except for mild spattering during the first few weeks) and the passive extrusion of degassed lavas. Corsaro and Miraglia (2005) also considered this magma to have evolved from that feeding the 2001 LV and 2002–2003 S vents.

3. Experimental techniques

He and Ar have been investigated in olivine and pyroxene FIs from lavas and pyroclastic deposits erupted at Mount Etna during the 2001 (UV and LV), 2002–2003 (N and S), and

2004–2005 eruptions. 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 were selected by hand under a binocular microscope. Separated minerals were ultrasonically cleaned in 5% HNO₃, 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 and pumped to an ultra high vacuum overnight baking at 130°C. The loaded quantities above reported were established considering the expected amount of noble gases produced by crushing. Gases were extracted by *in-vacuo* crushing at about 200 bar pressure, so as to minimize the contribution of noble gases in the crystal lattice due to radioactive decay (Hilton et al., 1999). Helium, neon, and argon were cleaned up in a stainless steel ultra-high-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 an other charcoal trap (cryogenic pump), cooled down at 12°K by a cold-head. This trap was strategically positioned close to the He mass spectrometer in order to concentrate each sample in a small volume (about few tens of cm³) before expansion in the mass spectrometer, thus reducing the analytical error during analysis. 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%.

The He and Ar abundances and isotope compositions were measured, as well the ⁴He/²⁰Ne ratios, were determined in all of the investigated samples. During the

experiments, typical He, Ne, and Ar blanks were negligible. The uncertainties in the noble-gases abundances were less than 10%. Five couples of cogenetic olivines and pyroxenes were analyzed twice in the INGV-Palermo (INGV-Pa) laboratory. The analytical results are listed in Table 1.

4. Results and discussion

The He and Ar abundances and relative isotope ratios are reported in table 1 and are in agreement with the values reported by Marty et al. (1994) for olivine and pyroxene FIs from Etnean historical lavas. It is noteworthy that the gas extracted by crushing technique represents a bulk sample resulting from many individual grains holding different number density and size of inclusions, thus the noble gas abundances cannot be easily related to any magmatic process. For this reason, little importance is usually placed on noble gas amount from FI bulk analysis. Nevertheless, the good reproducibility of our data when crushing different populations of crystals of the same products (Table 1), suggests that the analysed abundances represent a suitable estimation of the average content of noble gases in the magma.

The measured helium isotope ratios of olivine and pyroxene FIs vary widely, from 5.2 to 7.0 Ra, and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios are between 300 and 310, which is near to the atmospheric value of 295.5. The He and Ar contents generally decrease in both olivines and pyroxenes from the 2001 to the 2004–2005 products (Fig. 1). In fact, the He abundances in 2004–2005 products are particularly low, especially in pyroxenes. Finally, in our investigation, the He and Ar concentrations are generally higher in olivines than in pyroxenes. Although this behaviour has already been observed in Etnean vulcanites (Marty et al., 1994), it is not a general result of FI investigations, which also report suites of products having higher noble gas amounts in pyroxenes (Martelli et al., 2004; Shaw et al., 2006).

4.1 Evidence of air contamination

The measured $^{40}\text{Ar}/^{36}\text{Ar}$ ratios fall in the range of subduction-related volcanism, well below the typical mantle values (Burnard et al., 1997; Fischer et al., 2005), and close to the atmospheric signature. In order to assess if the low $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of FIs (max 310) can be considered the typical magmatic ones, we have also to take into account the Ar isotope compositions in peripheral gas emissions of Mount Etna. These gas discharges were sampled in 1994 and 1996 (Nakai et al., 1997), and displayed $^{40}\text{Ar}/^{36}\text{Ar}$ ratios well above the typical atmospheric signature, varying from about 620 to more than 1700. Ar isotopes of the peripheral gas emissions are also currently being monitored by the Etna group of INGV-Pa, and the analyzed samples exhibit $^{40}\text{Ar}/^{36}\text{Ar}$ ratios up to 1800. These values are significantly higher than those measured in FIs, indicating that the low argon isotope ratios of FIs cannot be considered the deep magmatic signature of Mt. Etna, but were probably achieved by air contamination at shallow levels or after eruption.

Accordingly, the measured $^4\text{He}/^{20}\text{Ne}$ ratios of FIs (expressed as $X = (^4\text{He}/^{20}\text{Ne})_{\text{sample}} / (^4\text{He}/^{20}\text{Ne})_{\text{air}}$), ranging from 5.7 to 349.5, are also lower than the values measured in the peripheral gases (X generally >3000 ; Caracausi et al., 2003a; Caracausi et al., 2003b; Rizzo et al., 2006), suggesting that air contamination of the olivine- and pyroxene-hosted FIs modifies their original magmatic values. The effects of air contamination are clear in Figure 2, which plots $^4\text{He}/^{20}\text{Ne}$ ratios versus He isotope ratios (Sano and Wakita, 1985). Upward air contribution are evident in figure when moving from 2001 to 2005 products, as well as from olivines to pyroxenes.

It is debatable how this contamination occurred. As it will be described below, it appears unlikely that the Etnean magmas were contaminated by fluids with an atmospheric-like signature in the shallow plumbing system. Instead, it could be a component that diffused

into FIs when the crystals were still hot and already erupted. Nevertheless, taking into account recent data of Ar diffusivity in olivines and pyroxenes (Watson et al., 2007), it would take months for Ar to penetrate into millimeter-sized crystals at the magmatic temperature (i.e., 1100°C), which is not compatible with our samples being collected only a few days after the eruptions. Moreover, the $^{40}\text{Ar}/^{36}\text{Ar}$ and $^4\text{He}/^{20}\text{Ne}$ ratios do not differ between phenocrysts from the 2001 LV pyroclastics (tephra) and samples from lava flows, which surely cooled more slowly. With the aim of formulating an hypothesis about the origin of this atmospheric component, it is noteworthy that the microscopic inspection of the investigated crystals revealed that most of them display a number of microcracks connected to the surface (see Fig. 3). Therefore, we propose that such microcracks can entrap the air component during the eruptive activity or later. The entrapped air may be readily released only when the crystal is crushed and the microcracks are consequently opened. Clearly, a given atmospheric contribution causes more significant effects when added to smaller gas amounts, thus it is not amazing that it is more evident in the products of the 2004–2005 eruption, having the lowest gas amount (Fig. 1).

4.2 Magmatic helium degassing versus diffusive loss from crystals

The couples of cogenetic olivines and pyroxenes show a clear disequilibrium, in terms of both elemental abundances and isotopic composition. Figure 4 displays that the content of entrapped helium is always higher for olivines than for the parental pyroxenes. The olivines in the products from 2001 LV show higher He abundance compared to the other eruption products. Pyroxene FIs show a similar characteristic, although those from 2001 LV and 2001 UV are within analytical uncertainty. The pyroxene FIs from 2004–2005 lavas display the lowest He abundance, being one order of magnitude less than that in the

cogenetic olivines. In accordance with the petrological evidence, our results suggest that the extent of volatile degassing in lavas increased from the 2001 to the 2002–2003 and 2004–2005 eruptions.

Before studying the isotopic disequilibria, we recall that the process of atmospheric contamination explains most of the variability in helium-isotope ratios of olivine and pyroxene FIs. Thus, we corrected the He-isotope values on the basis of the $^4\text{He}/^{20}\text{Ne}$ ratio (see Table 1). The corrected $^3\text{He}/^4\text{He}$ ratios are generally close to the lowest limit of MORB (8 ± 1 Ra), and overlap the compositional range of samples collected from gas discharges (e.g., bubbling gas, mud volcanoes) at the Mount Etna periphery (Caracausi et al., 2003a,b; Rizzo et al., 2006). Figure 5 plots respective $^3\text{He}/^4\text{He}$ ratios for the couples of cogenetic olivines and pyroxenes (below we quote the air-corrected values except where stated otherwise). As for He abundances, the helium isotopes differ systematically between all the cogenetic olivine–pyroxene couples, with a general tendency to be lower in pyroxenes than in olivines. Our results also highlight a general decrease in the isotope ratios from 2001 products to 2004–2005 products. The $^3\text{He}/^4\text{He}$ ratios are higher in olivines and pyroxenes from 2001 UV lavas (7.02 and 6.73 Ra, respectively), and the $^3\text{He}/^4\text{He}$ ratios for 2001 LV and 2002 N products are consistent within analytical uncertainty. As observed for He abundances, we found that helium-isotope ratios were lowest in the 2004–2005 products (6.56 and 6.13 Ra in olivines and pyroxenes, respectively). Therefore, we raise two questions that need to be explained: i) the decrease of the $^3\text{He}/^4\text{He}$ ratios of both olivines and pyroxenes in the period 2001 to 2005; ii) the isotopic disequilibria between olivines and pyroxenes.

4.2.1 He isotope variations over time

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. 5). When investigating this feature, a key constraint is that lavas from 2004-2005 belong to a strongly degassed magma remaining in the shallow plumbing system after 2001 event (Corsaro and Miraglia, 2005), thus we need to explain the decrease of the $^3\text{He}/^4\text{He}$ ratios within a few years. Starting from the U and Th contents in the investigated Etnean lavas (Corsaro et al., 2007), as well as the measured concentration of He per gram of rock (Table 1), we can exclude any type of magma aging that lowers the $^3\text{He}/^4\text{He}$ ratios by 0.5 Ra in 4-5 years. Production of ^4He by U-Th decay in crystal lattice is even less efficient, due to lower content of radioactive nuclides inside the minerals (Zindler and Hart, 1986). Also, by assuming the most favourable condition of zero helium content in magma, any ^4He contribution from crustal fluids diffuses through the magma by some tens of centimetres over times of a few years (based on He diffusivity in basalt melts; Lux, 1987). Indeed, the diffusion of crustal He into melt would be even less efficient when taking into account that the concentration of magmatic He is higher than zero and the recognized degassing processes cause an He flux from magma to country rocks. Thus, we believe that the addition of crustal He could hardly cause the observed decrease of $^3\text{He}/^4\text{He}$ ratios of the whole magmatic body in a so short period. For similar reasons related to the He diffusion, it is poorly probable that contamination of atmospheric He directly in the magma reservoir was important over a period of few years. Thus, the recognized $^3\text{He}/^4\text{He}$ decrease due to air contribution (see He isotope correction in Sec. 4.2) was more probably linked to post-eruptive processes (air entrapment in microcracks; see Sec. 4.1) rather than magma contamination. It seems to be also unlikely that the crustal contamination, as well as the atmospheric one, involved both 2001 LV and UV magmatic reservoirs by a similar extent, so that inducing a comparable

decrease of helium isotopic ratios between 2001 and 2005. Finally, other geochemical indicators (e.g. Sr and B isotopes) suggest that the contributions of crustal fluids at shallow levels in the Etnean system are negligible or only occasional (Tonarini et al., 2001; Armienti et al., 2004).

Based on the above discussion, a different process must be hypothesized to explain the $^3\text{He}/^4\text{He}$ decrease from 2001 to 2004-2005. 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. Therefore, we suggest that this process could also induce a preferential ^3He loss in the residual magma. According to the process described by Caracausi et al. (2003a), the exsolving bubbles in Etnean magmas could in fact grow far from equilibrium, and thus become kinetically enriched in ^3He . Paonita and Martelli (2007) modelled the non-equilibrium degassing of noble gases, and they concluded that when the diffusivity of noble gas is similar or up to some ten-folds higher than that of the bubble-dominating species, the noble gas exsolves far from equilibrium and it suffers kinetic isotopic fractionation. The growth of CO_2 -dominated bubbles in MORB melts does not cause He kinetic fractionation as He diffusivity is more than two orders of magnitude lower than CO_2 (Paonita and Martelli, 2007). Nevertheless, He isotopes fractionate kinetically by growth of H_2O -dominated bubbles, because He and H_2O diffusivities in basalt melts differ by about one order of magnitude ($10^{-8.3}$ vs. $10^{-9.5}$ m^2/s , respectively; Lux, 1987 and Zhang and Stolper, 1991). Based on melt inclusion data from 2001 and 2002-2003 Etnean products (Metrich et al., 2004; Spilliaert et al., 2006), the $\text{H}_2\text{O}/\text{CO}_2$ ratios of the magmatic phase range from ~ 1 at depth to much higher values at shallower conditions. Although the combined effect of $\text{H}_2\text{O}-\text{CO}_2$ vapour on He non-equilibrium degassing has not been investigated and we cannot quantitatively evaluate it,

we reasonably consider that the kinetic fractionation can emerge especially when the H₂O contents become higher than CO₂. Accordingly, the progressive outgassing of ³He-enriched bubbles can explain the decrease of the ³He/⁴He ratios measured in the FI of 2002-2003 and 2004-2005 phenocrysts with respect to the ones erupted in 2001. As shown by rock petrology and He abundances, the degassing process involved the two distinct magma series, so as to coherently decrease the He isotope ratios of both of them.

4.2.2 Olivine-pyroxene disequilibria

The decoupling between isotopic values of olivine and pyroxene-hosted FI has been already reported by previous investigations carried out in some historical lavas of Etna volcano (Marty et al., 1994), as well as in other FI from basalts (Hilton et al., 1995; Patterson et al., 1997; Shaw et al., 2006), and it is still matter of debate. On the basis of U and Th content in Etnean lavas, Marty et al. (1994) excluded pre-eruptive addition of radiogenic helium, because they estimated 20-40 kyrs to lower the olivine values down to pyroxene ones and they compared it to the much smaller refilling time of the Etnean magma reservoir (<10 kyr; Condomines et al., 1982 and 1987). A common idea is that pyroxene crystallization postdates olivine and traps helium at a later date within a parent magma having a decreasing ³He/⁴He ratio or, due to the lower effective closure temperature, pyroxene continues to exchange helium with the magma after the olivine had become closed (Marty et al., 1994; Hilton et al., 1995; Shaw et al., 2006). This hypothesis assumes a progressive lowering of the ³He/⁴He magmatic ratio, which can be ultimately caused by either magma aging (⁴He production by U and Th decay in melt) or crustal contamination of the residual magma through addition of radiogenic ⁴He during its storage in the magmatic reservoirs. Coupled to both of these processes, magma degassing must also be hypothesized when He amounts in pyroxenes is lower than in

olivines (Shaw et al., 2006). For the case of Mt Etna, Marty et al. (1994) preferred the crustal contamination hypothesis to the magma ageing, because the time scale of decay is too long with respect to He diffusion in crystals, thus both olivines and pyroxenes would have exhibited similar values. Based on our data, we already stated such a process to be unlikely in lowering $^3\text{He}/^4\text{He}$ ratios of Etnean magmas. Even if we assume ^4He contribution from crustal fluids to magma, it cannot explain the mineral disequilibria. In fact, both olivines and pyroxenes are early phases crystallizing from Etnean magmas (Clocchiatti et al., 2004; Corsaro et al., 2007; Armienti et al., 2007), thus they do not necessarily sample the magma at well distinct times and any changes of magmatic He isotope ratios would be recorded in both the minerals.

Harrison et al. (2004) proposed a model of diffusive kinetic fractionation of He from crystals, to explain the $^3\text{He}/^4\text{He}$ decrease of pyroxenes with respect to olivines from Siberian lavas. The $^3\text{He}/^4\text{He}$ kinetic fractionation can be described by a Rayleigh-like equation (Hoefs, 1987):

$$^3\text{He}/^4\text{He} = (^3\text{He}/^4\text{He})^\circ \times f^{(\alpha-1)} \quad (1)$$

where $^4\text{He}^\circ$ and $(^3\text{He}/^4\text{He})^\circ$ are the initial abundance and isotopic ratio of He respectively, f is the He residual fraction and α is a kinetic fractionation between ^3He and ^4He masses.

In a $\text{Log}(^3\text{He}/^4\text{He})$ vs. $\text{Log}(\text{He})$ diagram (Fig. 6), plotting Eq.1 gives a straight line having $\alpha-1$ as a slope. By assuming the abundance ratio of a pair of cogenetic pyroxene and olivine as a proxy of the residual fraction of He and by fitting Eq.1 to the selected pair in the Log-Log plot, we have estimated the kinetic fractionation factors for our olivine-pyroxene pairs. The estimated values range from 1.02 to 1.04, with a mean of 1.03 for the whole dataset (Fig. 6). The sole exception is the 2001 UV pair ($\alpha \sim 1.09$) that however displays the smallest difference in He abundance between olivines and pyroxenes and, as a consequence, the least confident estimation. The estimated range of α values, which

matches the average fractionation factor that can be expected for He diffusion from magmatic pyroxenes (~ 1.04 ; Trull and Kurz, 1993), suggests that the process of diffusion-driven kinetic fractionation from pyroxene can account for the isotope differences between the cogenetic olivine-pyroxene pairs.

Moreover, such a process would be quick enough to occur within a few years (Harrison et al., 2004). Despite of the changes of helium isotopic signature in magmas, we thus 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 and Lupton, 1976; Mamyrin and Tolstikhin, 1984; Ozima and Podosek, 1983; Martelli et al., 2004). Further evidences about the main retention of He in olivines will be also discussed in the following. The loss of entrapped gases from pyroxenes also makes the latter more susceptible of contamination by any addition of non-magmatic components.

4.3 Constraints on the magma source

When comparing 2001 LV versus 2001 UV olivines (Fig. 5), we note that the differences between the two pairs of $^3\text{He}/^4\text{He}$ values are slightly larger than analytical uncertainties. In detail, 2001 LV products display values lower than 2001 UV (6.85 vs. 7.0 Ra, respectively). As we stated that helium isotope signature can suffer slight changes by volatile degassing during magma dynamics (see Sec. 4.2.1), we cannot consider these minor differences as a pristine feature of the two different magmas.

Instead, what can be reasonably stated is that our olivine data fall in the range defined for historical Etnean lavas since 500 kyr b.p. (Marty et al., 1994). Therefore, our data confirm the narrow variability of the helium isotope signature of Etnean magmas over

geological time scale. This condition appears still more remarkable when considering that the 2001 and 2002-03 eruptions have confirmed the trends of increase of both $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and incompatible and fluid-mobile trace elements (Clocchiatti et al., 2004), already observed during the last ten thousand years of Mount Etna activity (Marty et al., 1994). Founded on these geochemical trends, several researchers have proposed that mantle source feeding Etnean magmatism is undergoing contamination by crustal fluids coming from dehydration of the subducting Ionian slab (Tonarini et al., 2001; Schiano et al., 2001; Clocchiatti et al., 2004). If we assume that U and Th of the recent Etnean lavas are mostly linked to slab-derived fluids, the amount of radiogenic He produced in the last ten thousand years would be in the order of 10^{-13} mol/g of melt. Taking into account the amount of He in undegassed Etnean magmas of about 10^{-11} mol/g or more (Marty et al., 1994), the effect of mantle metasomatism by slab-related fluids on the helium isotope signature can be calculated to be negligible. Accordingly, we cannot expect any significant variation of magmatic $^3\text{He}/^4\text{He}$ ratios to be related to other indicators of fluids from the slab.

4.4 He isotope relationship between FI and peripheral gases

We collected samples of gas venting at the periphery of Mount Etna during the period covering the investigated eruptive phases by weekly or two-weekly sampling frequency, and we analysed their helium isotopic composition (Caracausi et al., 2003a,b; Rizzo et al., 2006). Therefore, we gained the unique condition to compare the variations of FI isotope composition with that of volcanic gases within a narrow time range.

The long-term monitoring of the gases showed remarkable variations of both $^3\text{He}/^4\text{He}$ ratios (Fig. 7) and chemical composition, that have been related to magma dynamics of the volcano at depth. Particularly, before 2001 and 2002-2003 eruptions, those variations

were related to volatile-rich magma recharge from depth into the Etnean shallow plumbing system (Caracausi et al., 2003a). All the monitored sites displayed the highest Ra values (up to 7.6 Ra) during 2001, with the values measured during 2002 being slightly lower (the maximum recorded value was 7.2 Ra) and comparable to the 2004–2005 eruption period (6.9 Ra). This behaviour is similar to that of $^3\text{He}/^4\text{He}$ ratios measured in the investigated olivine FIs. In fact, the highest $^3\text{He}/^4\text{He}$ ratio of 7.02 Ra was measured in the olivines from 2001 products, with those in the olivines in 2002 and 2004–2005 lavas being 6.78 and 6.57 Ra, respectively (Fig. 5). These evidences provide a straightforward confirmation in favour of the fact that helium from the peripheral gas emissions is directly supplied by the degassing of the Etnean magmas. At the same time, they suggest that olivines entrap a fluid phase which carries the He isotope signature of the magma.

It is worth of note that the ratios obtained from olivine-hosted FI are somewhat in the middle with respect to those of the monitored gases, some emissions providing higher values while others being lower. Recalling that the olivines crystallize throughout the whole rising path of Etnean magmas (Spilliaert et al., 2006), it probably depends on the fact that we measure helium isotopes of FI trapped in a large population of olivine crystals, under different extents of magma degassing. Therefore, the measured isotope ratios in FIs represent average values of the magmatic system, where both maximal and minimal values are smoothed out. In contrast, the peripheral sites sample fluids from a well-defined range of depth of the plumbing system (see Caracausi et al., 2003b).

Comparison of the observed decreases in the values between the peripheral gases and the olivine FIs from 2001 to 2004–2005 allows inferences to be made about the crystallization time of the minerals. If we reasonably assume that: i) the $^3\text{He}/^4\text{He}$ ratio of the peripheral gases stands for that of the magmatic gas phase exsolved in close

proximity to the time of sampling; and ii) olivines entrap the exsolved phase during their crystallization, then the co-variation between FIs and gases over time suggests that the olivines crystallized and entrapped fluids close to the eruption time. Thus, olivines from 2001 lavas crystallized earlier with respect to those that erupted during 2002–2003 and 2004–2005, because all of them probably crystallized just before the respective eruptions. This supplies further constraints in favour of the fact that pyroxenes did not decouple from olivines due to the growing contribution of crustal fluids through 2001 to 2005. Indeed, 2004-2005 olivines show similar or higher isotope ratios than 2001 and 2002-2003 pyroxenes, although the latter ones formed early. The co-variation also excludes significant He loss and related $^3\text{He}/^4\text{He}$ fractionation by diffusion from olivines. In fact, the 2001 olivines would have had more time for diffusion than those of 2004-2005 which crystallized later, thus the former ones would have exhibited lower He abundances and isotope ratios.

The lack of significant isotope variations in peripheral gases during the 2004–2005 eruption was previously attributed to the effusion of strongly degassed magma that already resided in the shallow plumbing system (Rizzo et al., 2006). At that time we stated that a new input of undegassed magma appeared to be lacking during the 2004–2005 event, in accordance with this magma evolving from the 2001 and 2002-2003 melts. This mechanism is in agreement with both FIs and petrological data. These observations provide a straightforward confirmation that helium from the peripheral gas emissions is directly supplied by the degassing of Etnean magmas. The helium-isotope variations observed in these emissions can be linked to any in-progress changes of the magma dynamics in the plumbing system, and hence they represent a powerful tool for the real-time monitoring of Etnean activity.

5. Conclusions

During 2001–2005, Mount Etna was characterized by three distinct eruptions that simultaneously emitted two petrologically different magma types from several vents. FIs trapped in olivines and pyroxenes have been investigated in the erupted lavas, focusing on the abundance of rare gases and the ratios of their isotopes. The main results are summarized as follows:

- The He abundances and isotope ratios were systematically lower in pyroxenes than in cogenetic olivines. This effect has been attributed to the closure temperature being lower for pyroxenes than for olivines, that caused higher loss of magmatic volatiles and fractionation in the formers, coupled to more evident effects of air contamination.
- He abundances and isotope ratios, measured in the olivine FIs of each erupted magma, showed a decreasing trend of the values from 2001 to 2004-2005 products. This trend has been attributed to non-equilibrium volatile exsolution during magma degassing and depressurization in the shallow plumbing system.
- The $^3\text{He}/^4\text{He}$ ratios of present Etnean lavas fall in the range assessed for the historical ones. This is coherent with the hypothesis of a progressive mantle metasomatism by He-poor fluids from the Ionian slab.
- 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. 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.

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Table 1 – Noble-gas abundance and isotope ratios in the investigated minerals (Ol = olivines, Px = pyroxenes). Helium-isotope ratios are expressed as R/Ra, where R is the $^3\text{He}/^4\text{He}$ ratio of the sample and Ra is the same ratio in air (equal to 1.39×10^{-6} ; Ozima and Podosek, 1983). Rc/Ra values are He-isotope ratios corrected for atmospheric contamination on the basis of the $^4\text{He}/^{20}\text{Ne}$ ratio measured in the sample (Sano and Wakita, 1985). X is the $(^4\text{He}/^{20}\text{Ne})_s / (^4\text{He}/^{20}\text{Ne})_a$ ratio, where subscripts “s” and “a” refer to sample and atmosphere. Olivines 2001 LV* were separated from pyroclastites (tephra) ejected from 2100 mt vent.

Figure captions

Figure 1 – He versus Ar abundances in FIs of investigated olivines (Ol) and pyroxenes (Px). White and gray colours indicate the two parental magma series (see text for details). Squares and triangles have dimensions progressively smaller in size from 2001 products to 2004–2005 products. Each point represents an individual mineral sample. The line representing the He/Ar ratio in the atmosphere is also shown.

Figure 2 – Uncorrected R/Ra values versus $^4\text{He}/^{20}\text{Ne}$ ratios. The shadowed area defines a mixing trend by a magmatic end-member having $^3\text{He}/^4\text{He}$ of 6.6 to 7.0 Ra, mixed with air (R/Ra=1, $^4\text{He}/^{20}\text{Ne}=0.318$). The $^4\text{He}/^{20}\text{Ne}$ ratio of the magmatic member has been fixed to 1000, based on measurements made on most of the Etnean free gases (Caracausi et al., 2003a; Rizzo et al., 2006). However, the model curves are relatively insensitive to changes in the magmatic $^4\text{He}/^{20}\text{Ne}$ value.

Figure 3 – Microphotograph (left) and back-scattered electron image (right) showing a grain of olivine crossing out by microcracks. Some gas bubbles may also be noted in the optical microscope picture.

Figure 4 – Comparison of He abundance between investigated olivines and pyroxenes. White and gray colours indicate the two parental magma series as in Figure 1. Circles progressively decrease in size from 2001 products to 2004–2005 products. Each point represents an individual mineral sample.

Figure 5 – $^3\text{He}/^4\text{He}$ ratios (expressed as R_c/R_a) of the investigated olivines and pyroxenes. The legend is as in figure 4

Figure 6 – Bi-logarithm plot of He isotope ratios vs. abundances. The thick line is the fit of Eq.1 to the olivine-pyroxene pair of 2002 N ($\alpha \sim 1.023$, see text). The thin line is a best fit to the whole database ($\alpha \sim 1.03$), which assumes the same initial values of He isotope ratio and abundance for all the olivine-pyroxene pairs.

Figure 7 – Two-point moving averages (about 1 point per month) of R_c/R_a in two selected Etnean gas discharges [P39 and Fondachello sites; see Rizzo et al. (2006) for their locations and gas geochemistry]. R_c/R_a values of olivine FIs from 2001 LV, 2002 S, and 2004–2005 (red horizontal lines) and from 2001 UV and 2002 N (gray lines) are shown. Vertical dashed lines indicate the onset and the offset of investigated eruptions.