# Light-noble-gas isotopic ratios in gases from Mt. Etna (Southern Italy): Implications for mantle contamination and volcanic activity (*)(**)

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**Summary.** — Helium isotopic ratios in gases from Mt. Etna are in the range of 6–7 Ra (Ra = atmospheric $^{3}$He/$^{4}$He ratio $1.4 \times 10^{-6}$), below the MORB's typical range, and fall in the same range of those measured in xenoliths from the Northern part of Europe, where a crustal contamination of the sub-continental mantle has been recognized. Taking into account the light-noble-gas isotopic signature of gas samples coming from the Etnean area, it seems that in this area the crustal contamination played a minor role. Instead, processes that enriched the original MORB-type mantle in incompatible elements, have to be considered. The $^{3}$He/$^{4}$He ratios are, thus, lowered because of $^{4}$He produced by radioactive decay of U and Th. On the other hand, helium isotopic ratios have shown wide temporal variations sometimes reaching values as high as 7.6 Ra, out of the typical Etnean range. As these unusually high ratios have been measured during phases of unrest of the volcanic activity at Mt. Etna, this apparent discrepancy in the helium isotopic ratios is considered, as the effect of fractionation processes occurred during magma uprising.

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## 1. – Methods

Gas samples have been collected from sites located in the Eastern and Southern part of the volcano (fig. 1). The samples consist of bubbling gases, taken from mud volcanoes (Paterno' Stadio site) and from a river (Fondachello site), and soil gas

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Fig. 1. – Location of the sampling sites around Etna.

(Paternò P39 site). Samples for helium isotopic measurements have been taken over a time span of more than three years, while samples for noble-gas isotopes determinations have been taken twice (July 1994 and February 1996) during periods of quite degassing activity of the volcano.

The analyses have been performed by mass spectrometry on VG5400 mass-spectrometers, following procedures described elsewhere (Sano and Wakita, 1985; Nakai *et al.*, 1997).

Analytical results of the light-noble-gas isotopic ratios are shown in table I.

## 2. – Discussion

Noble-gas systematics of mantle xenoliths from Massif Central (France) and Eifel (Germany) highlight a crustal contamination of the North European sub-continental mantle (Dunai and Baur, 1995). The helium isotopic ratios measured in xenoliths samples from Eifel and Massif Central are in the range of 6.1–6.65 Ra, similar to the values recorded in gas samples from Mt. Etna. Considering the low $^3He/^4He$ ratios measured in other Italian volcanic areas (in the range 2.3–5.7; Sano *et al.*, 1989), it is possible that the sub-continental mantle of Southern Europe (*i.e.* the Mediterranean Sea) also suffered a contamination probably because of a subduction of crustal materials as Dunai and Baur (1995) observed for the Northern part of the continent.

On the other hand, the noble-gases isotopic signature ($^{20}Ne/^{21}Ne$, $^{40}Ar/^{36}Ar$) in samples from the Etna area is in accordance with a contaminated mantle source. Such a signature also revealed that the contamination processes are different from the
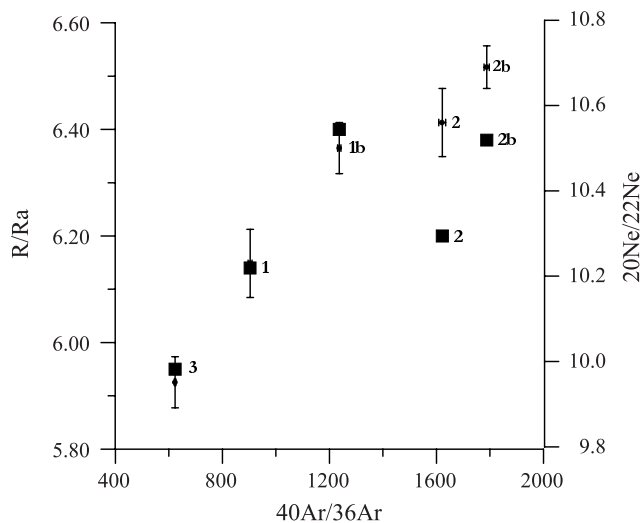
Fig. 2. – $^3$He/$^4$He and $^{20}$Ne/$^{22}$Ne isotopic ratios plotted *vs.* the $^{40}$Ar/$^{36}$Ar ratio. The helium isotopic ratios (black squares) are plotted without the error bars. Numbers on the graph show the sampling sites as follows: 1 and 1b: Vallone Salato (Paterno); 2 and 2b Mofeta dei Palici; 3 Fondachello (Mascali). Numbers without notation are referred to the July 1994 sampling; notation "b" shows February 1996 sample collection. See fig. 1 for sampling site locations.

subduction of crustal materials (Nakai *et al.*, 1997). Figure 2 shows the relationships of helium and argon isotopic ratios: while the $^{40}$Ar/$^{36}$Ar isotopic ratio (from 623 to about 1800) is within the MORB's values range, the $^3$He/$^4$He ratio varies in a narrow range (5.95–6.4 Ra), below the typical MORB's ratio (8 Ra). The good positive correlation indicates a common origin for both of the gases. The $^{20}$Ne/$^{22}$Ne isotopic ratios, that fall in the MORB's range, show the same good positive relationship if plotted *vs.* the $^{40}$Ar/$^{36}$Ar isotopic ratio, thus implying that Ar, He and Ne may have the same common "mantle" origin. As a consequence we consider that the radiogenic $^{40}$Ar is of a mantle origin and has not derived from an addiction of crustal components.

The Ne three isotopes are plotted on a plane $^{20}$Ne/$^{22}$Ne *vs.* $^{21}$Ne/$^{22}$Ne in fig. 3. The samples fall along a mixing line, in which end-members are the mantle and the "solar component" (Honda *et al.*, 1993). The $^{21}$Ne/$^{22}$Ne ratio increases because of nucleogenic production of $^{21}$Ne, which spontaneously happens inside the mantle. If we suppose that the original mantle source of the Etna area was a typical MORB, the $^{21}$Ne/$^{22}$Ne ratios should increase with the time following a pattern which depends on the U and Th concentrations and on the initial $^{21}$Ne/$^{22}$Ne ratio. If some event modified (increased) the U and Th concentrations (Condomines *et al.*, 1982), the $^{21}$Ne production rate changed and it would be possible to estimate the time of the event by using two functions of $^{21}$Ne production with the time: the former that considers MORB's type U and Th contents, the latter based on the calculated concentrations of an enriched mantle (about 30 and 120 ppb, respectively; Nakai *et al.*, 1997). Such estimation provided a mantle time enrichment (the two crossing points of the $^{21}$Ne production functions; fig. 4) of 200–400 My, which agrees with the estimations (200–500 My) carried on by Carter *et al.* (1978). Because of the enrichment in radioactive-elements
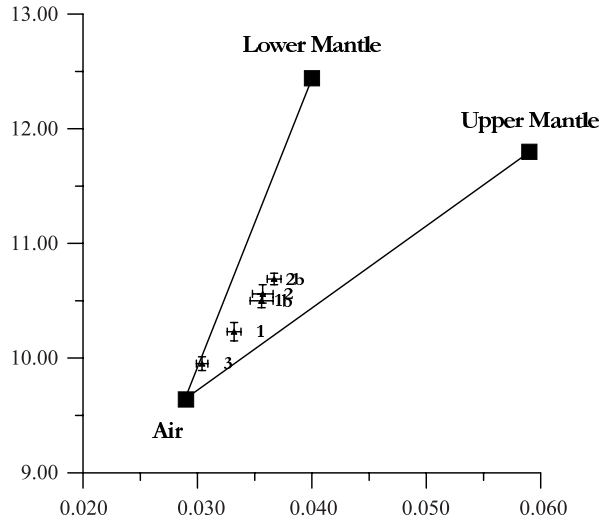
Fig. 3. – Three neon isotope plot for samples around Etna. The collected samples fall on a plane between the Ne isotopic mixing lines through air and lower mantle (MORB) and upper mantle, respectively. Numbers have the same meaning as those in fig. 2.
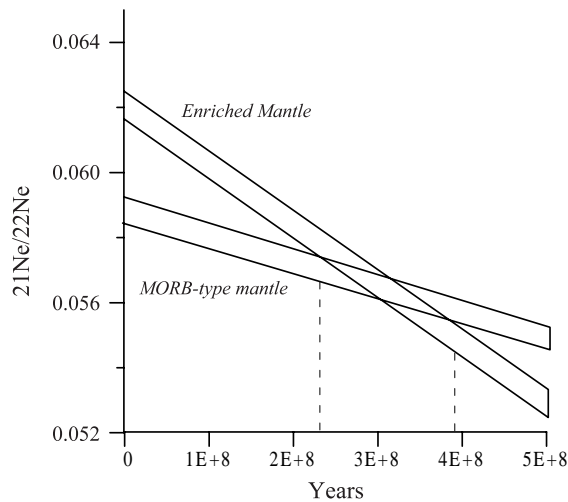


Fig. 4. – Neon isotopic evolution curves calculated for a MORB-type mantle and an enriched mantle, respectively. This calculation has been done assuming that a MORB source mantle existed beneath Etna before the metasomatism and $^{21}$Ne increased because of nucleogenic production $(U + Th \rightarrow \alpha \, ; \, ^{18}O(\alpha, n) \rightarrow \, ^{21}Ne)$, and no other reaction took place.

$\alpha$-decaying, the $^4$He production over the same time span should be taken into account, as it lowered the R/Ra values from the typical MORB, down to the measured ratios. Considering $1.5 \times 10^{-9}$ mol/g as representative of the He content in MORBs (Marty *et al.*, 1994), a $^3$He content of about $3.7 \times 10^{-10}$ cc/g can be estimated with a $^3$He/$^4$He ratio

of 8 Ra. To decrease this ratio down to 6.5–7 Ra, the $^4$He content should increase up to about $4.5$–$5 \times 10^{-5}$ cc/g, with an accumulation of about $7$–$10 \times 10^{-6}$ cc$_{4He}$/g.

The $^4$He accumulation rate from $^{238}$U and $^{232}$Th over the time "$t$" ending at present, can be estimated for an enriched mantle where the $^{238}$U and the $^{232}$Th content are about 30 and 120 ppb, respectively (Nakai $et~al.$, 1997). Considering He accumulation rates of $7.749 \times 10^2$ ($^{238}$U) and $5.796 \times 10^2$ ($^{232}$Th) (Ozima and Podosek, 1983) the total amount of $^4$He accumulated over 200–400 My would be in the range of $1.4$–$2.6 \times 10^{-6}$ cc$_{4\,He}$/g, thus in agreement with the observed ratios. All of these evidences lead to the consideration that a crustal contamination can probably be neglected for the Etna area, and, moreover, the noble-gas isotopic features fit well with an origin from a portion of the upper mantle enriched by metasomatic events.

2$^.$1. *Temporal variation of helium isotopic ratios.* – Figure 5 shows the variations in the helium isotopic ratio observed in three different sites. The samples collected at the P39 (Paternò) sampling site displayed the highest values, with $^3$He/$^4$He ratios up to 7.6 Ra that exceeded the normal range. It seems hard to reconcile the observed data with the above considerations about the Etna mantle source. The possibility that new different magma is supplying a volatile phase with a changed signature can also be neglected. In fact, as noted by Marty $et~al.$ (1994), the $\delta^{18}$O values and olivine $^3$He/$^4$He ratios are constant throughout the volcano's history, supporting the occurrence of a single mantle source feeding Etnean magmas. Because variations in the volcanic activity of Mt. Etna (from a quiet degassing state to Strombolian explosions, lava fountains and small lava flows) have been observed, during the three years sampling period, the observed discrepancy is considered to be only apparent. Following the degassing model proposed Nuccio and Valenza (1992), the observed results are considered as the effect of kinetic fractionation occurred during magma uprising, when depressuring allows a volatile phase to be separated. In this case the $^3$He diffuses
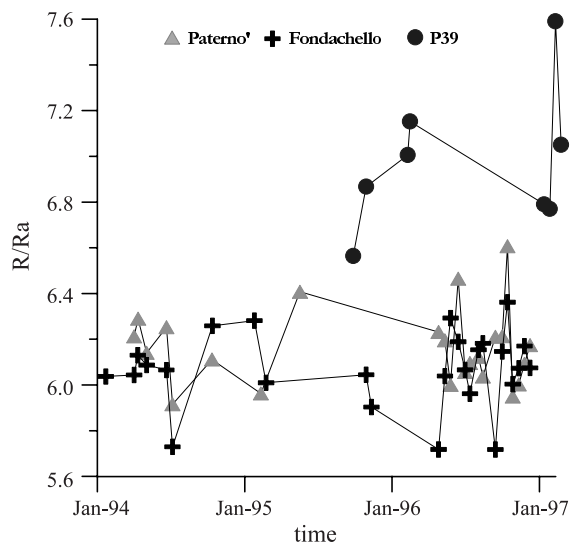


Fig. 5. – Helium isotopic ratio variations at three sampling sites around Mt. Etna from 1994 to 1997. The site "P39" (Paterno' village) shows the highest recorded values.

faster than the mass 4 isotope and it is enriched in the separated volatile phase. This effect disappears when the volcanic system degasses in quiet conditions simply because of diffusion of the dissolved volatile phase.

## 3. – Conclusions

The light noble gas systematics of gas samples from Mt Etna allowed to constrain important event occurred in the past (mantle contamination) and today's occurring phenomena (gas fractionation). The isotopic features of the noble gas show an origin from a contaminated source mantle, and agree with an enrichment of incompatible elements as a consequence of mantle metasomatism probably occurred 200–500 My ago. The $^4$He production from radioactive elements over the same time interval lowered the $^3$He/$^4$He ratio, in agreement with the measured helium isotopic ratios below the MORB's values. The unusually high values recorded during phases of unrest of the Etna volcanic activity are not in contrast with the presence of an enriched mantle, as they reflect non-equilibrium conditions of the magmatic system and are a sign of fractionation phenomena occurrence.

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