Bull Volcanol (2011) 73:395–408
DOI 10.1007/s00445-011-0448-1

RESEARCH ARTICLE

N_2, Ar, and He as a tool for discriminating sources of volcanic fluids with application to Vulcano, Italy

Yuri A. Taran

Received: 17 June 2009 / Accepted: 11 December 2010 / Published online: 17 May 2011

Abstract A detailed analysis of published data on the N_2, Ar, and He content and Ar and He isotopic composition of fumarolic fluids from Vulcano crater (south Italy) supports a model with two endmembers comprising magmatic and hydrothermal fluids with correspondingly low and high H_2O content. The magmatic component with the highest $^3He/^4He$ and highest absolute concentrations of N_2, Ar, and He also has the lowest N_2/Ar and N_2/He ratios (~300 and ~500, respectively). In contrast, the hydrothermal endmember, with the lower $^3He/^4He$ and lower absolute N_2, Ar, and He abundances, has high N_2/Ar (~1,000) and high N_2/He (>3,000) ratios. The hydrothermal component is also characterized by the highest $^{40}Ar/^{36}Ar$ ratios (>1,000) and is proposed to be the main carrier of metamorphic gases from the arc crust.

Keywords Vulcano · Volcanic gases · He and Ar isotopes · Sources of volatiles

Editorial responsibility: S. Inguaggiato

This paper constitutes part of a special issue. The complete citation information is as follows:

Taran Y (2011) N_2, Ar and He as a tool for discriminating sources of volcanic fluids with application to Vulcano, Italy. In: Inguaggiato S, Shinohara H, and Fischer T (eds) Geochemistry of volcanic fluids: a special issue in honor of Yuri A. Taran. Bull Volcanol 73(4):395–408

Y. A. Taran (✉)
Institute of Geophysics,
Universidad Nacional Autónoma de México,
Coyoacán, México, DF 04510, Mexico
e-mail: taran@geofisica.unam.mx

Introduction

Nearly two decades ago, Werner Giggenbach (1992a) introduced a N_2–Ar–He ternary diagram for studying geothermal and volcanic gases. This diagram is still quite popular because of its simplicity and its ability to distinguish at least three main sources of fluids: atmosphere, sediments, and mantle. The diagram (Fig. 1) does not allow for almost any terrestrial natural gas to be plotted below a mixing line between air-saturated water (ASW) and the He corner, which means that gases with $N_2/Ar<38$ are very rare (if they exist) in terrestrial fluids. Gases generated by organic-rich sediments ("thermogenic" gases, producing N_2 but not Ar), usually have $N_2/Ar>>100$ (e.g., Jenden et al. 1988), hence, plot close to the He–N_2 axis. Because of their relatively high He content with respect to N_2 and low N_2/Ar (Marty 1994; Marty and Zimmermann 1999), mantle fluids should plot close to the He corner. Taking into account that subduction-type magmatism commonly is induced by fluids released from the subducting oceanic slab carrying organic-rich oceanic sediments, one can suggest that the N_2–Ar–He relative contents of such a magmatic fluid should be similar to that of the sediments themselves. When applying this diagram to volcanic gases, Giggenbach (1992a) outlined three main areas on this plot: Air+ASW, "Andesitic" gases and "Basaltic" gases, keeping in mind that "Andesitic" gases are magmatic gases from subduction zones (subduction type or arc type), and "Basaltic" gases are those from rifts and hotspots (MORB–OIB type). This approach provides a convenient way for discriminating the main contributions to a fluid composition in terms of the relative amounts of N_2, Ar, and He.

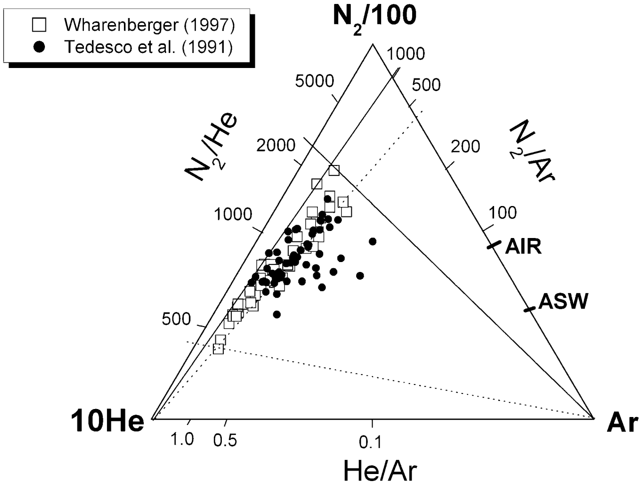

Fig. 1 N_2–Ar–He ternary plot (Giggenbach 1992a) with data points for Vulcano (Tedesco et al. 1991; Wahrenberger 1997). Intersections of the *dotted* and *solid* lines show two apparent endmember compositions

A single volcanic gas analysis always shows some mixing with air that occurs either during sampling and/or analysis, or naturally due to a permeable volcanic edifice near fumarolic vents. The volcanic water is always a mixture of magmatic and meteoric water and/or seawater, the latter two being a source of "atmogenic" N_2, Ar, He and other noble gases. Traces of air in a volcanic gas can drastically change N_2/Ar and N_2/He ratios. This is the main reason for fluctuations of N_2 and Ar concentrations and N_2/He and N_2/Ar ratios in a gas sample. Hence to determine and discriminate the non-atmospheric fraction of N_2 and Ar for a given volcano, it is necessary to have a statistically reasonable dataset.

Such datasets exist for only a few volcanoes. The largest sets containing N_2, Ar, and He have been obtained for the Italian volcanoes Vulcano, La Solfatara, and Vesuvius (Chiodini et al. 1993, 1995; Tedesco et al. 1991; Tedesco 1995; Tedesco and Scarsi 1999; Magro and Pennisi 1991; Wahrenberger 1997; Caliro et al. 2007). The points shown in Fig. 1 are the compositions of gases from Vulcano taken from Wahrenberger (1997) and Tedesco et al. (1991). Chiodini et al. (1995) suggested that the He-enriched gas from Vulcano is more magmatic, and thus, the trend on the ternary diagram (Fig. 1) is a mixing line between a He-rich magmatic endmember and a He-poor endmember which most authors term "hydrothermal".

Using this ternary diagram, however, it is impossible to distinguish the mantle and crustal (from the old metamorphic crust) gases which both have a high relative He content and a low N_2/He ratio (e.g. Hilton et al. 2002). A relative enrichment in He may indicate both crustal and mantle contributions. On the other hand, relatively low He contents and a high N_2/He are compatible with subduction-type magmatic fluids derived from subducted sediments (Giggenbach 1996; Hilton et al. 2002) or with fluids derived from organic-rich sediments of the continental crust (Jenden et al. 1988). Isotopic compositions of He and Ar are a powerful additional tool for resolving such kind of problems.

The aim of this contribution is to focus on the N_2–Ar–He systematics of volcanic gases from Vulcano Island using a more complicated approach than a simple ternary plot. The published data on N_2, Ar, and He are used here to determine their non-atmospheric fractions in volcanic gases. I also attempt to distinguish magmatic, hydrothermal, and crustal contributions to the N_2+Ar+He system using data for other components (HCl, S, CO_2) as well as $^3He/^4He$ and $^{40}Ar/^{36}Ar$ isotopic data.

Geochemical models for Vulcano fumaroles

One of the best geochemical datasets comes from fumaroles of La Fossa crater at Vulcano Island (Aeolian Archipelago, south Italy). This dataset is continuously increasing and is used by different groups for geochemical models. One of the first models was the Carapezza et al. (1981) "pressure cooking" model (pressurized geothermal reservoir with a two-phase brine–vapor fluid) based on the available data up to 1979. On the basis of theoretical constraints, Cioni and D'Amore (1984) postulated a "dry" model with fluid chemistry the result of mixing between a gas of magmatic origin and a vapor derived from lateral seepage and evaporation of a brine of marine origin. There also have been debates on the interpretation of the vapor isotopic composition (Panichi and Noto 1992; Capasso et al. 1997; Bolognesi and D'Amore 1993), in particular the nature of magmatic endmember and the importance of the seawater contribution to Vulcano fluids. Chiodini et al. (1993, 1995) suggested three endmembers with one magmatic (with water isotopic composition close to typical subduction-type water in agreement with the Panichi and Noto model) and two hydrothermal sources. These debates were partly the result of interpretative biases because the oxygen isotopic exchange between H_2O and CO_2 was not considered. According to Chiodini et al. (2000), oxygen isotope exchange between CO_2 and steam is fast enough in natural gas phases to allow rapid isotopic reequilibration within a wide temperature range (100–1,000°C). A way to annul or minimize the effects of this process is simply to consider the oxygen isotope balance of the whole H_2O+CO_2 gas system (Chiodini et al. 2000). After such correction of analytical data, the isotopic composition of the fumaroles of Vulcano clearly shows mixing between hydrothermal fluids whose water has a marine origin, minor contributions from meteoric waters, and a magmatic component with an isotopic composition of H_2O typical of subduction zones and with relatively high contents in CO_2, N_2 and He. The Chiodini et al. (2000) model suggests magmatic source with apparently constant geochemical characteristics in terms of Cl–H_2O–S–N_2–He–δD.

In contrast, Nuccio et al. (1999), Nuccio and Paonita (2001), Paonita et al. (2002), and Di Liberto et al. (2002) developed a model where a magmatic endmember, highly variable in its chemical and isotopic composition, mixes with a vapor from a hot (380–400°C), saline (24–30% NaCl) hydrothermal brine of marine origin. Leeman et al. (2005) proposed a three endmember model with magmatic, hydrothermal, and mixed magmatic–hydrothermal sources.

In any case, all authors are in agreement with two main sources for the Vulcano fumaroles: magmatic gases and hydrothermal brine. There is also a generally accepted compromise that magmatic fluid of Vulcano has a complex origin, consisting of significant portion of crustal gases and recycled volatiles from the subducted African slab (Tedesco and Scarsi 1999; Capasso et al. 1997, 2001; Leeman et al. 2005).

The main controversy appeared after 1992, when drastic changes in the chemical composition and in the ratios of the main components marked a new stage in the activity of Vulcano. Simple, quasi-linear, two endmember trends such as H_2O–HCl and H_2O–S_{tot} have broken down, and highly variable and lowered HCl and S_{tot} contents, independent from the H_2O concentration or δD values, have became a common behavior for all fumaroles of Vulcano to the present day (Wahrenberger 1997; Di Liberto et al. 2002).

Two stages of Vulcano fumarolic activity revealed from He and other components

Figure 2 shows a difference between "stage 1" (1987–1991) and "stage 2" (after 1992) on plots where H_2O, CO_2, HCl S_{tot}, and N_2 are plotted against He concentration. These plots, based on data from different sources, demonstrate that between 1987 and 1992, a two-endmember "dry" model was reliable, because all components, including acid (HCl, S_{tot}) and uncondensable (CO_2, N_2), showed a similar strong positive trend when compared with He concentrations. After 1992, HCl and S_{tot} lost their determinant behavior, but the correlation between CO_2 and N_2 did not change; the same or nearly the same quasi-linear trend continued for these components after 1992. In other words, two endmember mixing is valid for "non-condensable" species N_2 and CO_2 for the whole period of observations, but not for "acid" species such as HCl and SO_2 which after 1992 do not correlate with He. However, a good correlation between HCl and $S_{tot}=SO_2+H_2S$ is found during the whole period as shown in Fig. 3 (data from Chiodini et al. 1995; Tedesco et al. 1991, and Wahrenberger 1997). Strong linear correlations between H_2O, CO_2, N_2, He, and δD have already been shown for the datasets obtained before 1991 by Chiodini et al. (1993) and Tedesco (1995).

These effects may indicate that the "dry" case, which provided a simple two endmember mixing pattern for all species, has changed to a "wet" situation, when magmatic gas from a deep source passes through a liquid formed by mixing of the magmatic gas condensate with the hydrothermal brine. The poorly soluble CO_2, N_2, Ar, and He essentially retain their proportions passing through this brine, but vapor concentrations of acid HCl and $S_{tot}=SO_2+H_2S$ begin to depend on the vapor/liquid ratio and on the relative solubility of HCl and SO_2 in the brine. Solubilities of HCl and SO_2, in turn, depend on pH, salinity, and chemical composition of the brine. The SO_2 concentrations and SO_2/H_2S also depend on the redox conditions (Di Liberto et al. 2002). Therefore, the two endmember model, as well as an apparently constant He/Ar, He/N_2, and He/CO_2 ratios of the magmatic component, still makes sense, with the acid species may varying not because of changes in the magmatic fluid composition, but due to "bubble-liquid" fractionation of acidic gases or gas–brine interaction.

In the two endmember mixing model, the high CO_2 (high N_2, high He), low H_2O endmember was attributed to the magmatic component because of its water isotopic composition, which is typical for other subduction zones (−25‰<δD<−15‰, Sakai and Matsubaya 1977; Taran et al. 1989; Giggenbach 1992b), although Mediterranean seawater is about 10‰ isotopically heavier that oceanic water (Chiodini et al. 1993, 1995, 2000; Bolognesi and D'Amore 1993; Capasso et al. 1992). Further support for this idea are data on the isotopic composition of the CO_2–carbon and $^3He/^4He$ reported by Tedesco and Scarsi (1999) for the Vulcano gases sampled during 1986–1993. Together with the interpretation of the $\delta^{13}C$–CO_2 correlation by Paonita et al. (2002) based on data by Tedesco (1995) and Capasso et al. (1997, 2001) that the high CO_2 endmember has isotopically heavier CO_2 (+0.5‰ V–PDB), the data of Tedesco and Scarsi (1999) clearly show that this CO_2-rich endmember also has high $^3He/^4He$ with maximum values close to $6.2R_a$ (where R_a is the atmospheric value of 1.4×10^{-6}).

N_2–Ar–He in gases of Vulcano

Relative and absolute concentrations of N_2, Ar, and He in endmembers

To investigate the N_2–He–Ar system, we refer here to published data. The data with simultaneous analyses of N_2, Ar, and He have been reported by Magro and Pennisi (1991), Tedesco et al. (1991, 1995) (F5 fumarole, $O_2+Ar\approx Ar$) and

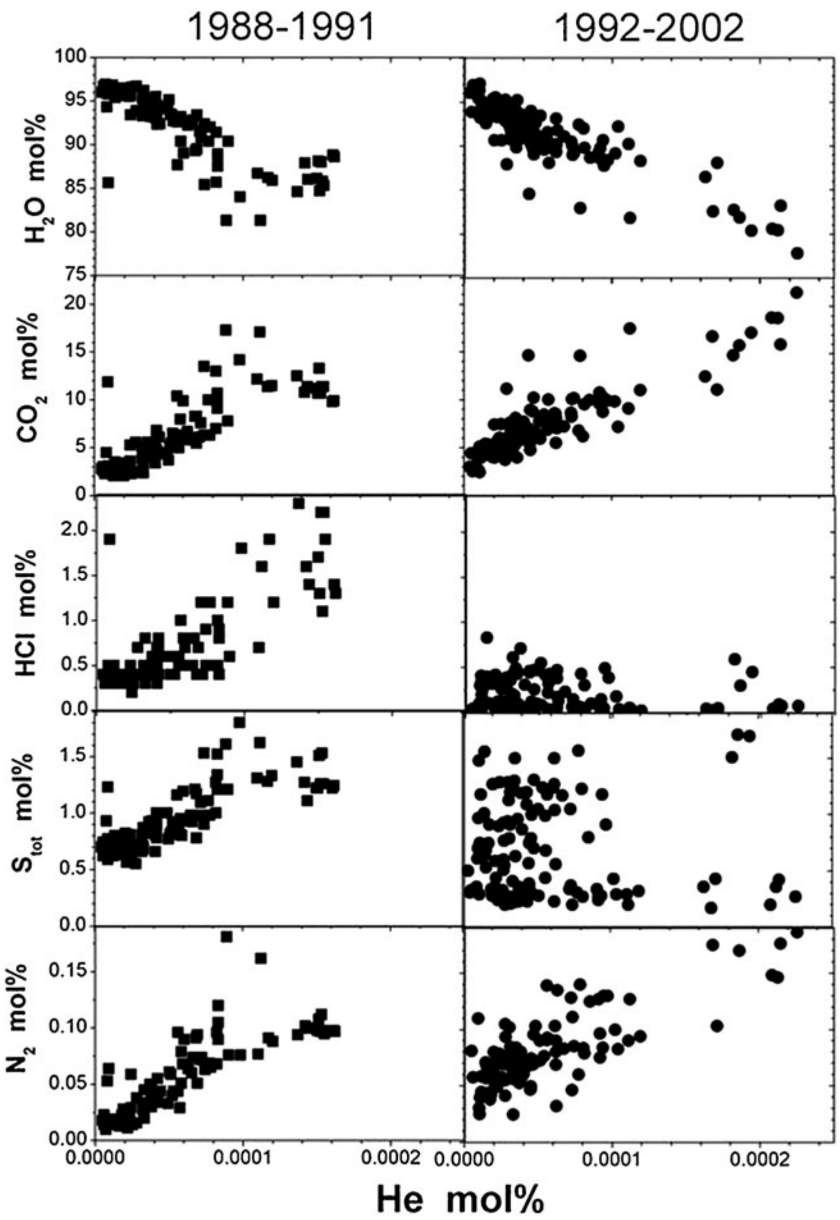

Fig. 2 Relationships between He and macro-components of the Vulcano gases during 1988–1991 (*left*) and 1992–2002 (*right*). Data from Tedesco et al. (1991); Chiodini et al. (1995); Wahrenberger (1997); Paonita et al. (2002)

Wahrenberger (1997). A large data set by Chiodini et al. (1995) does not report Ar concentrations. Furthermore, we refer also to $^3He/^4He$ and $^{40}Ar/^{36}Ar$ data of Vulcano fumaroles published by Tedesco et al. (1995); Magro and Pennisi (1991); Tedesco (1995); Italiano and Nuccio (1997); Tedesco and Nagao (1999), and Tedesco and Scarsi (1999).

A mixing trend for gases of Vulcano does not define the origin and the absolute concentrations of N_2, Ar, and He in the endmembers (Fig. 1). The two extreme positions of the data points are characterized by different N_2/Ar and N_2/He ratios. From Fig. 1, these ratios could be estimated as following: (1) the N_2-enriched endmember apparently should have $N_2/Ar \sim 1{,}000$ and $N_2/He \sim 3{,}000$; (2) the N_2-depleted endmember may be characterized by $N_2/Ar \sim 400$ and $N_2/He \sim 500$. It is generally accepted for Vulcano fumarolic gas that the magmatic endmember is characterized by a high CO_2 and a low H_2O content. This endmember also has the highest N_2 and He absolute concentrations (Fig. 2).

N_2 and N_2/He are plotted in Fig. 4 vs He. Data of Chiodini et al. (1995) before 1992, Wahrenberger (1997) for 1994–1996 and Paonita et al. (2002) for 1996–1998 are used. The high He, high N_2 component has N_2/He ratio <1,000. Both linear and hyperbolic trends in Fig. 4 correspond to a situation when variable batches of a high He fluid with $N_2/He \approx 500$ are mixed with a low He fluid with relatively low N_2 but high N_2/He ratio (>2,000). However, the lowest He component is characterized by N_2 close to 0.02 mol% (200 ppm), much higher than the ASW value of 0.0015% (15 ppm). Such a high concentration of

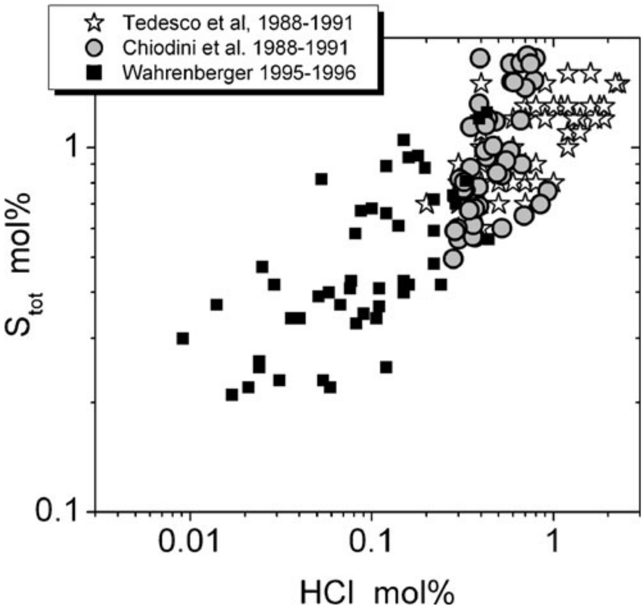

Fig. 3 Relationship between S_{tot} and HCl in gases of Vulcano collected in 1988–1996

nitrogen in the ASW-derived vapor may occur as the result of partial boiling of meteoric water. Some 3–4 wt.% of steam in the two-phase meteoric steam–water mixture is necessary to produce a batch of steam with ~400 ppm of N_2 ($X_{N2,vapor} \approx X_{N2,water}/Y$, where Y is the weight fraction of steam). This amount of N_2 should be accompanied by ~7–8 ppm of Ar. However, as can be seen in Fig. 5, the low N_2 component with ~500 ppm (data by Wahrenberger 1997) has low Ar (~0.5 ppm), close to its concentration in ASW of ~0.3 ppm, hence N_2/Ar ~1,000. This indicates that most N_2 in the low He and low N_2 endmember has a non-atmospheric origin. Thus, the low N_2 (low CO_2, high H_2O) component which is attributed to the hydrothermal end-member is characterized by high N_2/Ar (~1,000, Fig. 5) and high N_2/He (>2,000, Fig. 4) ratios. Apparently, this fluid is associated with a long-living hydrothermal system above an old intrusive body (beneath the Caldera del Piano?). The high He, high N_2, and high Ar component is characterized by significantly lower N_2/He (~500) and N_2/Ar (~300; Figs. 4 and 5). The output rate of this component, which is attributed to direct magma degassing, is variable. The fluid may originate from a younger magmatic body beneath the Vulcano crater.

Air contamination

All estimates above for ratios of N_2/Ar and N_2/He (and hence, He/Ar) have large uncertainties, more than 50%. These uncertainties include natural fluctuations such as fractionation during magma degassing (Nuccio et al. 1999; Nuccio and Paonita 2001), fractionation during boiling of the deep brine, irregular contributions of meteoric water, and air contamination during sampling and analysis. The air contamination can significantly alter the natural relationships between N_2, Ar, and He because of the relatively large Ar excess in air compared with the parent gas of Vulcano. Figure 6a, b shows a series of modeled mixing lines of two endmembers (M, magmatic; H, hydrothermal) with characteristics approximately corresponding to the Vulcano gases with maximum and minimum N_2 contents. It is assumed that the M component has 1,400 ppm of N_2, 3 ppm of He and 3 ppm of Ar, whereas the H component contains 400 ppm of N_2, 0.2 ppm of Ar, and 0.1 ppm of He. Each combination of these endmembers is mixed with a

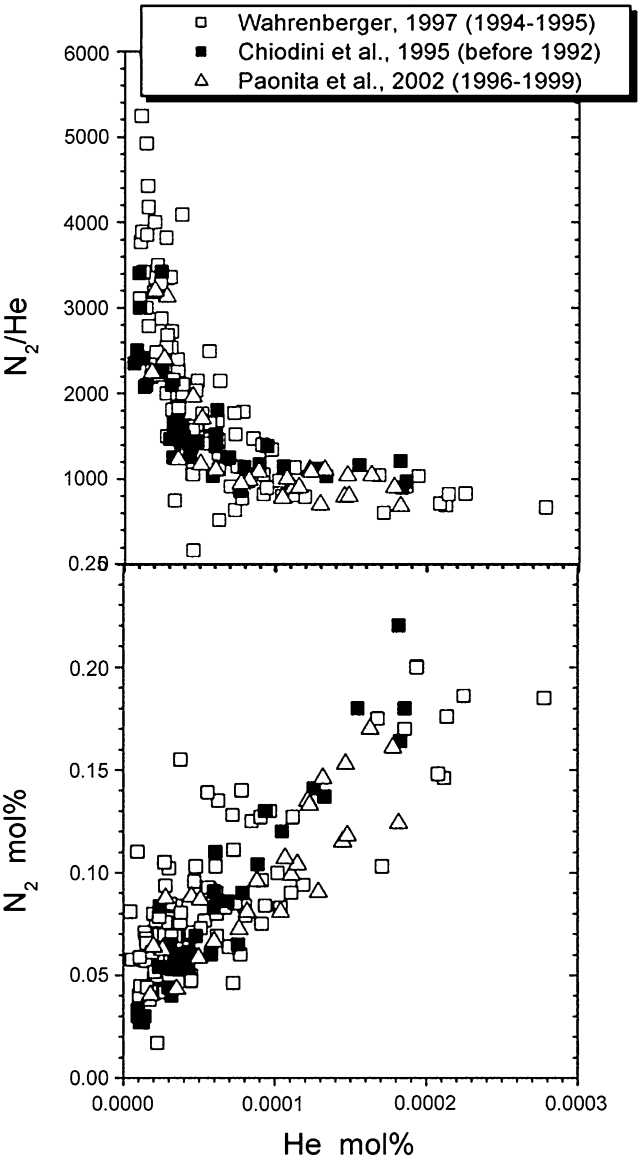

Fig. 4 N_2 vs. He and N_2/He vs. He for Vulcano; data from Wahrenberger (1997), Chiodini et al. (1995) and Paonita et al. (2002). Note that the "zero-He" extrapolation apparently gives non-zero N_2

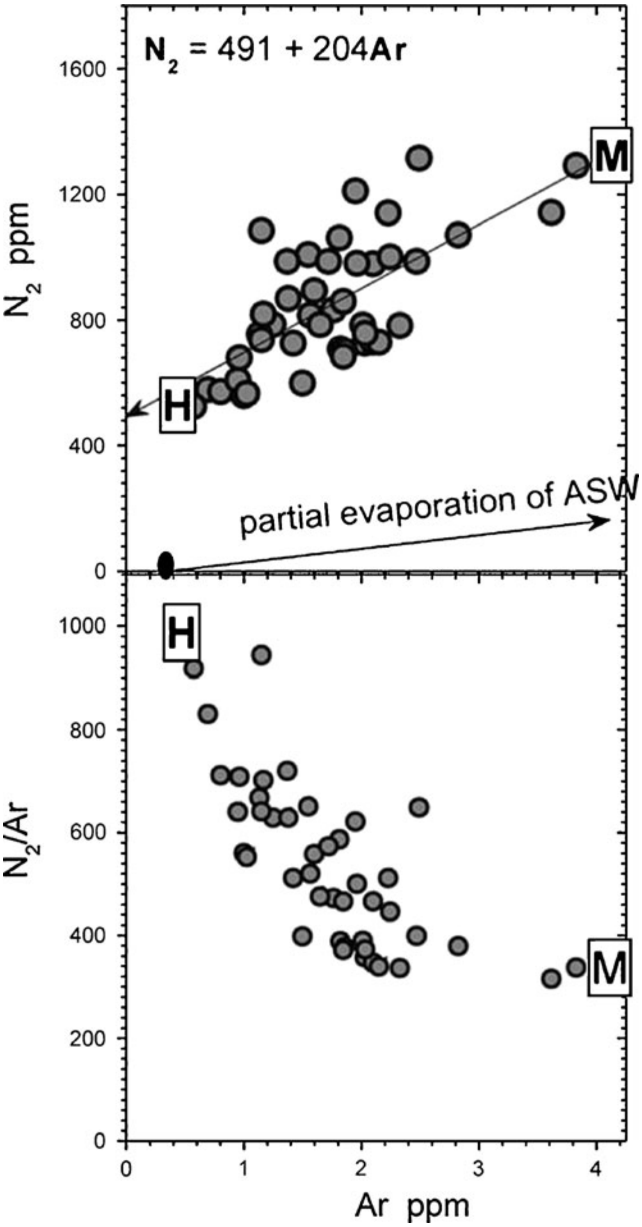

Fig. 5 N_2 vs Ar and N_2/Ar vs Ar (data from Wahrenberger 1997). The low Ar gases have Ar ~0.3 ppm which is close to its concentration in ASW, but high N_2 and N_2/Ar indicating a high fraction of non-atmospheric nitrogen

random but small amount of air (as log-normal random numbers with the mean of 0.1 mol%). The resulting compositions are plotted together with the ideal mixing lines. Qualitatively, the modeled and observed plots are similar (Fig. 6a). Moreover, it can be seen from the modeled ternary plot (Fig. 6b) that all modeled points are shifted to the right relative to the ideal mixing line, and the apparent extrapolation to the N_2–Ar axis leads to the incorrect conclusion regarding N_2/Ar of the magmatic component.

As already mentioned, samples with high He (and high N_2 and CO_2) have the highest $^3He/^4He$ ($6R_a$ to $6.2R_a$, Shinohara and Matsuo 1984; Italiano and Nuccio 1997; Tedesco and Scarsi 1999). The low He hydrothermal component is characterized by a high N_2/Ar (~1,000), and according to Magro and Pennisi (1991), by high values of $^{40}Ar/^{36}Ar$ which are much higher than the atmospheric value of 296. Values of $^{40}Ar/^{36}Ar$~1,000 correspond to the highest N_2/Ar. Tedesco and Scarsi (1999) also reported $^{40}Ar/^{36}Ar$~1,000 for the least air contaminated samples (He/Ne~4,000). The same authors, however, measured the Ne isotope ratios for the least air-contaminated Vulcano samples with low $^{20}Ne/^{22}Ne$ and high $^{21}Ne/^{22}Ne$ of 9.4 and 0.04, respectively, indicating a high proportion of crustal gases involved in the degassing of Vulcano. The N_2–Ar–He relationships shown above, along with the published isotopic data, may suggest that the main contribution of crustal gases to Vulcano volcanic gases comes through the hydrothermal component. This suggestion is in agreement with data of Magro (1997) on He and Ar isotopes; the highest $^{40}Ar/^{36}Ar$ ratio in the Vulcano fluids (~1,700) corresponds to the lowest $^3He/^4He$ (~$4.2R_a$). However, according to Magro (1997) this high $^{40}Ar/^{36}Ar$, low $^3He/^4He$ component is derived from an older, more crustal-contaminated magma in contrast to the high $^3He/^4He$ fluid derived from a fresh basaltic magma injected into the old magma chamber. This suggestion could be partially argued because volcanic rocks of Vulcano contain Ar with low $^{40}Ar/^{36}Ar$, close to the atmospheric value of ~300 (Magro 1997; Tedesco and Scarsi 1999), indicating that the main source of radiogenic Ar is not magma and is decoupled from the ^3He magmatic source. It should also be noted that Ar in the hydrothermal endmember, although it has a concentration close to the ASW value of ~0.3 ppm, is characterized by a high $^{40}Ar/^{36}Ar$ ratio, exceeding 1,000. This indicates that at least 2/3 of this argon has a non-atmospheric, radiogenic origin, and that only ~1/3 of Ar in the hydrothermal endmember may account for the direct atmospheric or mixed atmospheric+magmatic source.

Compositions of magmatic and magmatic–hydrothermal endmembers in fumarolic gases of Vulcano deduced from N_2–Ar–He systematics

The estimated N_2, Ar, and He concentrations, $^{40}Ar/^{36}Ar$ and $^3He/^4He$ (R/R_a) values for the M and H endmembers are shown in Table 1. The H_2O, CO_2, and S+HCl+HF concentrations and the δD, $\delta^{13}C$, for the same components of the Vulcano fluids have been reported earlier (Chiodini et al. 1993, 1995; Leeman et al. 2005).

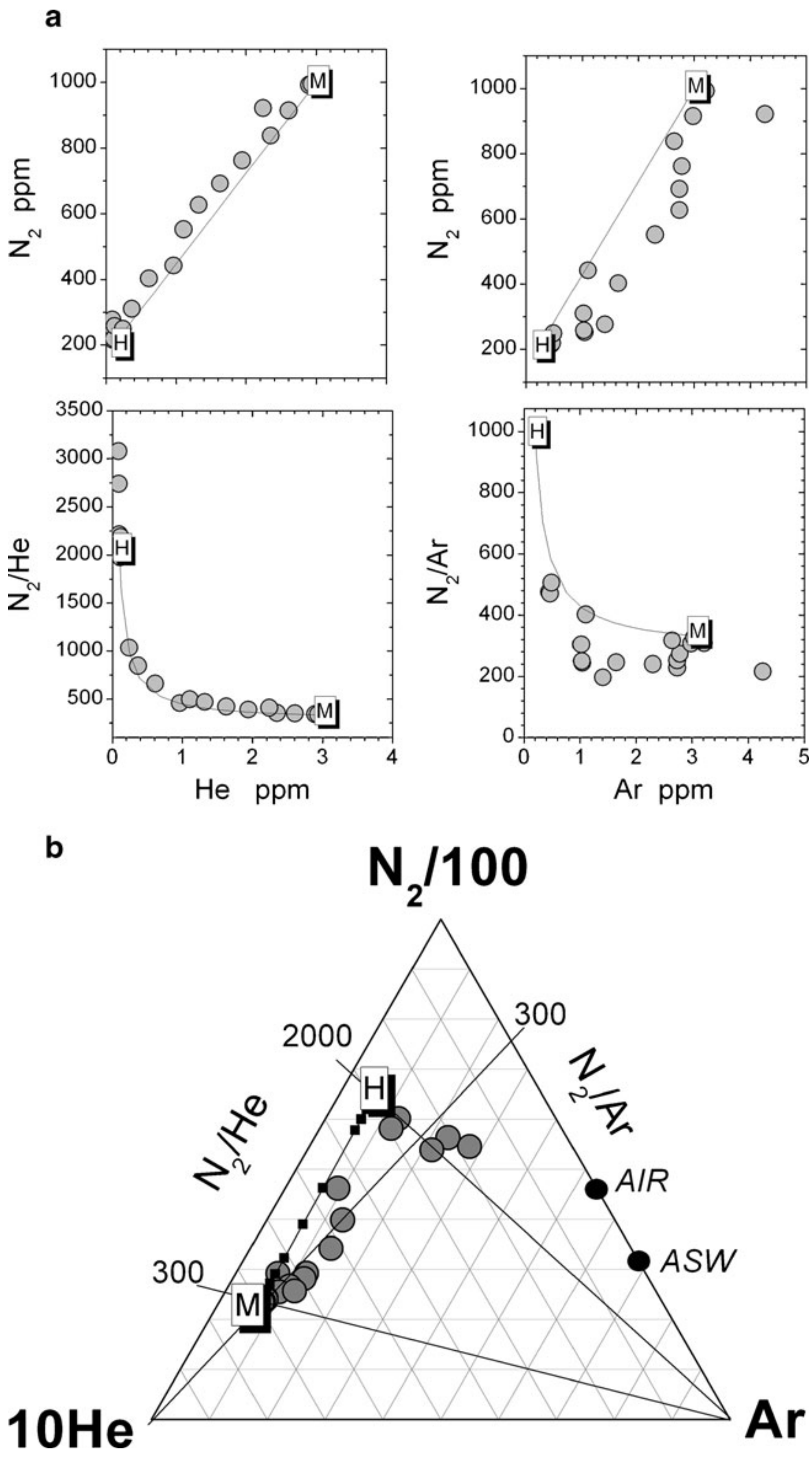

Fig. 6 **a** Modeled compositions of mixtures of H and M gases (see text) disturbed by a random injection of air (log-normal with the mean 0.1%). Note that the most scattered are plots with Ar because of the high relative proportion of Ar in air. **b** Results of the same modeling plotted on the ternary diagram. Note a large scattering of points with a trend to the air composition. The best-fit line gives a N$_2$/Ar ratio much lower than for the end-member enriched in N$_2$ (see text for details)

The magmatic endmember (M) is atypical for high-temperature subduction-type volcanic gases (e.g., Shinohara et al. 1993; Symonds et al. 1994; Taran et al. 1995; Giggenbach 1996). The most unusual are low H_2O and high CO_2 concentrations and relatively high He concentrations; the values are more typical for the hot spot volcanoes such as Kilauea, Hawaii, or Sierra Negra, Galapagos (Symonds et al. 1994; Giggenbach 1996; Goff and McMurtry 2000).

Taking into account the $\delta^{13}C$ value of CO_2 (+0.5‰) which is typical for limestone and marine carbonates, one can suggest a significant contribution of CO_2 to magmatic

Table 1 Composition of the two endmember components (*M* magmatic and *H* hydrothermal) for the Vulcano fumarolic gases including N_2, Ar, and He

	H_2O mol%	CO_2 mol%	S+Cl+F mol%	N_2 mol%	Ar ppmV	He ppmV	$^3He/^4He$ R/R_a	$^{40}Ar/^{36}Ar$	δD ‰ V-SMOW	$\delta^{13}C$ ‰ V-PDB
M	75	20	4	0.14	4	3	6.2	<400	−15	+0.5
H	96	3	<1?	0.02	0.2	0.1	4.2	>1,000	+10	−3

The estimates are made on the base of the published chemical and isotopic data (see text) and the data analysis made in this work

fluids from a crustal source. The problem is what crust to choose. One of the probable scenarios is that a very high amount of CO_2 from the subducting African continental lithosphere (Ionian slab) and Mediterranean carbonate-rich marine sediments participates in the magma generation process within the mantle wedge beneath this part of the Aeolian arc. This amount of CO_2 is much higher than in the case of an intra-oceanic setting or at continental margins with subducting oceanic plates. The total amount of CO_2 cannot be completely dissolved in magma at relatively deep levels due to its limited solubility; therefore, it forms a separate fluid phase, extracting other magmatic volatiles. This idea is in agreement with the finding of CO_2-rich high-pressure fluid inclusions in quartz xenoliths from Vulcano lavas, corresponding to depths of >20 km, at the crust–mantle interface (Zanon and Nikogosian 2006; Peccerillo et al. 2004). Decarbonation and and/or melting of carbonate-rich lithologies from a subducted African lithosphere proposed by Frezzoti et al. (2009) also suggest the presence of high CO_2 fluids or a carbonated partially molten CO_2-rich mantle at depths of the magma-generation zone. Low CO_2 contents in mafic melt inclusions of some Vulcano rocks is not contradictory to the existence of a separate fluid phase and may be caused by low-pressure crystallization of magmas in the shallow magma chamber beneath La Fossa crater (Gioncada et al. 1998; De Astis et al. 1997).

It is interesting that the H endmember in Vulcano gases is much more similar to a typical arc-type volcanic gas if its water isotopic composition is ignored. According to the above definition, the H endmember consists of the water vapor derived from a boiling-concentrated brine (Nuccio et al. 1999; Nuccio and Paonita 2001; Di Liberto et al. 2002). This brine, in turn, can be considered as a mixture of partially absorbed "magmatic" fluid and significantly evaporated seawater which has evolved due to water–rock interaction. The water–rock interaction is also the main reason for the contribution of a significant fraction of crustal gases (N_2, Ar, He) to fumarolic discharges.

Using the volatile balance calculations, it was estimated that the main source of volatiles (except He) in the subduction-type magmas are subducted sediments and altered oceanic basalts (Tatsumi et al. 1986; Plank and Langmuir 1998; Hilton et al. 2002; Jarrard 2003; Wallace 2005; Fischer 2008; Taran 2009). These produce a water-rich fluid with CO_2 from subducted carbonates and organic material, sedimentary and seawater sulfur, and Cl predominantly from the subducted seawater. The main feature of the South Italy subduction zone is that the subducting slab is probably not really oceanic, with Mediterranean marine sediments consisting of a large proportion of continental material (Nile sediments and Sahara dust). These sediments are also rich in biogenic material (e.g., Emeis et al. 1996; Bouloubassi et al. 1999). The mechanisms and amounts of this material involved into the magma generation process remains a significant problem, nevertheless, the behavior of H_2O and CO_2, which are the predominant components of regional magmatic fluids, is drastically different from those of "standard" volcanic arcs. On the other hand, high N_2/Ar ratios (>>100) are common for many volcanic arcs, but high He concentrations and He/Ar ratios are a special feature of the South Italy volcanism, as well as relatively low $^3He/^4He$ ratios.

Vulcano gas with relatively high $^3He/^4He$ of ~6R_a (Shinohara and Matsuo 1984; Italiano and Nuccio 1997; Tedesco et al. 1995) has about 85% of mantle He (7R_a is the highest value recorded in Mt. Etna fluids, which may be representative for the mantle beneath the Aeolian arc (Marty et al. 1994; Allard et al. 1997)). This mantle He is transported to the surface from the magma generation zone in the Aeolian mantle wedge together with other volatiles released from the subducting slab and the overlying mantle. The remaining 15% of the He is from the arc crust and the subducted slab. This He, which is mostly radiogenic from the continental crust beneath the volcano and the African lithosphere (Tedesco and Nagao 1999), should be accompanied by some CO_2, N_2, Ar, Ne, and other gases from the slab and the crustal surrounding magma chambers and conduits. A conclusion based on the analysis of the N_2–Ar–He system is that most of the crustal fluids in the Vulcano fumarolic gases are transported by the hydrothermal component.

Comparison with potential source fluids and gases from other subduction-type volcanoes

It is interesting to compare both the magmatic and hydrothermal components of Vulcano gases with the accepted compositions for upper mantle volatiles, some crustal gases and volatile components of oceanic sediments and altered oceanic crust. Oceanic sediments and altered oceanic crust are thought to be the main contributors of almost all species except He to volcanic gases of subduction zones. However, the subducting Ionian slab beneath the Aeolian arc may not be similar to an oceanic plate. According to Emeis et al. (1996), in the Ionian Sea, the Mediterranean sediments near the Calabrian accretionary wedge beneath the Pliocene layer consists of at least 2 km of Messinian evaporites and more than 10 km of a sedimentary complex underlain by Tethyan oceanic crust of Cretaceous age. Bouloubassi et al. (1999) reported the geochemistry of Pliocene (~3 Ma) organic sediments in cores of Ocean Drilling Project (ODP) site 964 drilled in the Ionian Basin. The organic carbon and nitrogen from this site, and in general from all ODP sites in the Mediterranean, are characterized by lower $\delta^{15}N$ (+3‰) compared with the average value of oceanic pelagic sediments (+6‰, Li and Bebout 2005). The composition of other volatiles in Mediterranean sediments is still unknown, as well as the amount of sediments involved in Ionian slab subduction.

Table 2 shows ranges in elemental ratios and isotopic compositions of N_2, Ar, and He in the main reservoirs; these are potential contributors of volatiles to volcanic gases of subduction zones. The characteristics of crustal gases are from different sources: Apennines (Collettini et al. 2008), KTB deep well in Germany (Bach et al. 1999; Lippmann et al. 2005), and deep wells of a giant oil field in Kansas, USA (Ballentine and Sherwood-Lollar 2002). The data on He and Ar concentrations and isotopic ratios in altered oceanic crust have been reported only by Staudacher and Allegre (1988). They also reported the abundances of Ar and He in a few samples of pelagic oceanic sediments, isotopic compositions of Ar and He in altered basalts, and Ar isotopes in sediments. The published data on He abundances and isotopes in pelagic sediments (see Ozima and Podosek 2002 for a review) show very high $^3He/^4He$ (30–100R_a) due to a constant (though at a very low rate) contribution from cosmic dust. However, Hilton et al. (2002) argued against subducting sediments transporting He into the mantle based on the high mobility of He. Nitrogen in oceanic sediments and altered crust was analyzed by Sadofsky and Bebout (2004), Li and Bebout (2005), and Li et al. (2007).

Table 2 Relative concentrations and isotopic compositions of N_2, Ar, and He in different terrestrial reservoirs, potential contributors to the subduction-type magmas and in some subduction-related volcanic gases

Reservoir	N_2/Ar	N_2/He	He/Ar	R/R_a	$^{40}Ar/^{36}Ar$	$N_2/^3He$	1σ%	Refs
Mantle								
MORB	100	25	4	8	3E+04	2.3E+08	30	Marty (1994); Marty and Zimmermann (1999); Hilton et al. (2002)
Subducting slab								
AOC	10,000	20,000	0.5	0.1	360	1.4E+11	100	Staudacher and Allegre (1988)
SED	30,000	2E+05	1	??	400	2.18E+11	100	Staudacher and Allegre (1988)
Continental crust								
KTB	700	120	5	0.07	950	4.2e+09	30	Bach et al. (1999); Lippmann et al. (2005)
Italy	5,000	3,300	1	0.04	–	1E+11	100	Collettini et al. (2008)
Kansas	300	35	8	0.2	990	1.8E+08	20	Ballentine and Sherwood-Lollar (2002)
Arc-type volcanoes								
Kudryavy	440	1,500	0.3	6.76	–	1.6E+08	30	Fischer et al. (1998);
Mutnovsky	1,200	2,000	0.6	7.5	301	1.9E+08	20	Zelensky and Taran (2011); Rozhkov and Verkhovsky (1990)
Vulcano								
M	350	460	0.76	6.2	300	5.3E+07	50	This work
H	1,000	2,000	0.5	4.2	1000	3.4E+08	70	This work
Air	83.6	1.49E+05	5.61E-04	1	296	1.1E+11		
ASW 20°C	38	2.64E+05	1.46E-04	1	296	1.9E+10		

The 1σ uncertainties are given very approximately, to give an idea about the natural scatter of data. 1σ of 100% indicates that the observed variations may be more than one order of magnitude

AOC altered oceanic crust

Distinguishing between various sources of volatiles (mantle wedge, subducted slab, sub-arc crust) is possible by considering the coupled components (i.e., N_2, ^{40}Ar, ^{36}Ar, ^4He, ^3He) together. In this case, the concentration of each component of the parent magmatic gas X_i is a weighted sum

$$X_i = \sum f_j X_{ij}, \tag{1}$$

where f_j is the fraction of fluid from each source (endmember) and X_{ij} is the concentration of each species normalized by the sum N_2+^{40}Ar+^{36}Ar+^4He+^3He. If there are four reservoirs (Mt, mantle; S, slab; C, crust; and A, atmosphere (ASW)), then we have five equations for four variables. Taking into account the mass balance equation $f_M + f_S + f_C + f_A = 1$, we can use three equations for concentrations and one for the mass balance. This approach is considered in detail by Albarede (1995). If all parameters are chosen correctly, the solution (f_j) of the system with the observed or presumed composition of the parent (or any) gas X_i is a set of f_j values with $0 \le f_j \le 1$. This solution should be the same for any set of three equations for concentrations, for example, (^{40}Ar, ^4He, N_2), (^3He, N_2, ^4He), (N_2, ^3He, ^{40}Ar), etc. In practice, all parameters (concentrations) of endmembers are mean values with large standard deviations. The observed or presumed gas compositions at the surface also have certain errors or ranges of values. Therefore, this “ideal” approach sometime does not work, giving either different reasonable solutions for different sets of equations, or solutions that do not make sense (f_j negative and/or >1). Therefore, such a formulation may be used for optimization of parameters (concentrations) of endmembers if we know exactly that any observed composition is a mixture of N-1 components from N reservoirs. For the Vulcano gas endmembers “M” and “H”, the set (N_2+^{40}Ar+^{36}Ar+^3He+^4He) gives consistent values of f_i (Table 3) independent of the chosen set of equations in the system (1).

Two plots with mixing lines between the main potential reservoirs of N_2, Ar, and He are shown in Figs. 7 and 8. The ratios N_2/Ar, N_2/He, and $^3He/^4He$ are plotted in Fig. 7 vs. the fraction of the mantle component. Values of $6.2R_a$ and $4.2R_a$ are used for the M (magmatic) and H (hydrothermal) components, respectively. Table 3 shows the calculated fractions Mt, S, C, and A in M and H endmembers for different sets of components. It can be seen from Table 3 that the major contribution to both endmembers comes from the “slab” source. It should be understood that this source, as well as the “crust” source, is not well defined for the Aeolian arc (see above). The crustal CO_2-rich gases with low $^3He/^4He$ collected by Collettini et al. (2008) from Central Italy, are much more similar in their N_2+Ar+He component to the “slab” component derived from data for oceanic pelagic sediments and altered oceanic crust than to metamorphic, N_2-rich gases from the KTB well or oil–gas fields. The least air-contaminated samples from Collettini et al. (2008) have very high N_2/Ar and high N_2/He, similar to the “slab” gases (Table 2). In other words, the S+C source for Vulcano (and maybe for other Italian volcanoes such as Campi Flegrei or Vesuvius) may be considered as a generalized “crustal” source without distinguishing the continental crust beneath the volcano and the subducting African lithosphere.

Table 3 Fractional contributions of MORB (M), slab (S), continental crust (C) and atmosphere (A) to magmatic (M) and hydrothermal (H) components of Vulcano fumarolic gases

Fraction	M	H
N_2+^4He+Ar		
M	0.055	0.013
S	0.85	0.95
C	0.0029	0.000
A	0.094	0.034
N_2+^4He+^3He		
M	0.043	0.007
S	0.81	0.94
C	0.048	0.022
A	0.096	0.035
N_2+Ar+^4He+^3He		
M	0.043	0.007
S	0.81	0.94
C	0.048	0.022
A	0.096	0.035
Ar+^4He+^3He		
M	0.043	0.007
S	0.81	0.94
C	0.048	0.022
A	0.096	0.035
^{36}Ar+^{40}Ar+N_2+^3He		
M	0.043	0.006
S	0.17	0.41
C	0.73	0.58
A	0.058	0.004

The fractions are obtained as a solution of Eq. 1 for the N_2–^{40}Ar–^{36}Ar–^4He–^3He system in Vulcano gases (Table 2) with different sets of species

Figure 7 shows that only ~5% of the mantle N_2+Ar+He is present in the “m” component (“m” and “h” instead of capital “M” and “H” are used in Figs. 7 and 8 to avoid confusion with the mantle source M) yet this mixture contains almost 5% of the mantle N_2, more than 80% of the total mantle He and more than 95% of the total ^3He. The “hydrothermal” (H) component is characterized by only ~1% of the mantle N_2+Ar+He mixture and ~95% of

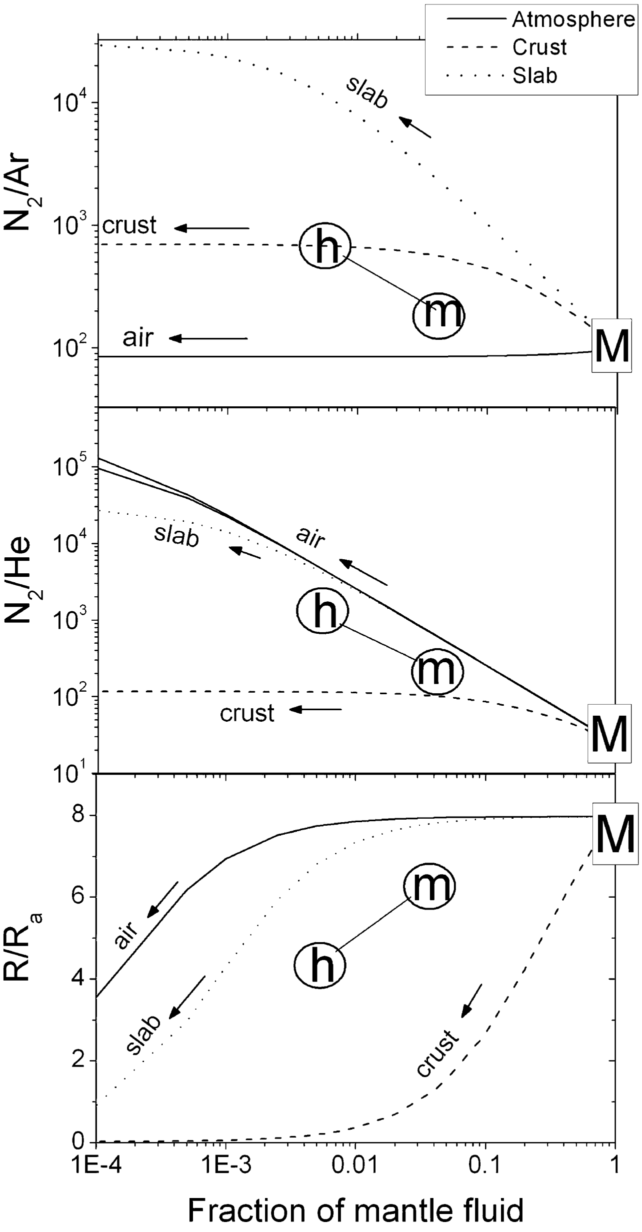

Fig. 7 N_2–Ar–He characteristics of endmembers (*h* hydrothermal, *m* magmatic) as a function of the fraction of the mantle contribution to N_2+Ar+He in gases of Vulcano. The mantle fraction is calculated using Eq. 1. Mixing lines between the mantle endmember (*M*) and other reservoirs are also shown

the S+C fraction against ~85% of the S+C for the "magmatic" (M) component. Both M and H components contain a significant fraction of atmospheric gases (3.5–9.6%).

N_2/He and ^{40}Ar/^{36}Ar vs N_2/Ar for fumarolic gases of Vulcano are shown in Fig. 8a and b together with the compositions of M and H endmembers ("m" and "h"). The points for main reservoirs and mixing lines are calculated using data of Table 2; the continental crust (CC) area corresponds to the KTB well. On the N_2/He vs N_2/Ar diagram (Fig. 8a), points for Vulcano and La Solfatara (shown for comparison) form compact clusters close to the mixing line between the mantle and C+S endmembers. Note that the CC (crustal) composition lies close to the M–slab mixing line. Central Italy CO_2-rich gases (Collettini et al. 2008) with the highest N_2/Ar ratios also plot close to the M–CC–slab mixing line, supporting the idea that some of these gases (with maximum N_2/Ar ratios and high N_2/He) may represent crustal gases of Central and South Italy.

The data of Magro and Pennisi (1991) plotted in the ^{40}Ar/^{36}Ar vs N_2/Ar diagram (Fig. 8b) demonstrate a

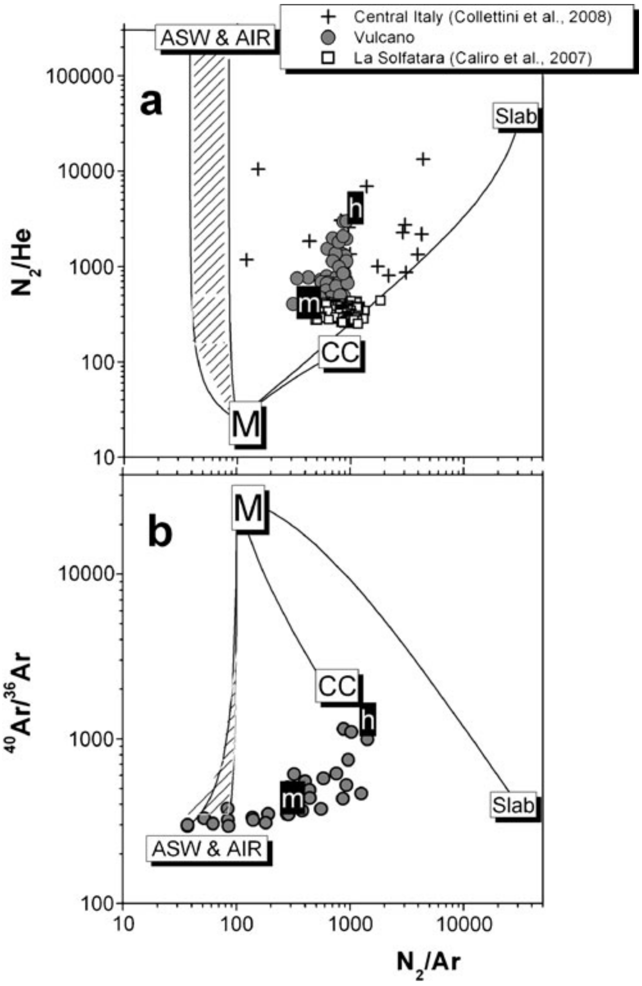

Fig. 8 **a** N_2/He vs N_2/Ar for fumarolic gases of Vulcano. Data of Caliro et al. (2007) for La Solfatara and Collettini et al. (2008) for cold CO_2-rich gases of Central Italy are also shown for comparison. Points for main reservoirs and mixing lines are calculated using data of Table 2. *CC* continental crust endmember is assumed to be close to the KTB well gases (see Table 2 and text for details). Except for the atmosphere each endmember is characterized by strong variations in compositions, and the plotted values for endmembers are mean values with large dispersions. **b** Variations of ^{40}Ar/^{36}Ar as a function of the N_2/Ar ratio in Vulcano gases (modified from Magro and Pennisi 1991). The proportion of radiogenic Ar increases with increasing non-atmospheric N_2. This indicates that the main source for both non-atmospheric N_2 and radiogenic Ar is the continental crust

mixing relationship from a low $^{40}Ar/^{36}Ar$, low N_2/Ar air-contaminated component, through a low $^{40}Ar/^{36}Ar$, moderate N_2/Ar magmatic endmember, to a high $^{40}Ar/^{36}Ar$, high N_2/Ar crustal (hydrothermal) endmember.

Concluding remarks

This study has focused on N_2–Ar–He systematics of gases from Vulcano Island. It is an attempt to use the existing database on the geochemistry of Vulcano fluids to consider how the behavior of "inert" components can be used as indicators of primary sources of volcanic gases, and also the mechanism of volcano degassing. This study indicates that the following topics deserve more detailed attention in the near future:

1. Although the He concentrations and isotopic composition have been measured in a number of papers, a statistically reasonable dataset with simultaneous determinations of concentrations of N_2, Ar, He, and $^3He/^4He$ still does not exist.
2. There remains a wide gap in measured Ar isotopes together with the full set of other components. After the very promising results by Tedesco and Scarsi (1999), more data are also required on Ne isotopes, also accompanied by a full set of the measured components.
3. It is also very important to correlate data on H, C, He, Ar, C, and N isotopes with their abundances and elemental ratios.
4. There are no constraints for the south Italy subduction zones regarding the input parameters. Subduction rate, ages, volatile compositions, and amount of subducting sediments are unknown; this is also the case for the upper, volatile-bearing part of the sub-sediment Ionian plate.

Acknowledgments I gratefully acknowledge funding from CONACyT, Mexico and INGV, Palermo, for the opportunity to visit Vulcano and other volcanic fields in Italy. I thank Giovanni Chiodini for helpful discussion of an earlier version of the manuscript, Salvatore Inguaggiato for keeping me informed about the latest scientific news from Vulcano Island, and William Bandy for his review of the manuscript. Reviews by Franco Tassi and Walter D'Alessandro significantly improved the manuscript.

References

Albarede F (1995) Introduction to geochemical modeling. Cambridge University Press, Cambridge

Allard P, Jean-Baptist P, D'Alessandro W, Parello F, Parisi B, Flehoc C (1997) Mantle derived helium and carbon in groundwaters and gases of Mt. Etna, Italy. Earth Planet Sci Lett 148:501–516

Bach W, Naumann D, Erzinger J (1999) Helium, argon and nitrogen of the upper continental crust (KTB drill holes, Oberpfalz, Germany): implications for crustal degassing. Chem Geol 160:81–101

Ballentine CJ, Sherwood-Lollar B (2002) Regional groundwater focusing of nitrogen and noble gases into the Hugoton–Panhandle giant gas field, USA. Geochim Cosmochim Acta 66:2483–2497

Bolognesi L, D'Amore F (1993) Isotopic variation of the hydrothermal system on Vulcano Island, Italy. Geochim Cosmochim Acta 9:2069–2082

Bouloubassi I, Rullkotter J, Meyers FA (1999) Origin and transformation of organic matter in Pliocene–Pleistocene Mediterranean sapropels: organic geochemical evidence reviewed. Mar Geol 153:177–197

Caliro S, Chiodini G, Moretti R, Avino R, Granieri D, Russo M, Fiebig J (2007) The origin of the fumaroles of La Solfatara (Campi Flegrei, South Italy). J Volcanol Geotherm Res 71:3040–3055

Capasso G, Dongarra G, Haiser S, Favara R, Valenza M (1992) Isotope composition of rain water, well wáter and fumarolic steam on the island of Vulcano, and their implications for volcani survellance. J Volcanol Geotherm Res 49:147–155

Capasso G, Favara R, Inguaggiato S (1997) Chemical features and isotopic gaseous manifestation on Vulcano Island (Aeolian Islands): an interpretative model of fluid circulation. Geochim Cosmochim Acta 61:3425–3442

Capasso G, D'Alessandro W, Favara R, Inguaggiato S, Parello F (2001) Interaction between the deep fluids and the shallow groundwaters on Vulcano island (Italy). J Volcanol Geotherm Res 108:187–198

Carapezza M, Nuccio PM, Valenza M (1981) Genesis and evolution of the fumaroles of Vulcano (Aeolian Islands, Italy): a geochemical model. Bull Volcanol 44:547–563

Chiodini G, Cioni R, Marini L (1993) Reactions governing the chemistry of cráter fumaroles from Vulcano island, Italy, and implications for volcanic surveillance. Appl Geochem 8:357–371

Chiodini G, Cioni R, Marini L, Panichi C (1995) Origin of fumarolic fluids of Vulcano Island, Italy and implications for volcanic surveillance. Bull Volcanol 57:99–110

Chiodini G, Allard P, Caliro S, Parello F (2000) 18° Exchange between steam and carbón dioxide in volcanic and hydrothermal gases. Implications for the source of water. Geochim Cosmochim Acta 64:2479–2488

Cioni R, D'Amore F (1984) A genetic model for the fumaroles of Vulcano island (Sicily, Italy). Geothermics 13:375–384

Collettini C, Cardellini C, Chiodini G, De Paola N, Holdsworth RE, Smith SAF (2008) Fault weakening due to CO_2 degassing in the Northern Apennines: short- and long-term processed. Geol Soc Lond Spec Pub 299:174–194

De Astis G, La Volpe L, Peccerillo A, Civetta L (1997) Evoluzione vulcanologica e magmatologica dell'isola di Vulcano. In: La Volpe L, Dellino P, Nuccio PM, Privitera E, Sbrana A (eds) Progetto Vulcano: Rizultati dell'attivita di Ricerca 1993–95. Felici Editore, Pisa, pp 155–177

Di Liberto V, Nuccio PM, Paonita A (2002) Genesis of chlorine and sulfur in fumarolic emissions at Vulcano Island (Italy): assessment of pH and redox conditions in the hydrothermal system. J Volcanol Geotherm Res 116:137–150

Emeis K-C, Robertson AHF, Richter C (1996) Site 964. Proc Ocean Drill Program Initial Rep 160:85–123

Fischer TP, Giggenbach WF, Sano Y, Williams SN (1998) Fluxes and sources of volatiles discharged from Kudryavy, a subduction zone volcano, Kurile Islands. Earth Planet Sci Lett 160:81–96

Fischer TP (2008) Fluxes of volatiles (H_2O, CO_2, N_2, Cl, F) from arc volcanoes. Geochem J 42:21–38

Frezzoti ML, Peccerillo A, Panza G (2009) Carbonate metasomatism and CO_2 lithosphere–asthenosphere degassing beneath the Western Mediterranean: an integrated model arising from petrological and geophysical data. Chem Geol 262:108–120

Giggenbach WF (1992a) The composition of gases in geothermal and volcanic systems as a function of tectonic setting. Proc Int Symp Water Rock Interact WRI-8:873–878

Giggenbach WF (1992b) Isotopic shift in waters from geothermal and volcanic systems along convergent plate boundaries and their origin. Earth Planet Sci Lett 113:495–510

Giggenbach WF (1996) Chemical composition of volcanic gases. In: Scarpa R, Tilling R (eds) Monitoring and mitigation of volcano hazards. Springer, Berlin, pp 221–256

Gioncada A, Clocciatti R, Sbrana A, Bottazzi P, Massare D, Ottolini L (1998) A study of melt inclusions at Vulcano (Aeolian Islands, Italy): insights on the primitive magmas and on the volcanic feeding system. Bull Volcanol 60:286–306

Goff F, McMurtry G (2000) Tririum and stable isotopes of magmatic waters. J Volcanol Geotherm Res 97:347–396

Hilton DR, Fischer TP, Marty B (2002) Noble gases and volatile recycling at subduction zones. In: Porcelli D, Ballentine CJ, Wieler R (eds). Noble gases in cosmochemistry and geochemistry. Rev Mineral 47(1): 319–370

Italiano F, Nuccio PM (1997) Variazione del raporto isotópico dell'elio nelle fumarole di Vulcano. In: La Volpe L, Dellino P, Nuccio PM, Privitera E, Sbrana A (eds) Progetto Vulcano: Rizultati dell'attivita di Ricerca 1993–95. Felici Editore, Pisa, pp 124–127

Jarrard RD (2003) Subduction fluxes of water, carbon dioxide, chlorine and potassium. Geochem Geophys Geosys 4:U1–U50. doi:10.1029/2002GC000392

Jenden PD, Kaplan IR, Poreda RJ, Craig H (1988) Origin of nitrogen-rich gases in the Californis Great Valley: evidence from helium, carbón and nitrogen isotope ratios. Geochim Cosmochim Acta 52:851–861

Leeman WP, Tonarini S, Pennisi M, Ferrara G (2005) Boron isotope variations in fumarolic condensates and thermal waters from Vulcano Island, Italy: implications for evolution of volcanic fluids. Geochim Cosmochim Acta 69:143–163

Li L, Bebout GE (2005) Carbon and nitrogen geochemistry of sediments in the Central American convergent margin: insights regarding subduction input fluxes, diagenesis, and paleoproductivity. J Geophys Res 110:B11202. doi:10.1029/2004JB003276

Li L, Bebout GE, Ildelman BD (2007) Nitrogen concentration and $\delta^{15}N$ of altered oceanic crust obtained on ODP Legs 129 and 185: insight into alteration-related nitrogen enrichment and the nitrogen subduction budget. Geochim Cosmochim Acta 71:2344–2360

Lippmann J, Erzinger J, Zimmer M, Schloemer S, Eichinger JL, Faber E (2005) On the geochemistry of gases and noble gas isotopes (including ^{222}Rn) in deep crustal fluids. The 4,000 m KTB-pilot hole fluid production test 2002/03. Geofluids 5:52–66

Magro G (1997) La composizione isotopic dell'elio e dell'argon nei prodotti di Vulcano: inclusion fluide e gas fumarolici. In: La Volpe L, Dellino P, Nuccio PM, Privitera E, Sbrana A (eds) Progetto Vulcano: Rizultati dell'attivita di Ricerca 1993–95. Felici Editore, Pisa, pp 128–132

Magro G, Pennisi M (1991) Noble gases and nitrogen: mixing and temporal evolution in the fumarolic fluids of Vulcano, Italy. J Volcanol Geotherm Res 47:237–247

Marty B (1994) Nitrogen content of the mantle inferred from N_2/Ar correlations in oceanic basalts. Nature 377:326–329

Marty B, Zimmermann L (1999) Volatiles (He, C, N, Ar) in mid-ocean ridge basalts: assessment of shallow-level fractionation and characterization of source composition. Geochim Cosmochim Acta 63:3619–3633

Marty B, Trull T, Lussiez P, Basile I, Tanguy JC (1994) Helium, argon, oxygen, strontium and neodymium isotope constraints on the origin and evolution of Mt Etna magmatism. Earth Planet Sci Lett 126:23–39

Nuccio PM, Paonita A (2001) Magmatic degassing of multicomponent vapors and assessment of magma depth: application to Vulcano Island (Italy). Earth Planet Sci Lett 193:467–481

Nuccio PM, Paonita A, Sortino F (1999) Geochemical modeling of mixing between magmatic and hydrothermal gases. The case of Vulcano, Italy. Earth Planet Sci Lett 167:321–333

Ozima M, Podosek F (2002) Noble gas geochemistry, 2nd edn. Cambridge University Press, Cambridge

Panichi C, Noto P (1992) Isotopic and chemical composition of water, steam and gas samples of the island of Vulcano (Aeolian Arc, Italy). Acta Vulcanol 2:297–312

Paonita A, Favara R, Nuccio PM, Sortino F (2002) Genesis of fumarolic emissions as inferred by isotope mass balance: CO_2 and water at Vulcano Island, Italy. Geochim Cosmochim Acta 66:759–772

Peccerillo A, Frezzotti ML, De Astis G, Ventura G (2004) Modeling the magma plumbing system of Vulcano (Aeolian Islands, Italy) by integrated fluid-inclusion geobarometry, petrology, and geophysics. Geol Mag 141:525–540

Plank T, Langmuir CH (1998) The chemical composition of subducting sediments and its consequences for the crust and the mantle. Chem Geol 145:325–394

Rozhkov AM, Verkhovsky AB (1990) Geochemistry of noble gases in high temperature hydrothermal systems. Nauka, Moscow

Sadofsky SJ, Bebout GE (2004) Nitrogen geochemistry of subducting sediments: new results from Izu–Bonin–Mariana margin. Geochem Geophys Geosys 5:Q03115. doi:10.1029/2003GC000543

Sakai H, Matsubaya O (1977) Stable isotope study of Japanese geothermal systems. Geothermics 5:97–124

Shinohara H, Matsuo S (1984) Results and analysis of fumarolic gases from F-1 and F-5 fumaroles of Vulcano, Italy. Geothermics 15:211–215

Shinohara H, Giggenbach WF, Kazahaya K, Hedenquist JW (1993) Geochemistry of volcanic gases and hot springs of Satsuma–Iwojima, Japan: following Matsuo. Geochem J 27:271–285

Staudacher T, Allegre C (1988) Recycling of oceanic crust and sediments: the noble gas subduction barrier. Earth Planet Sci Lett 89:173–183

Symonds RB, Rose WI, Bluth GJS, Gerlach TM (1994) Volcanic-gas studies: methods, results and applications. Rev Miner 30:1–66

Taran YA (2009) Geochemistry of volcanic and hydrothermal fluids and volatile budget of Kamchatka–Kuriles subduction zone. Geochim Cosmochim Acta 73:1134–1163

Taran YA, Pokrovsky BG, Dubik YM (1989) Isotopic composition and origin of water in andesitic magmas. Dokl Earth Sci 304:440–443

Taran YA, Hedenquist JW, Korzhinsky MA, Tkachenko SI, Shmulovich KI (1995) Geochemistry of magmatic gases from Kudryavy volcano, Kuril Islands. Geochim Cosmochim Acta 59:1749–1761

Tatsumi Y, Hamilton DL, Nesbitt RW (1986) Chemical characteristics of fluid phase released from a subducted lithosphere and origin of arc magmas: evidence from high-pressure experiments and natural rocks. J Volcanol Geotherm Res 29:293–309

Tedesco D (1995) Fluid geochemistry at Vulcano Island: a change in volcanic regime or fluctuations in the mixing of different systems? J Geophys Res 100:4157–4167

Tedesco D, Nagao K (1999) Radiogenic ^{4}He, ^{21}Ne and ^{40}Ar in fumarolic gases of Vulcano: implications for the presence of continental crust beneath the island. Earth Planet Sci Lett 144:517–528

Tedesco D, Scarsi P (1999) Intensive gas sampling of noble gases and carbon at Vulcano (Southern Italy). J Geophys Res 104:10499–10510

Tedesco D, Toutain JP, Allard P, Losno R (1991) Chemical variations in fumarolic gases at Vulcano Island: seasonal and volcanic effects. J Volcanol Geotherm Res 45:325–334

Tedesco D, Miele G, Sano Y, Toutain JP (1995) Helium isotopic ratio in Vulcano island fumaroles: temporal variations in shallow level mixing and deep magmatic supply. J Volcanol Geotherm Res 64:117–128

Wahrenberger CM (1997) Some aspects of the chemistry of volcanic gases. PhD thesis, Swiss Federal Insitute of Technology, Zurich

Wallace PJ (2005) Volatiles in subduction zone magmas:concentrations and fluxes based on melt inclusions and volcanic gas data. J Volcanol Geotherm Res 140:217–240

Zanon V, Nikogosian I (2006) Evidence of crustal melting events below the island of Salina (Aeolian arc, southern Italy). Geology 3:17–20

Zelensky M, Taran Y (2011) Chemical and isotopic compositions of volcanic and hydrothermal gases of Mutnovsky volcano, Kamchatka: Evidence for mantle, slab and atmosphere contributions to fluids of a typical arc volcano. Bull Volcanol. doi:10.1007/s00445-011-0449-0