frontiers | Frontiers in Earth Science

TYPE Brief Research Report
PUBLISHED 07 November 2022
DOI 10.3389/feart.2022.1011203

Check for updates

OPEN ACCESS

EDITED BY
Ying Li,
Institute of Earthquake Forecasting,
China Earthquake Administration, China

REVIEWED BY
David Graham,
Oregon State University, United States
Ian Ernest Masterman Smith,
The University of Auckland,
New Zealand
Eemu Ranta,
Faculty of Science, University of
Helsinki, Finland

*CORRESPONDENCE
Fabrizio Gherardi,
f.gherardi@igg.cnr.it

SPECIALTY SECTION
This article was submitted
to Geochemistry,
a section of the journal
Frontiers in Earth Science

RECEIVED 03 August 2022
ACCEPTED 21 October 2022
PUBLISHED 07 November 2022

CITATION
Gherardi F, Barsanti M, Principe C and
Magro G (2022), Helium isotopes in
Plinian and inter-Plinian volcanic
products of Vesuvius, Italy.
Front. Earth Sci. 10:1011203.
doi: 10.3389/feart.2022.1011203

COPYRIGHT
© 2022 Gherardi, Barsanti, Principe and
Magro. This is an open-access article
distributed under the terms of the
Creative Commons Attribution License
(CC BY). The use, distribution or
reproduction in other forums is
permitted, provided the original
author(s) and the copyright owner(s) are
credited and that the original
publication in this journal is cited, in
accordance with accepted academic
practice. No use, distribution or
reproduction is permitted which does
not comply with these terms.

Helium isotopes in Plinian and inter-Plinian volcanic products of Vesuvius, Italy

Fabrizio Gherardi[1]*, Mattia Barsanti[2], Claudia Principe[1] and Gabriella Magro[1]

[1]National Research Council of Italy (CNR) - Institute of Geosciences and Georesources (IGG), Pisa, Italy, [2]ENEA Italian National Agency for New Technologies, Italian National Agency for New Technologies (ENEA) - Energy and Sustainable Economic Development, Marine Environment Research Centre S.Teresa, La Spezia, Italy

We investigated helium isotopes on gas extracted by crushing from melt and fluid inclusions in minerals from Plinian and inter-Plinian tephra and lavas of Vesuvius, Italy. Erupted products of different ages were considered, from Avellino eruption (1995 BCE) to the last eruption of 1944, with special focus on the *79 AD* Plinian eruption. $^{3}He/^{4}He$ ratios between 1.5 and 2.7 R_A were measured, with the highest values associated with rocks representative of the roof and the walls of the magma chambers (cumulates). Lowest values occurred in sanidines representative of magma-skarn interfaces. Noteworthy, the highest measured values of the *79 AD* pumices were comparable with both lavas and tephra emitted from flank vents and under open-conduit conditions during the *Medieval Period* and *Present Period* of Vesuvius activity, and present-day fumarolic discharges. $^{3}He/^{4}He$ values are buffered within an extended, deep-seated reservoir at about 10 *km* filled with magma rising from the mantle. A fact that might potentially limit the accuracy of future eruption forecasting through monitoring of $^{3}He/^{4}He$ changes in Vesuvius fumaroles. Ageing and interaction with crustal rocks emerged as possible mechanisms that lowered the $^{3}He/^{4}He$ ratio of the melt during its intra-crustal magma chambers stay, with highest values associated with more dynamic conditions.

KEYWORDS

Helium isotopes, Carbon isotopes, melt and fluid inclusions, Plinian eruptions, Sub-Plinian eruptions, Violent Strombolian eruptions, flank eruptions, Vesuvius

Introduction

The volcanoes of Monte Somma, Vesuvius, and Phlegraean Fields occupy the southern part of the Campania Plain, southern Italy, and border a densely populated region currently inhabited by more than two million people that also includes the metropolitan city of Naples. Starting in the 1980s', the high volcanic risk related with the possible renewal of activity of one of these volcanoes fostered an intense scientific effort to increase knowledge on the eruptive history and mechanisms of these volcanoes (e.g., Barberi et al., 1984; De Vivo et al., 1993). Present volcanic activity mostly consists of active

seismicity, ground deformation with alternation of deflation/inflation episodes (mostly in the Phlegraean Fields area), moderate fumarolic emissions, and hot spring discharges.

At Vesuvius, over the last decades, a large number of rock and fluid samples have been collected, and an extended database of mineralogical and geochemical analyses of various deposits is now available (De Vivo et al., 2010; Peccerillo, 2020). The historic activity of the Vesuvius volcanic system is characterized by occasional Plinian eruptions (Avellino, *79 AD*, *472 AD*, 1631) separated by periods of inactivity or semi-persistent activity (Arnò et al., 1987). During semi-persistent phases of activity, the volcano experienced an open-conduit behavior, and produced effusive, often from flank vents (Principe et al., 2004), and mixed (effusive and explosive) eruptions, from Strombolian, to Violent Strombolian and Sub-Plinian type (Arrighi et al., 2001).

As the last eruption occurred in 1944, most of the current scientific interest is in the possible correlation between ongoing observed dynamics and past geological record. In particular, the link between present-day fluid composition and magma degassing at depth is considered a key element in understanding the mechanisms that could control any possible future volcanic activity.

Due to its well-defined isotopic signature for different geological settings (e.g., Kurz et al., 1982; Ozima and Podosek, 1983; Mamyrin and Tolstikhin, 1984; Burnard, 2013), the helium isotope composition (expressed as the $^3He/^4He$ ratio measured in the sample, R, normalized to same isotope ratio measured in air, $R_A = 1.39 \times 10^{-6}$) has the potential to be usefully employed to investigate eruptive mechanisms and magma dynamics. As a general statement, under closed conduit conditions, a number of information on the primary magma source could be lost due to the long residence time of a magma into shallow intra-crustal magmatic chambers. Despite this uncertainty, the R/R_A signature of gases extracted from fluid inclusions can disclose important information on the evolution of melts inside the magmatic chambers, and on the interactions between magma and wall rocks. Further to this, the comparison of $^3He/^4He$ ratios measured on fluid inclusions of phenocrysts with values from present-day fluids (fumaroles, hot springs, gas dissolved in water, mofettes, etc.) provide additional insights on the time evolution of the magmatic-hydrothermal system, because variations in the chemical and isotopic composition of fluids may reveal the onset of a new phase of volcanic activity (e.g., Ozima and Podosek, 1983; Mamyrin and Tolstikhin, 1984; Porcelli et al., 2002; Burnard, 2013).

At Vesuvius, $^3He/^4He$ ratios have been mostly determined on olivine and pyroxene phenocrysts separated from lavas emitted under open conduit conditions during the last 400 years (from 1,631 to 1,944; Graham et al., 1993; Graham and Lupton, 1999; Martelli et al., 2004). Until today, no He isotope were available for products—such as Plinian pumices—emitted after long periods of permanence in a magmatic chamber under closed conduit condition—or from Violent Strombolian and Sub-Plinian products—deriving from the refilling of the open conduit with gas-rich magma from a deep-seated reservoir. This paper aims at filling this gap, by integrating the existing He isotope composition data with new data on minerals from tephra and lavas belonging to all these types of eruptions. Special emphasis is on volcanic products emitted during the *79 AD* Plinian eruption.

Geological-volcanological setting

Monte Somma is a complex volcanic structure affected by several calderas and structural collapses (e.g., Principe et al., 2021). In the middle of the resulting morphological depression, the volcanic cone of Vesuvius has grown. Along with the Phlegraean Fields volcanic area and the Roccamonfina stratovolcano, Monte Somma-Vesuvius volcano is hosted in a large graben within the Campania plain (Figure 1) that originated during the Upper Pliocene-Lower Pleistocene. This graben is part of a macro-regional extensional system that stretches along the Tyrrhenian margin of the Apennine mountainous chain, from southern Toscana to northern Calabria. This belt experienced widespread volcanism in Pleistocene (e.g., Scandone, 1979; Turco et al., 2006).

The volcanic activity in the area now occupied by Monte Somma and Vesuvius started about 400 ka BP (Brocchini et al., 2001). The outcropping deposits all belong to the volcanic activity following the Campanian Ignimbrite eruption (about 39 ka ago; Rosi and Sbrana, 1987). Dated to about 22 ka BP (Cioni et al., 2008), the *Pomici di Base* eruption—the oldest eruption considered in the present work—is the first one and the major Plinian eruption occurred in Vesuvius area (Bertagnini et al., 1998). Other major explosive eruptions followed, such as the *Greenish Pumices* Sub-Plinian eruption (about 20 ka BP; Cioni et al., 2003), and the *Pomici di Mercato* Plinian eruption (about 8,900 years BP; Mele et al., 2011). The activity occurred at Vesuvius during the last 4 ka BP has been subdivided into four synthematic units, on the basis of major geological events, marked by depositional unconformities (Paolillo et al., 2016): 1) *Proto -Vesuvius*, between the Plinian eruptions of *Pomici di Avellino* (about 4 ka ago) and *79 AD*; 2) *Ancient Vesuvius*, between *79 AD* Plinian eruption and *472 AD* Sub-Plinian eruption; 3) *Medieval Vesuvius*, from the *472 AD* Sub-Plinian eruption and the 1631 small-scale Plinian eruption; 4) *Present Vesuvius*, between 1631 and 1944 eruptions.

The *Medieval Vesuvius* activity is characterized by the emission of lava flows from flank vents opened on the slopes of the Vesuvius cone, and of Strombolian and Violent Strombolian scoriae fallout (Principe et al., 2004; Paolillo et al., 2016). During the *Present Vesuvius* period, the volcano passed from effusive and markedly Strombolian activity to episodes of violent Strombolian and Sub-Plinian eruptions

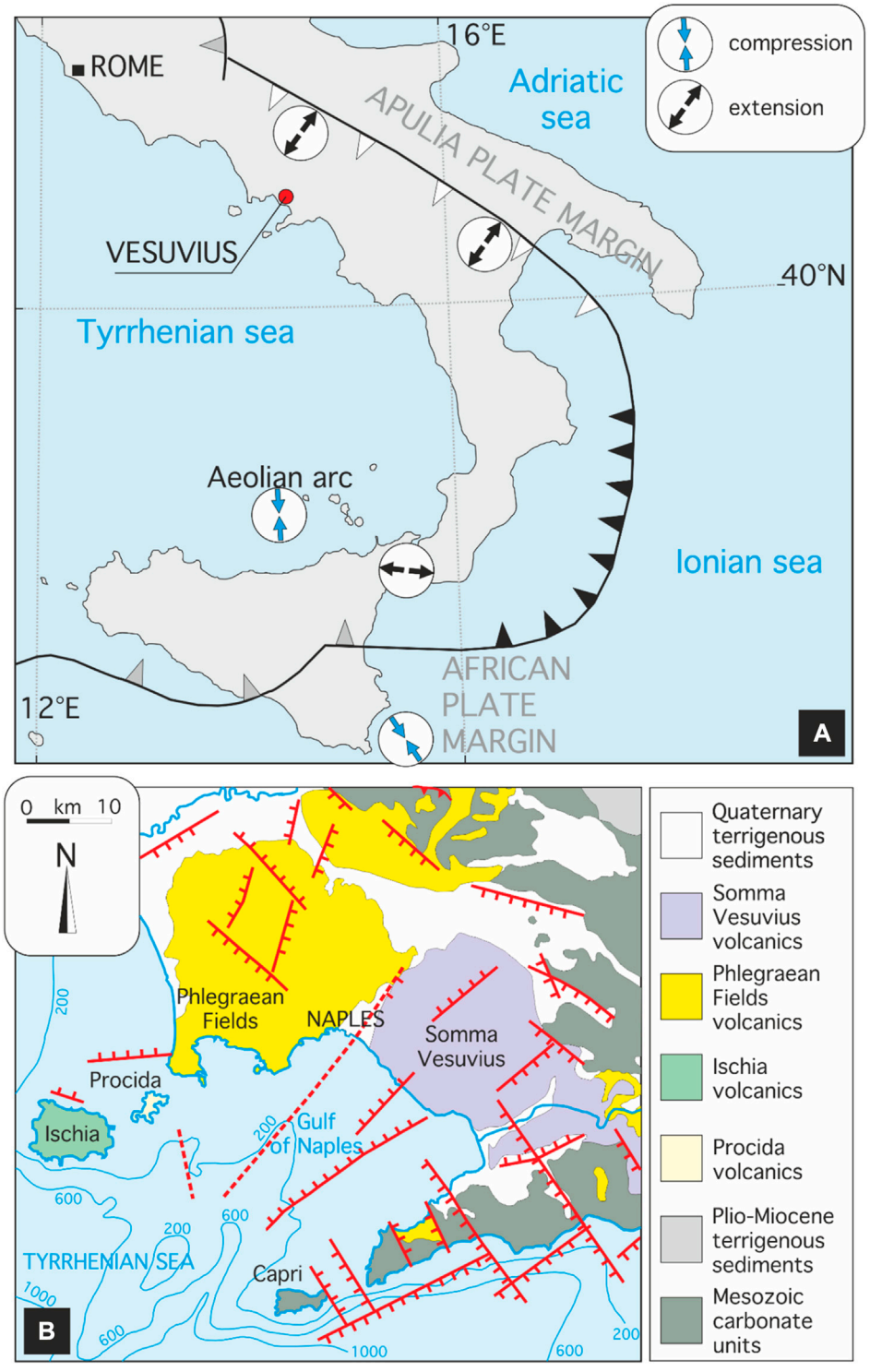

FIGURE 1
(A) Geodynamical sketch map of Southern Italy, with location of the Monte Somma and Vesuvius (modified after Montone et al., 1999). Bold lines = structural arcs; shaded triangles = active compressional fronts; solid triangles = active oceanic subduction; open triangles = front of the Plio-Pleistocene thrust, now prevalently affected by extension. **(B)** Simplified geological map of the Campania plain and volcanic districts.

with mixed effusive and explosive character (Arrighi et al., 2001).

Since the last eruption of 1944, Vesuvius entered a period of eruptive rest. In the crater area, temperatures between 600 and 800°C were recorded in the fumaroles during the period 1944–1960 (Chiodini et al., 2001), before starting to gently decrease close to the boiling point of water at the crater altitude (around 95°C) during the 1990s, down to present-day sub-boiling temperatures (about 72°C). The residual activity consists of fumaroles, diffuse degassing (e.g., Baubroun et al., 1991; Chiodini et al., 2001; Federico et al., 2002; Frondini et al., 2004), general subsidence and low-magnitude seismicity (e.g., Ricco et al., 2021; and references therein). The present-day, mildly fumarolic activity is concentrated near the crater only, whereas diffuse soil emissions widely occur around the flanks of the volcano, in correspondence of structural and volcano-tectonic elements (Paolillo et al., 2016). In this area, the extensive interaction between rising magmatic fluids and groundwater has been revealed by C-He systematics of dissolved species (Federico et al., 2002).

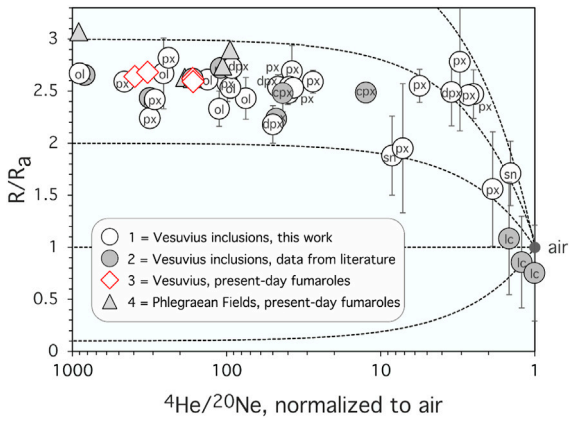

FIGURE 2
R/R_a vs. $^4He/^{20}Ne$ ratio (normalized to air) diagram for Monte Somma and Vesuvius samples. 1 = Monte Somma and Vesuvius fluid inclusions (this work); 2 = Monte Somma and Vesuvius fluid inclusions (data from literature); 3 = Vesuvius present-day fumaroles (this work); 4 = Phlegraean Fields present-day fumaroles (this work). Labels are as follows: cpx, clinopyroxene; dpx, diopside; lc, leucite; ol, olivine; px, pyroxene; sn, sanidine. The black dashed lines represent binary mixing trends between the atmospheric end-member (air) and a number of deep components with different $^3He/^4He$ signature and fixed $^4He/^{20}Ne$ ratio ($^4He/^{20}Ne$ = 10,000).

Methods

Bulk rocks samples were disaggregated and the mineral phases of interest separated with a magnet separator. Then, olivine and pyroxene crystals were carefully collected from the enriched fraction by handpicking under binocular microscope, and cleaned ultrasonically. Mineral samples successively underwent several hours under-vacuum degassing at 100–150°C to minimize air contamination on crystal surfaces. Fluid inclusions gases were then extracted by under-vacuum crushing of 1–2 g of the selected mineral fragments (grain size from 0.5 to 1 mm). The crushing efficiency was checked by verifying that the granulometric size of the powder was below 20 μm for all samples.

Both fumarolic gases and minerals were processed on a stainless-steel vacuum line equipped with cold and hot Ti getters to separate noble gases from the gaseous mixture. The extraction line was connected to both a magnetic mass spectrometer (MAP 215-50) equipped with ion counting detector, and a quadrupole mass spectrometer (Spectralab 200, VG-Micromass; Magro et al., 2003).

The $^3He/^4He$ resolution was close to 600 AMU for HD_^{3}He at 5% of the peak. Typical blanks, during the measurement period, were on the order of 0.6–1 × 10^{-9} cc STP for ^4He, with R close to air. No blank corrections were applied to R values of fumarolic gases, as the He concentration of these samples was several orders of magnitude higher than the blank (a few hundred ppm in the samples vs. ppb level concentrations in the blank). Minerals samples with He concentrations below the arbitrary threshold of five times the concentration of the blank, or with $^4He/^{20}Ne$ ratios lower than five times the air ratio were marked as "low-gas samples" in Supplementary Table S1A.

A standard volume of air at different pressures (from 1,013 to 10.13 mbar) was introduced into the extraction line and processed like the samples. The reproducibility of $^3He/^4He$ and 4/(20 + 22) mass ratios measurements on air samples was better than 10% and 5%, respectively, over the analysis period. To check He isotopes results, we performed duplicate analyses on: 1) the gas extracted from an olivine crystal from the 1983 Mt. Etna eruption ($^3He/^4He$ between 6.0 and 6.7 R_A; Marty et al., 1994); 2) the gas extracted from a pyroxene crystal of the 1906 lava flow of Vesuvius ($^3He/^4He$ = 2.61 ± 0.08 R_A; Graham et al., 1993); 3) the gas extracted from an olivine and a pyroxene crystal of the 1944 lava flow of Vesuvius ($^3He/^4He$ = 2.42 ± 0.14 R_A; Graham et al., 1993). These results are summarized in Supplementary Table S1C.

The CO_2 fraction extracted from three sanidine samples was first entrapped in a stainless-steel finger equipped with high-vacuum valves, and then analyzed in a stable isotope mass spectrometer (Europe lab) for the determination of $\delta^{13}C$ values.

Cross controls were performed to exclude C isotopic fractionation during crushing, and in particular, we verified that CO_2 could be not released by the crushing device by comparing the analytical results of "standard" samples with a quartz sample without inclusions.

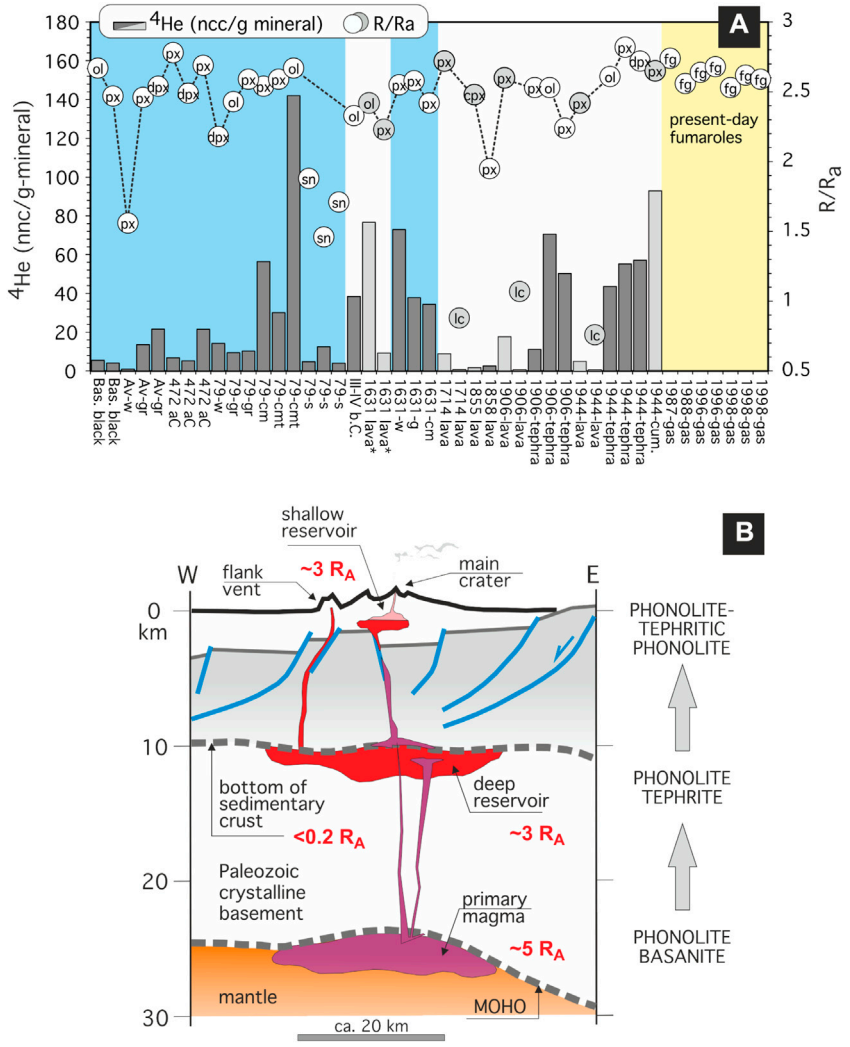

FIGURE 3
(A) R/R_A ratios (dots) and ^4He contents (bars) for different, individual eruptions (abundances are in ncc/grams of crushed mineral). Empty dots/grey bars: data from this work. Pale grey dots/pale grey bars: data after Graham et al. (1993). Leucites after Graham et al. (1993) were likely compromised by air contamination (low He concentrations, and air-like $^4He/^{20}Ne$ and $^3He/^4He$ ratios). The dashed line connects olivine and pyroxene samples. (*) 1,631 lava samples should be attributed to Medieval age activity Principe et al. (2004). Pale blue background: closed conduit activity; white background: open conduit activity; pale yellow background: present-day fumarolic activity. **(B)** Simplified conceptual model of Vesuvius, with indication of various hypothetical levels of magma accumulation and differentiation (modified after Stoppa et al., 2017). Volcanic activity is driven by the recurrent arrival of primitive mafic magma batches from the mantle into an extended deep-seated reservoir ("deep reservoir"), where homogenization occurs with resident, pre-existing magmas. From this reservoir, magmas can be directly emitted at the surface, or stored into shallow magma chambers ("shallow reservoir"), giving origin to the different eruptive styles and types of volcanic deposits of Vesuvius. Numbers in red are approximate $^3He/^4He$ signatures of different domains/reservoirs.

Results and discussion

The concentration and the isotopic composition of He, and the $^4He/^{20}Ne$ ratios of fluid and melt inclusions, and fumarolic gases analyzed for this study are reported in Supplementary Table S1A (data from this work) and Supplementary Table S1B (data from the literature).

The $^3He/^4He$ ratio (normalized to air) of olivine and cogenetic pyroxenes range between 2.25 and 2.84 R_A, in close agreement with literature values (2.2–2.7 R_A; Graham et al., 1993; Graham and Lupton, 1999). The lowest $^3He/^4He$ values measured in olivine and clinopyroxene correspond to an olivine phenocryst from white pumices of the *79 AD* Plinian eruption, the highest ones to a pyroxene of the 1944 tephra fallout. Sialic minerals, leucites from 1631 to 1944 period (*Present Vesuvius*), and sanidines from magma-skarn interface of *79 AD* eruption, show the lowest $^3He/^4He$ values, in the range 0.7–1.8 R_A. The $^3He/^4He$ values for fumarolic gases range

from 2.64 to 2.78 R_A, that are of the same range of the highest values measured in pyroclastic products of 1944 eruption. For comparison, present-day fluids discharged in the neighboring volcanic area of Phlegraean Fields (mostly in the range 2.4–3.2 R_A, up to about 3.53 R_A; Tedesco et al., 1990; Chiodini et al., 1996; Tedesco and Scarsi, 1999) partially overlap with the upper values of Vesuvius range.

The R/R_A vs. $^4He/^{20}Ne$ correlation plot (Figure 2) shows that most of samples from this work plot along mixing lines connecting the atmospheric end-member with a possible deep-seated component having a $^3He/^4He$ signature of 2–3 R_A. Samples with lowest $^4He/^{20}Ne$ values possibly suggest the mixing with a correspondingly ^3He- enriched component (up to about 3.5 R_A), but the R/R_A ratios of these samples are affected by a relatively large error due to the low amount of He extracted from minerals, and should be treated with caution. Only sialic minerals from leucites (data from literature) do not follow this trend, plotting at comparatively lower $^3He/^4He$ values (~1 R_A). Overall, all plotted values are markedly lower than most ^3He- enriched values measured in most volcanic arcs (7–9 R_A; Poreda and Craig, 1989), and the average range of subduction zones worldwide (5.4 ± 1.9 R_A; Hilton et al., 2002). The compositional resemblance between mineral separates from the considered eruptive units, and present-day fluids indicates a common magmatic source that has remained almost unchanged over time.

$^3He/^4He$ time patterns over the course of different phases of activity of the volcano (Figure 3) indicate that: 1) coexisting olivines and pyroxenes are characterized by similar R/R_A values; 2) the two generations of dark (i.e., ferrosalitic) and light (i.e., diopsidic) green pyroxenes of 1944 tephra have by similar R/R_A values; 3) grey and white pumices of the *79 AD* eruption have a significantly lower He content (one order of magnitude less) compared to cumulates of the same eruption. Vesuvius cumulates are typically dunites, wherlites, and biotite-bearing pyroxenites (e.g., Joron et al., 1987; Belkin and De Vivo, 1993), with clinopyroxene, phlogopite, biotite, apatite, plagioclase, and fosteritic olivine ($Fo_{80–90}$) as main phases; 4) the He content of olivine and pyroxene from lavas of the 1631–1944 Vesuvius phase of activity is generally lower than cogenetic tephra, despite similar $^3He/^4He$ values, whereas the products of 1944 and 1906 eruptions do not show the same differences in helium abundance; 5) R/R_A values systematically decrease from femic to sialic minerals, and sanidines are characterized by the lowest He contents, despite the presence of volatile-rich fluid inclusions (mostly CO_2-enriched).

Data from literature suggest low $^3He/^4He$ ratios and He total content typically associated with leucites can be tentatively attributed to a relatively minor efficiency in volatile trapping of this mineral during magma transport and cooling. Structural reasons (i.e., a less compact structure of sanidine crystals compared to more retentive minerals like pyroxene and olivine) can be invoked to explain gas loss phenomena affecting sanidines (Graham et al., 1993).

Data from this work point to a negligible effect (at least on He isotope distribution) of processes such as later crystallization and/or wall rock assimilation in magma chambers, because pyroxenes are not characterized by a ^4He-richer signature than coexisting olivine, as found elsewhere, where these processes are active (e.g., Hilton et al., 1995; Marty et al., 1994; Shaw et al., 2006). Overall, highest $^3He/^4He$ ratios were observed in *79 AD* cumulates, representative of the roof and the walls of the magma chambers (e.g., Cioni et al., 1995). Lowest values occur in sanidines representative of the magma-skarn interface (e.g., Fulignati et al., 1998, 2005). Noteworthy, the highest measured values of the *79 AD* paleo-fluids are comparable with both lavas and tephra emitted under open-conduit conditions during the 1631–1944 period, and present-day fumarolic discharges. *Medieval Period* lavas are phonolitic basanites, with primitive magmatic composition (i.e., the Vesuvius parental melts). These lavas have modal olivine ~10%, MgO content >7 wt%, high Mg# (83–86) and high Cr + Ni (usually in the 200–270 ppm range), which are reasonable figures for primitive, mantle-derived melts (Stoppa et al., 2017). Lavas and tephra of the *Present Period* are phono-tephrites (Figure 3B).

A tendency of $^3He/^4He$ ratios to decrease from South to North in Central-Southern Italy has been recognized long ago, based on data from present-days fluids and from fluid/melt inclusions (e.g., Sano et al., 1989; Graham et al., 1993; Marty et al., 1994; Tedesco, 1997; Martelli et al., 2004; Martelli et al., 2008). This trend has been put in relation with the geodynamic context of this part of the Mediterranean area, dominated during the last 30 Ma by the subduction of the Ionian-Adriatic plate. As a result of this subduction process, a large spatial and temporal heterogeneity of the volcanic products has been identified in the Tyrrhenian Sea region, associated with a variety of tectonic regimes (subduction-related, intraplate, rifting, e.g., among many others, Peccerillo, 2020). The noble gas signature of present-day fluids and products of Plio-Quaternary volcanism has been used to constrain the deep sources of the regional volcanism, and a 6.7–7.1 R_A range has been identified as representative of the mantle component in Southern Italy (Marty et al., 1994; Martelli et al., 2008). Crustal contamination acts in the direction of lowering the $^3He/^4He$ value of this component, and a northward increase in ^4He is generally observed in association with an increase in radiogenic Sr and Pb, and unradiogenic Nd (Martelli et al., 2008, and references therein). Based on data from Procida Island (Martelli et al., 2004), we can assume a value of 5.2 R_A for this modified mantle component in the Neapolitan area.

Low R/R_A ratios in fumarolic gases and basalt phenocrysts have been explained in many arc-related environments either by degassing of subducted sediments or continental crust, or by the assimilation of crustal material by magma stored in an intra-crustal condition (Hilton et al., 1993a; Hilton et al., 1993b). A metasomatized mantle with a He isotope signature of 2.4 ± 0.4 R_A

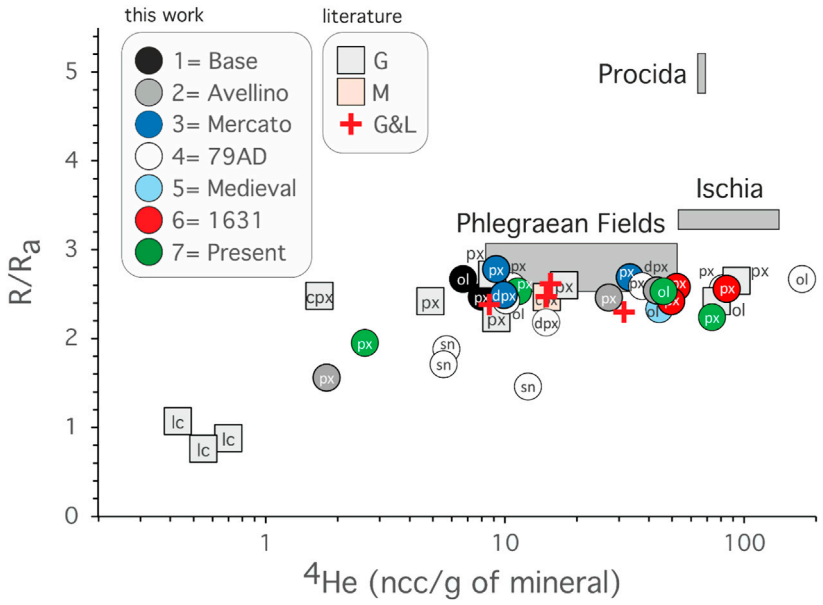

FIGURE 4
R/R_A vs. ^4He correlation diagram. Data from this work: 1 = *Pomici di Base* Plinian eruption black pumice; 2 = *Pomici di Avellino* Plinian eruption; 3 = *Pomici di Mercato* Plinian eruption; 4 = *79 AD* Plinian eruption; 5 = *Medieval Vesuvius*, Calastro lava; 6 = 1,631 small-scale Plinian eruption; 7 = *Present Vesuvius* activity. Data from literature: G = Graham et al. (1993); M = Martelli et al. (2004); G&L = Graham and Lupton (1999). The compositional fields for Phlegraean Fields, Procida and Ischia islands are also shown for comparison (data from Martelli et al., 2004). Labels as in Figure 2.

was suggested by Graham et al. (1993) for the area under study. Geochemical features of Monte Somma, Vesuvius, Phlegraean Fields, and Ischia-Procida rocks have been linked by some authors to a dominant fertile OIB-type (Ocean Island Basalts) source, probably contaminated by subducted terrigenous (Ayuso et al., 1998), or pelagic sediments (Gasperini et al., 2002). Some authors more recently claimed that the release of metasomatic fluids from the subducting Ionian-Adriatic plate could be realistically invoked to explain the low-^3He signature and the He-Sr isotope trends of Plio-Quaternary volcanism over all Central-Southern Italy (Martelli et al., 2008).

Irrespective of these hypotheses, the correlation between He amounts and R/R_A (Figure 4) highlights a relatively uniform and lower R/R_A compositional range for Vesuvius fluid/melt inclusions, compared to other volcanoes of the Campania magmatic province. In particular, a partial overlapping with R/R_A values from Phlegraean Fields is recognizable, along with a clear separation from values from Ischia (about −1 R_A) and Procida (about −2 R_A) islands. Noteworthy, all these volcanoes are only a few kilometers from each other (up to a maximum of about 40 *km* between Vesuvius and Ischia Island; Figure 1), and the observed differences cannot be easily ascribed to short-scale compositional heterogeneities of the mantle wedge.

Numerical models and laboratory experiments on site-specific rocks have emphasized the importance of crustal contamination/assimilation processes at mid-crustal depth (e.g., Iacono-Marziano et al., 2008; Iacono-Marziano et al., 2009; Pichavant et al., 2014), in agreement with the geology of the Vesuvius substratum, that comprises: 1) about 10 km of Mesozoic carbonates above the Paleozoic crystalline basement (e.g., Berrino et al., 1998; Brocchini et al., 2001; Improta and Corciulo, 2006; Di Renzo et al., 2007); 2) a possibly large (400 km^2), deep reservoir zone identified by tomography imaging at a depth of 8–10 km, well above the supposed depth of the Moho discontinuity (about 30 *km* depth; De Natale et al., 2006).

Supporting observations to this conjecture include the following points. 1) The occurrence of effective interactions between magma and rocks hosting the magma chamber, as testified by the mineralogical and geochemical characterization of cognate xenoliths and skarn fragments ejected during the different eruptions of the volcano (e.g., Barberi and Leoni, 1980; Belkin et al., 1985; Cioni et al., 1995; Fulignati et al., 1998; Gilg et al., 2001; Pascal et al., 2009; Stoppa et al., 2017). 2) The possibility that magma contamination by carbonate rocks widely occurs in the plumbing system of the volcano, as corroborated by Sr systematics (e.g., Civetta et al., 1991; Piochi et al., 2006), and quantitatively modelled by several authors (e.g., Pappalardo et al., 2004; Pappalardo and Mastrolorenzo, 2010). 3) The emission of large amounts of CO_2 generated by sidewall assimilation processes after the intrusion of alkali-basaltic magma into the sedimentary carbonate basement (Iacono-Marziano et al., 2008,

2009). In addition, the presence of a mantle source affected by the incorporation of U-rich carbonated melts has been recently advanced on the basis of data on U-Th disequilibria and Sr-Nd-Pb-U isotope systematics (Avanzinelli et al., 2018), supporting the hypothesis that interactions between carbonate-rich lithologies and magma may also occur below the local crystalline basement (Figure 3B).

However, other studies questioned the thermodynamic and geochemical grounds of conceptual models that consider extensive (i.e., >10%) country-rock assimilation processes active in the roots of Vesuvius (e.g., Bailey, 2005; Woolley et al., 2005; Bell and Kjarsgaard, 2006; Stoppa et al., 2017). Overall, despite the large amount of geoscientific data now available, there is no agreement on the actual effectiveness of carbonate assimilation, and whether the crustal component was involved at the time of melting of the source, or subsequently during the ascent of magma, or in what proportions the two processes can possibly overlap at Vesuvius.

In this complex picture, the main result of our work is to highlight the striking constancy of the He isotope signal of fluid/melt inclusions, and its close similarity to the composition of present-day gaseous emanations. This temporal stability points to a common deep source beneath the volcano, and to a mechanism of compositional homogenization that has the potential to smooth variations possibly related to the ascent of new magma batches. In the frame of the currently accepted multi-depth magma chamber (MDMC) model, this entails that magma ageing and interaction with crustal rocks could be effective in lowering the $^3He/^4He$ ratio of the primitive melt during its intra-crustal storage, most likely during the stay inside the "deep reservoir" of Figure 3B. The MDMC model foresees the presence of a shallow reservoir, possibly migrating up and down over time within the upper 8 *km* under Vesuvius (Auger et al., 2001; Scaillet et al., 2008; Pappalardo and Mastrolorenzo, 2010; and references therein), and of a large, deep-seated reservoir at about 10 *km* (De Natale et al., 2006). The longer is the storage time, the more effective is the expected re-equilibration of fluid inclusions in femic minerals like olivine and pyroxene. Even though, the efficiency of this process may also depend on additional, ill-defined parameters, such the volume ratio of the reservoir and of the recharge, the feeding frequency of the new batches of magma and their possible channeling, or any other structural element which may locally enhance or prevent magma-rock interactions. Conditions of homogenization are expected to be easily achieved for helium, due to its high diffusivity in melts. Based on data from literature (Trull and Kurz, 1993), we speculate that this homogenization can occur over a spatial scale of about 1 mm over less than about 1,060 and 2.5 years for olivine and pyroxene, respectively, at temperatures of about 965°C, with these numbers decreasing to less than 32 years and 10 days at about 1,100°C. These features are compatible with the hypothesized large range of temperatures (possibly betweeen 850 and more than 1,150°C) and residence times (from few months up to thousands of years) experienced during the magmatic history of Somma-Vesuvius (e.g., among many others, Macdonald et al., 2016; Scheibner et al., 2008; Di Renzo et al., 2007; Morgan et al., 2004).

The carbon-isotope composition of CO_2 extracted from fluid inclusions in sanidines of *79 AD* plinian syenites further supports this scenario. The $\delta^{13}C$ values of these samples ranges in fact from +1.3‰ to +2.1‰ (vs. V-PDB; Supplementary Table S2), higher than present-day crater fumarolic emissions (~0‰; Federico et al., 2002), and significantly different from both the typical mantle range ($\delta^{13}C$ = −4‰ to −7‰; Pineau et al., 2004), and the regional mantle end-member of Pantelleria Island, southern Italy ($\delta^{13}C$ = −4.2‰ to −5.8‰; Parello et al., 2000).

The positive $\delta^{13}C(CO_2)$ values of sanidines are compatible with both a decarbonation process at near magmatic temperature (>500°C; Valley, 1986) of local unmetamorphosed carbonates ($\delta^{13}C$ = −0.5‰ to +1.3‰; Fulignati et al., 2005) and/or metalimestones and metadolostones ($\delta^{13}C$ = −2‰ to +2‰; Gilg et al., 2001), and the degassing (by decompression during its ascent towards the surface) of a magma that underwent increasing carbonate assimilation at depth (e.g., Iacono-Marziano et al., 2008). Independent on the predominant mechanism between these two, in a more general sense, also the C-isotope signature of fluid inclusions supports an important involvement of crustal materials in the mechanisms of magma generation, transport and physical-chemical evolution at Vesuvius.

Conclusion

With the aim of shedding light on the precursory path of a possible future reactivation of Vesuvius, we investigated helium isotope abundances in gases extracted by crushing from melt and fluid inclusions of volcanic products of different type and age, and we compared them with present-day fumarolic discharges.

For the first time, we analyzed pyroxene, olivine and sanidine crystals from both lavas and tephra coming from Plinian and inter-Plinian eruptions. In particular, we focused on volcanic products emitted after long periods of permanence in a magmatic chamber under closed conduit condition, by paying special attention to *79 AD* Plinian eruption.

We measured $^3He/^4He$ ratios between 1.5 and 2.7 R_A, with the highest values for the deposits emitted from the *79 AD* magma chamber. This striking constancy of the $^3He/^4He$ signal, regardless of the occurrence of open vs. closed conduit conditions, and its similarity with values obtained on present-day fumarolic discharges, suggests that helium isotope patterns are consistent with an efficient mechanism of homogenization at depth, under Vesuvius.

We related this homogenization mechanism to the existence of a deep-seated (about 10 *km* b.g.l.), extended magma reservoir filled with magma rising from the mantle. This reservoir directly

fed lava flows emitted from flank vents during the *Medieval Period*, and the overlying magma chambers that produced mixed and explosive eruptions during other phases of Vesuvius history, through the ascent of pulses of mafic magma. Our data indicate that, independently of the effectiveness of carbonate assimilation processes, minor variations in $^3He/^4He$ are associated either with the ascent of magma along the upward path above the main, deep storage region, or with the formation of shallow magma chambers, as in the case of *79 AD* Plinian eruption. The hypothesis that crustal contamination/assimilation processes at mid-crustal depth played a role at Vesuvius, is corroborated by the occurrence of positive $\delta^{13}C$ values of the CO_2 extracted from fluid inclusions in sanidines of the *79 AD* event.

Overall, our data emphasize the fundamental role of the multiple-chamber structure in the magma dynamics of the Vesuvius volcanic system, and suggest that magma ponding at crustal depth could be considered a key mechanism that might have the potential to homogenize the helium isotope signal. Should this hypothesis be confirmed, the accuracy of future eruption forecasting through monitoring of $^3He/^4He$ changes in Vesuvius fumaroles would be questioned.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

Author contributions

FG: Noble gas analysis, data interpretation, writing of the original draft, review and editing; MB: Mineral separation, noble gas analysis, data interpretation, review and editing; CP: Field work, data interpretation, review and editing; GM: Conceptualization, methodology, noble gas analysis, data interpretation, writing the original draft, review and editing.

Acknowledgments

We warmly acknowledge the three reviewers for their constructive criticisms.

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

All claims expressed in this article are solely those of the authors and do not necessarily represent those of their affiliated organizations, or those of the publisher, the editors and the reviewers. Any product that may be evaluated in this article, or claim that may be made by its manufacturer, is not guaranteed or endorsed by the publisher.

Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/feart.2022.1011203/full#supplementary-material

References

Arnò, V., Principe, C., Rosi, M., Santacroce, R., Sbrana, A., and Sheridan, M. F. (1987). "Eruptive history," in *Somma-vesuvius*. Editor R. Santacroce (Roma: CNR Edizioni), Vol. 114, 53–104.8

Arrighi, S., Principe, C., and Rosi, M. (2001). Violent strombolian and subplinian eruption at Vesuvius during the post-1631 activity. *Bull. Volcanol.* 63, 126–150.

Auger, E., Gasparini, P., Virieux, J., and Zollo, A. (2001). Seismic evidence of an extended magmatic sill under Mt. Vesuvius. *Science* 294, 1510–1512. doi:10.1126/science.1064893

Avanzinelli, R., Casalini, M., Elliott, T., and Conticelli, S. (2018). Carbon fluxes from subducted carbonates revealed by uranium excess at Mount Vesuvius, Italy. *Geology* 46, 259–262. doi:10.1130/g39766.1

Ayuso, R. A., De Vivo, B., Rolandi, G., and Seal, R. R. (1998). Seal II R., Paone AGeochemical and isotopic (Nd-Pb-Sr-O) variations bearing on the Genesis of volcanic rocks from Vesuvius, Italy. *J. Volcanol. Geotherm. Res.* 82, 53–78. doi:10.1016/s0377-0273(97)00057-7

Bailey, D. K. (2005). Carbonate volcanics in Italy: Numerical tests for the hypothesis of lava-sedimentary limestone mixing. *Period. Mineral.* 74 (3), 205–208.

Barberi, F., Corrado, G., Innocenti, F., and Luongo, G. (1984). Phlegraean fields 1982–1984: Brief chronicle of a volcano emergency in a densely populated area. *Bull. Volcanol.* 47, 175–185. doi:10.1007/bf01961547

Barberi, F., and Leoni, L. (1980). Metamorphic carbonate ejecta from vesuvius plinian eruptions: Evidence of the occurrence of shallow magma chambers. *Bull. Volcanol.* 43, 107–120. doi:10.1007/bf02597615

Baubron, J.-C., Allard, P., Sabroux, J.-C., Tedesco, D., and Toutain, J.-P. (1991). Soil gas emanations as precursory indicators of volcanic eruptions. *J. Geol. Soc. Lond.* 148, 571–576. doi:10.1144/gsjgs.148.3.0571

Belkin, H. E., and De Vivo, B. (1993). Fluid inclusion studies of ejected nodules from plinian eruptions of Mt. Somma-Vesuvius. *J. Volcanol. Geotherm. Res.* 58, 89–100. doi:10.1016/0377-0273(93)90103-x

Belkin, H. E., De Vivo, B., Roedder, E., and Cortini, M. (1985). Fluid inclusion geobarometry from ejected Mt. Somma-vesuvius nodules. *Am. Mineral.* 70, 288–303.

Bell, K., and Kjarsgaard, B. (2006). Discussion of Peccerillo (2004) "carbonate-rich pyroclastic rocks from central apennines: Carbonatites or carbonate-rich rocks?" *Period. Mineral.* 75 (1), 85–92.

Berrino, G., Corrado, G., and Riccardi, U. (1998). Sea gravity data in the gulf of naples: A contribution to delineating the structural pattern of the vesuvian area. *J. Volcanol. Geotherm. Res.* 82, 139–150. doi:10.1016/s0377-0273(97)00061-9

Bertagnini, A., Landi, P., Rosi, M., and Vigliargio, A. (1998). The Pomici di Base plinian eruption of Somma-Vesuvius. *J. Volcanol. Geotherm. Res.* 83, 219–239. doi:10.1016/s0377-0273(98)00025-0

Brocchini, D., Principe, C., Castradori, D., Laurenzi, M., and Gorla, L. (2001). Quaternary evolution of the southern sector of the campanian plain and early somma–vesuvius activity: Insights from the trecase 1 well. *Mineral. Pet.* 73, 67–91. doi:10.1007/s007100170011

Burnard, P. (2013). *The noble gases as geochemical tracers*. Berlin Heidelberg: Springer-Verlag.

Chiodini, G., Cioni, R., Magro, G., Marini, L., Panichi, C., Raco, B., et al. (1996). Chemical and isotopic variations of bocca grande fumarole (solfatara volcano, phlegrean fields). *Acta Vulcanol.* 8, 228–232.

Chiodini, G., Marini, L., and Russo, M. (2001). Geochemical evidence for the existence of high-temperature hydrothermal brines at Vesuvio volcano, Italy. *Geochim. Cosmochim. Acta* 65, 2129–2147. doi:10.1016/s0016-7037(01)00583-x

Cioni, R., Civetta, L., Marianelli, P., Metrich, N., Santacroce, R., and Sbrana, A. (1995). Compositional layering and syn-eruptive mixing of a periodically refilled shallow magma chamber: The AD 79 plinian eruption of vesuvius. *J. Petrology* 36, 739–776. doi:10.1093/petrology/36.3.739

Cioni, R., D'Oriano, C., and Bertagnini, A. (2008). Fingerprinting ash deposits of small scale eruptions by their physical and textural features. *J. Volcanol. Geotherm. Res.* 177, 277–287. doi:10.1016/j.jvolgeores.2008.06.003

Cioni, R., Sulpizio, R., and Garruccio, N. (2003). Variability of the eruption dynamics during a subplinian event: The greenish pumice eruption of somma-vesuvius (Italy). *J. Volcanol. Geotherm. Res.* 124, 89–114. doi:10.1016/s0377-0273(03)00070-2

Civetta, L., Galati, R., and Santacroce, R. (1991). Magma mixing and convective compositional layering within the Vesuvius magma chamber. *Bull. Volcanol.* 53, 287–300. doi:10.1007/bf00414525

De Natale, G., Troise, C., Pingue, F., Mastrolorenzo, G., and Pappalardo, L. (2006). The Somma–Vesuvius volcano (southern Italy): Structure, dynamics and hazard evaluation. *Earth. Sci. Rev.* 74, 73–111. doi:10.1016/j.earscirev.2005.08.001

De Vivo, B., Petrosino, P., Lima, A., Rolandi, G., and Belkin, H. E. (2010). Research progress in volcanology in the neapolitan area, southern Italy: A review and some alternative views. *Mineral. Pet.* 99, 1–28. doi:10.1007/s00710-009-0098-6

B. De Vivo, R. Scandone, and R. R. Trigila (Editors) (1993). *Mount Vesuvius: Special issue of J. Volcanol. Geotherm. Res.*, Vol. 58, 1–381.

Di Renzo, V., Di Vito, M. A., Arienzo, I., Carandente, A., Civetta, L., D'Antonio, M., et al. (2007). Magmatic history of Somma–Vesuvius on the basis of new geochemical and isotopic data from a deep borehole (Camaldoli della Torre). *J. Petrology* 48 (4), 753–784. doi:10.1093/petrology/egl081

Federico, C., Aiuppa, A., Allard, P., Bellomo, S., Jean-Baptiste, P., Parello, F., et al. (2002). Magma-derived gas influx and water-rock interactions in the volcanic aquifer of Mt. Vesuvius, Italy. *Geochim. Cosmochim. Acta* 66, 963–981. doi:10.1016/s0016-7037(01)00813-4

Frondini, F., Chiodini, G., Caliro, S., Cardellini, S., Granieri, D., and Ventura, G. (2004). Diffuse CO_2 soil degassing at Vesuvio, Italy. *Bull. Volcanol.* 66, 642–651. doi:10.1007/s00445-004-0346-x

Fulignati, P., Gioncada, A., and Sbrana, A. (1998). The 79AD vesuvius magma chamber: A SEM-EDS study of doughter minerals in hypersaline fluid inclusions from cognate syenites. *N. Jb. Mineral. Abh.* 9, 403–416.

Fulignati, P., Panichi, C., Sbrana, A., Caliro, S., Gioncada, A., and Del Moro, A. (2005). Skarn formation at the walls of the 79AD magma chamber of Vesuvius (Italy): Mineralogical and isotopic constraints. *njma.* 181, 53–66. doi:10.1127/0077-7757/2005/0181-0007

Gasperini, D., Blichert-Toft, J., Bosch, D., Del Moro, A., Macera, P., and Albarède, F. (2002). Upwelling of deep mantle material through a plate window: Evidence from the geochemistry of Italian basaltic volcanics. *J. Geophys. Res.* 107 (B12), ECV 7-1–ECV 7-19. doi:10.1029/2001jb000418

Gilg, H. A., Lima, A., Somma, R., Belkin, H. E., De Vivo, B., and Ayuso, R. A. (2001). Isotope geochemistry and fluid inclusion study of skarns from Vesuvius. *Mineral. Pet.* 73, 145–176. doi:10.1007/s007100170015

Graham, D. W., Allard, P., Kilburn, C. R. J., Spera, F. J., and Lupton, J. E. (1993). Helium isotopes in some historical lavas from Mount Vesuvius. *J. Volcanol. Geotherm. Res.* 58, 359–366. doi:10.1016/0377-0273(93)90117-a

Graham, D. W., and Lupton, J. E. (1999). Helium isotopes in historical lavas from Mount Vesuvius. *Earth Planet. Sci. Lett.* 174, 241–244. doi:10.1016/s0012-821x(99)00268-x

Hilton, D. R., Barling, J., and Wheller, G. E. (1995). Effect of shallow-level contamination on the helium isotope systematics of ocean-island lavas. *Nature* 373, 330–333.

Hilton, D. R., Fischer, T. P., and Marty, B. (2002). "Noble gases and volatile recycling at subduction zones," in *Noble gases in geochemistry and cosmochemistry*. Editors D. P. Porcelli, C. J. Ballentine, and R. Wieler (Washington, DC: Reviews in Mineralogy and Geochemistry), Vol. 47, 319–370.

Hilton, D. R., Hammerschmidt, K., Loock, G., and Friedrichsen, H. (1993a). Helium and argon isotope systematics of the central Lau Basin and Valu Fa Ridge: Evidence of crust/mantle interactions in a back-arc basin. *Geochim. Cosmochim. Acta* 57, 2819–2841. doi:10.1016/0016-7037(93)90392-a

Hilton, D. R., Hammerschmidt, K., Teufel, S., and Friedrichsen, H. (1993b). Helium isotope characteristics of Andean geothermal fluids and lavas. *Earth Planet. Sci. Lett.* 120, 265–282. doi:10.1016/0012-821x(93)90244-4

Iacono-Marziano, G., Gaillard, F., and Pichavant, M. (2008). Limestone assimilation by basaltic magmas: An experimental re-assessment and application to Italian volcanoes. *Contrib. Mineral. Pet.* 155, 719–738. doi:10.1007/s00410-007-0267-8

Iacono-Marziano, G., Gaillard, F., Scaillet, B., Pichavant, M., and Chiodini, G. (2009). Role of non-mantle CO_2 in the dynamics of volcano degassing: The Mount Vesuvius example. *Geology* 37, 319–322. doi:10.1130/g25446a.1

Improta, L., and Corciulo, M. (2006). Controlled source nonlinear tomography: A powerful tool to constrain tectonic models of the southern apennines orogenic wedge, Italy. *Geol.* 34, 941–944. doi:10.1130/g22676a.1

Joron, J. L., Metrich, N., Rosi, M., Santocroce, R., and Sbrana, A. (1987). "Chemistry and petrography," in *Somma-vesuvius*. Editor R. Santacroce (Rome, Italy: CNR, Quaderni De La Ricerca Scientifica), Vol. 114, 105–174.

Kurz, M. D., JenkinsSchilling, W. J, J. G., and Hart, S. R. (1982). Helium isotopic variations in the mantle beneath the central North Atlantic Ocean. *Earth Planet. Sci. Lett.* 58, 1–14. doi:10.1016/0012-821x(82)90099-1

Macdonald, R., Baginski, B., Rolandi, G., De Vivo, B., and Kopczynska, A. (2016). Petrology of parasitic and eccentric cones on the flanks and base of Somma-Vesuvius. *Min. Pet.* 110, 65–85. doi:10.1007/s00710-015-0410-6

Magro, G., Ruggieri, G., Gianelli, G., Bellani, S., and Scandiffio, G. (2003). Helium isotopes in paleofluids and present-day fluids of the Larderello geothermal field: Constraints on the heat source. *J. Geophys. Res.* 108, ECV 3-1–ECV 3-12. doi:10.1029/2001jb001590

Mamyrin, B. A., and Tolstikhin, I. N. (1984). *Helium isotopes in nature*. Amsterdam, Netherlands: Elsevier, 273.

Martelli, M., Nuccio, P. M., Stuart, F. M., Burgess, R., Ellam, R. M., and Italiano, F. (2004). Helium–strontium isotope constraints on mantle evolution beneath the Roman Comagmatic Province, Italy. *Earth Planet. Sci. Lett.* 224, 295–308. doi:10.1016/j.epsl.2004.05.025

Martelli, M., Nuccio, P. M., Stuart, F. M., Di Liberto, V., and Ellam, R. M. (2008). Constraints on mantle source and interactions from He-Sr isotope variation in Italian Plio-Quaternary volcanism. *Geochem. Geophys. Geosyst.* 9, Q02001. doi:10.1029/2007GC001730

Marty, B., Trull, T., Lussiez, P., Basile, I., and Tanguy, J. C. (1994). He, Ar, O, Sr and Nd isotope constraints on the origin and evolution of Mount Etna magmatism. *Earth Planet. Sci. Lett.* 126, 23–39. doi:10.1016/0012-821x(94)90240-2

Mele, D., Sulpizio, R., Dellino, P. F., and La Volpe, L. (2011). Stratigraphy and eruptive dynamics of a pulsating plinian eruption of somma-vesuvius: The Pomici di Mercato (8900 years B.P.). *Bull. Volcanol.* 73, 257–278. doi:10.1007/s00445-010-0407-2

Montone, P., Amato, A., and Pondrelli, S. (1999). Active stress map of Italy. *J. Geophys. Res.* 104, 25595–25610. doi:10.1029/1999jb900181

Morgan, D. J., Blake, S., Rogers, N. W., DeVivo, B., Rolandi, G., Macdonald, R., et al. (2004). Time scales of crystal residence and magma chamber volume from modelling of diffusion profiles in phenocrysts: Vesuvius 1944. *Earth Planet. Sci. Lett.* 222, 933–946. doi:10.1016/j.epsl.2004.03.030

Ozima, M., and Podosek, F. A. (1983). *Noble gas geochemistry*. Cambridge: Cambridge University Press.

Paolillo, A., Principe, C., Bisson, M., Gianardi, R., Giordano, D., and La Felice, S. (2016). Volcanology of the southwestern sector of Vesuvius volcano, Italy. *J. Maps* 12, 425–440. doi:10.1080/17445647.2016.1234982

Pappalardo, L., and Mastrolorenzo, G. (2010). Short residence times for alkaline Vesuvius magmas in a multi-depth supply system: Evidence from geochemical and textural studies. *Earth Planet. Sci. Lett.* 296, 133–143. doi:10.1016/j.epsl.2010.05.010

Pappalardo, L., Piochi, M., and Mastrolorenzo, G. (2004). The 3800 yr BP–1944 AD magma plumbing system of somma-vesuvius: Constraints on its behaviour and present satte through a review of isotope data. *Ann. Geophys.* 47, 1363–1375.

Parello, F., Allard, P., D'Alessandro, W., Federico, C., Jean-Baptiste, P., and Catani, O. (2000). Isotope geochemistry of Pantelleria volcanic fluids, sicily channel rift: A mantle volatile end-member for volcanism in southern europe. *Earth Planet. Sci. Lett.* 180, 325–339. doi:10.1016/s0012-821x(00)00183-7

Pascal, M. L., Di Muro, A., Fonteilles, M., and Principe, C. (2009). Zirconolite and calzirtite in banded fosterite-spinel-calcite skarn ejecta from vesuvius 1631 eruption: Inferences for the magma-wallrock interactions. *Mineral. Mag.* 73 (1), 149–172.

Peccerillo, A. (2020). "Campania volcanoes: Petrology, geochemistry, and geodynamic significance." in *Vesuvius, campi flegrei, and campanian volcanism*. Editor B. De Vivo, H. E. Belkin, and G. Rolandi (Amsterdam, Netherlands: Elsevier), 79–120.

Pichavant, M., Scaillet, B., Pommier, A., Iacono-Marziano, G., and Cioni, R. (2014). Nature and evolution of primitive vesuvius magmas: An experimental study. *J. Petrology* 55, 2281–2310. doi:10.1093/petrology/egu057

Pineau, F., Shilobreeva, S., Hekinian, R., Bideau, D., and Javoy, M. (2004). deep-sea explosive activity on the mid-atlantic ridge near 34°50′N: A stable isotope (C, H, O) study. *Chem. Geol.* 211, 159–175. doi:10.1016/j.chemgeo.2004.06.029

Piochi, M., Ayuso, R. A., De Vivo, B., and Somma, R. (2006). Crustal contamination and crystal entrapment during polybaric magma evolution at Mt. Somma–Vesuvius volcano, Italy: Geochemical and Sr isotope evidence. *Lithos* 86, 303–329. doi:10.1016/j.lithos.2005.05.009

Porcelli, D., Ballentine, C. J., and Wieler, R. (2002). An overview of noble gas geochemistry and cosmochemistry. *Rev. Mineralogy Geochem.* 47, 1–19. doi:10.2138/rmg.2002.47.1

Poreda, R., and Craig, H. (1989). Helium isotope ratios in circum-Pacific volcanic arcs. *Nature* 338, 473–478. doi:10.1038/338473a0

Principe, C., Paolillo, A., La Felice, S., and Arrighi, S. (2021). "Forma vesuvii-2 volcanic morphology at the time of the 79AD plinian eruption," in *Physis*. Editor L. Olschki, 289–303. Firenze. 2021/1-2 (LVI).

Principe, C., Tanguy, J. C., Arrighi, S., Paiotti, A., Le Goff, M., and Zoppi, U. (2004). Chronology of Vesuvius' activity from AD 79 to 1631 based on archeomagnetism of lavas and historical sources. *Bull. Volcanol.* 66, 703–724. doi:10.1007/s00445-004-0348-8

Ricco, C., Petrosino, S., Aquino, I., Cusano, P., and Madonia, P. (2021). Tracking the recent dynamics of Mt. Vesuvius from joint investigations of ground deformation, seismicity and geofluid circulation. *Sci. Rep.* 11, 965. doi:10.1038/s41598-020-79636-w

M. Rosi and A. Sbrana (Editors) (1987). *Phlegraean fields* (Roma: Collana Quaderni della Ricerca Scientifica, Consiglio Nazionale delle Ricerche), 175.

Sano, Y., Wakita, H., Italiano, F., and Nuccio, M. P. (1989). Helium isotopes and tectonics in southern Italy. *Geophys. Res. Lett.* 16, 511–514. doi:10.1029/gl016i006p00511

Scaillet, B., Pichavant, M., and Cioni, R. (2008). Upward migration of Vesuvius magma chamber over the past 20, 000 years. *Nature* 455, 216–219. doi:10.1038/nature07232

Scandone, P. (1979). Origin of the Tyrrhenian Sea and calabrian arc. *Boll. Soc. Geol. It.* 98, 27–34.

Scheibner, B., Heumann, A., and Wörner, C. L. (2008). Crustal residence times of explosive phonolite magmas: U–Th ages of magmatic Ca-garnets of Mt. Somma-vesuvius (Italy). *Earth Planet. Sci. Lett.* 276, 293–301. doi:10.1016/j.epsl.2008.09.028

Shaw, A. M., Hilton, D. R., Fisher, T. P., Walker, J. A., and de Leew, G. A. M. (2006). Helium isotope variations in mineral separates from Costa Rica and Nicaragua: Assessing crustal contributions, timescale variations and diffusion-related mechanisms. *Chem. Geol.* 230, 124–139. doi:10.1016/j.chemgeo.2005.12.003

Stoppa, F., Principe, C., Schiazza, M., Liu, Y., Giosa, P., and Crocetti, S. (2017). Magma evolution inside the 1631 Vesuvius magma chamber and eruption triggering. *Open Geosci.* 9, 24–52. doi:10.1515/geo-2017-0003

Tedesco, D., Allard, P., Sano, Y., Wakita, H., and Pece, R. (1990). Helium-3 in subaerial and submarine fumaroles of Campi Flegrei caldera, Italy. *Geochim. Cosmochim. Acta* 54, 1105–1116. doi:10.1016/0016-7037(90)90442-n

Tedesco, D. (1997). Systematic variations in the 3He/4He ratio and carbon fumarolic fluids from active volcanic areas in Italy: Evidence for radiogenic 4He and crustal carbon addition by the subducting African plate? *Earth and Planetary Science Letters* 151, 255–269.

Tedesco, D., and Scarsi, P. (1999). Chemical (He, H_2, CH_4, Ne, Ar, N_2) and isotopic (He, Ne, Ar, C) variations at the solfatara crater (southern Italy): Mixing of different sources in relation to seismic activity. *Earth Planet. Sci. Lett.* 171, 465–480. doi:10.1016/s0012-821x(99)00137-5

Trull, T. W., and Kurz, M. D. (1993). Diffusivity of ^{3}He and ^{4}He in olivine and clinopyroxene at magmatic and mantle temperatures. *Geochim. Cosmochim. Acta* 57, 1313–1324. doi:10.1016/0016-7037(93)90068-8

Turco, E., Schettino, A., Pierantoni, P. P., and Santarelli, G. (2006). "The Pleistocene extension of the Campania plain in the framework of the southern tyrrhenian tectonic evolution: Morphotectonic analysis, kinematic model and implications for volcanism," in *Developments in volcanology*. *Developments in volcanology*. Editor B. De Vivo, Vol. 9, 27–51.

Valley, J. W. (1986). "Stable isotope geochemistry of metamorphic rocks," in *Stable isotopes in high temperature geological processes. Reviews in mineralogy*. Editors J. W. Valley, H. P. TaylorJr., and J. R. O'Neil, Vol. 16, 445–489.

Woolley, R. A., Bailey, D. K., Castorina, F., Rosatelli, G., Stoppa, F., and Wall, F. (2005). Reply to: "Carbonate-rich pyroclastic rocks from central apennines: Carbonatites or carbonated rocks? A commentary". A. Peccerillo. *Period. Mineral.* 74 (3), 183–194.