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# Revealing magma degassing below closed-conduit active volcanoes: Geochemical features of volcanic rocks versus fumarolic fluids at Vulcano (Aeolian Islands, Italy)



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# ABSTRACT

The elemental and isotopic compositions of noble gases (He, Ne, and Ar) in olivine- and clinopyroxene-hosted fluid inclusions have been measured for rocks at various degrees of evolution and belonging to high-K calcalkaline-shoshonitic and shoshonitic-potassic series in order to cover the entire volcanological history of Vulcano Island (Italy). The major- and trace-element concentrations and the Sr- and Pb-isotope compositions for whole rocks were integrated with data obtained from the fluid inclusions. <sup>3</sup>He/<sup>4</sup>He in fluid inclusions is within the range of 3.30 and 5.94 R/Ra, being lower than the theoretical value for the deep magmatic source expected for Vulcano Island (6.0–6.2 R/Ra). <sup>3</sup>He/<sup>4</sup>He of the magmatic source is almost constant throughout the volcanic history of Vulcano. Integration of the He- and Sr-isotope systematics leads to the conclusion that a decrease in the Heisotope ratio of the rocks is mainly due to the assimilation of 10–25% of a crustal component similar to the Calabrian basement. <sup>3</sup>He/<sup>4</sup>He shows a negative correlation with Sr isotopes except for the last-erupted Vulcanello latites (Punta del Roveto), which have anomalously high He isotope ratios. This anomaly has been attributed to a flushing process by fluids coming from the deepest reservoirs, since an input of deep magmatic volatiles with high <sup>3</sup>He/<sup>4</sup>He values increases the He-isotope ratio without changing <sup>87</sup>Sr/<sup>86</sup>Sr. A comparison of the He-isotope ratios between fluid inclusions and fumarolic gases shows that only the basalts of La Sommata and the latites of Vulcanello have comparable values. Taking into account that the latites of Vulcanello relate to one of the most-recent eruptions at Vulcano (in the 17th century), we infer that the most probable magma which actually feeds the fumarolic emissions is a latitic body that ponded at about 3–3.5 km of depth and is flushed by fluids coming from a deeper and basic magma.

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# 1. Introduction

Volcanoes that exhibit explosive activity can also undergo periods of quiescence lasting from hundreds to thousands of years, during which the magmas can experience closed-system storage conditions. During these long-lasting phases, volcanic degassing mainly occurs via fumarolic activity at the crater bottom and/or flanks, in addition to diffuse soil degassing and hydrothermal circulation. This activity testifies to the presence of magmas that exsolve volatiles at depth and are likely to lead to future increases in the volcanic activity. Hence, an increased awareness of these degassing magma bodies is of primary importance to volcanic surveillance. The main questions to be addressed relate to the localization, composition, and volatile contents of the magma bodies that feed the volcanic degassing. All of these features

\* Corresponding author. E-mail address: antonio.paonita@ingv.it (A. Paonita). can be interdependent and have a strong impact on the magnitude and type of the expected eruptive events (Parfitt and Wilson, 2008).

The volcanic system of Vulcano (Aeolian Islands, Italy) is a suitable natural laboratory for exploring this topic. The last eruptive event at Vulcano occurred during 1888–1890 AD, and since this time the volcano has been in a state of quiescence, with volcanic manifestations mainly characterized by intense exhalations and moderate seismic activity related to the migration of magmatic and hydrothermal fluids (Cannata et al., 2011; Peccerillo et al., 2006). There have been several phases of unrest since the last eruption, as testified by geochemical anomalies measured in fumarolic gases emitted at the La Fossa cone. Various authors have attributed this unrest to an increasing contribution of fluids coming from magmas at depth (Chiodini et al., 2000; Nuccio et al., 1999; Paonita et al., 2002, 2013; Taran, 2011). With the aim of understanding the types of magma involved in these deep dynamics, several geochemical and petrological studies have been carried out (Clocchiatti et al., 1994a; Granieri et al., 2006; Magro, 1997;



Nuccio et al., 1999; Paonita et al., 2002, 2013). The results have suggested that the compositions of these degassing magmas can range from basaltic to intermediate, although Paonita et al. (2013) recently constrained the composition to latite.

The most intriguing goal of this work is the search for relationships between the magma that is actually degassing within the plumbing system and the fumarolic fluids. A comparison between the composition of the volatiles entrapped in erupted products and that of the fumarolic fluids has been conducted in order to achieve this. Attention has been focused on He isotopes, which are regarded to be the best tracers of magma-derived fluids and make it possible to obtain a posteriori information on magmatic conditions before an eruptive event (Hilton et al., 2002; Marty et al., 1994; Nuccio et al., 2008). In this regard, a large set of He isotopic data of the fumarolic fluids are already available from previous studies (Tedesco and Nagao, 1996; Capasso et al., 1997; Nuccio et al., 1999; Nuccio and Paonita, 2001; Tedesco and Scarsi, 1999; Paonita et al., 2002, 2013; Taran, 2011). Measurements of the elemental and isotopic compositions of He and Ar retained in fluid inclusions hosted by mafic minerals-together with the major and trace elements and the Sr- and Pb-isotope ratios for the whole rocks-have been obtained from rocks at different evolutionary degree (from basalt to trachyte), covering all of the main stages of volcanic activity at Vulcano Island. The data obtained in the present study extend and complete the data set reported by Magro (1997) and Martelli et al. (2008). The new results presented here suggest the presence of a wellstructured feeding system that is characterized by small and shallow batches of latitic magmas flushed by volatiles coming from a deep magma chamber with a basaltic composition.

## 2. Geological and volcanological setting

#### 2.1. Geology and petrology

Vulcano is the southernmost island of the Aeolian Islands, a Quaternary volcanic arc generated by subduction of the oceanic Ionian plate underneath the Calabrian arc (Finetti and Del Ben, 1986). The Aeolian Islands are located on 15- to 20-km-thick continental crust (Peccerillo et al., 2006) related to the Hercynian metamorphic and granitic rocks and Mesozoic sediments of the Calabrian basement (Del Moro et al., 1998; Frezzotti et al., 2004; Keller, 1980). Vulcano is part of a volcanic complex including Lipari Island that has developed inside a graben-like structure controlled by the NNW–SSE strike-slip Tindari–Letojanni fault system (Gioncada et al., 2003; Ventura, 2013).

The subaerial volcanic activity at Vulcano started at about 120-100 ka (Keller, 1980) in the southern sector of the island with the building of Primordial Vulcano stratocone. A volcano tectonic collapse occurred at 100 ka that led to the formation of the Piano Caldera (Keller, 1980), where intracaldera activity took place until 21 ka. Poorly evolved products belonging to the high-K calcalkaline (HKCA) and shoshonitic (SHO) series were emitted during these two stages of activity, whereas more-evolved rocks erupted during the emplacement of rhyolitic domes and trachytic lava flows of the Lentia Complex between 25 and 15 ka (De Astis et al., 1997, 2013; Keller, 1980). After the collapse of the Lentia domes at 15 ka, phreatomagmatic activity shifted toward the north, with the formation of several vents active along an N-S direction (Saraceno, La Fossa cone, Faraglione, and Vulcanello), with the emission of volcanic products with compositions varying from latitic to rhyolitic [SHO and potassic (KS) series], and only minor amounts of shoshonites (De Astis et al., 1997; Gioncada et al., 2003; Keller, 1980). The La Fossa cone formed at about 5.5 ka through accretion due to the deposition of pyroclastic products and minor lava flows. The Vulcanello peninsula is a 123-m-high composite edifice comprising a shoshonitic to latitic lava platform and three partially overlapping scoria cones aligned in an NE-SW direction along the northern ring fault of the La Fossa caldera (Davì et al., 2009a; De Astis et al., 2013). Although the age of Vulcanello products is still debated, some recent studies using archaeomagnetic investigations have suggested that the lava platform was built up during continuous volcanic activity from 1100 to 1250 AD (Arrighi et al., 2006; Davì et al., 2009a; Di Traglia et al., 2013 and references therein). The three stratocones at Vulcanello formed between  $1050 \pm 70$  AD and the 17th century (Fusillo et al., 2015 and references therein). The last eruption at Vulcano Island occurred during 1888–1890, with the characteristic eruptive activity defined as "Vulcanian" by Mercalli and Silvestri (1891).

## 2.2. Geochemistry of fluids

Vulcano Island is currently in a state of intense fumarole activity chiefly localized in the northern rim of the La Fossa cone and in the area of Baia Levante, while CO<sub>2</sub> soil degassing occurs around the cone (Capasso et al., 1997; Inguaggiato et al., 2012). These manifestations are characterized by gas emissions with differing temperature and chemical compositions. The fluids emitted from the fumarole field at the La Fossa crater are characterized by high temperatures (100–450 °C) and a typical magmatic origin with high concentrations of CO<sub>2</sub>, N<sub>2</sub>, and He, and  $\delta^{13}C_{CO2}$  of near to 0‰ versus PDB. The fumaroles at Vulcano Porto have low emission temperatures (<100 °C) and compositions that are more typical of hydrothermal systems rich in H<sub>2</sub>O, CH<sub>4</sub>, and H<sub>2</sub>S, and more positive values of  $\delta D_{H2O}$  (Capasso et al., 1997; Nuccio et al., 1999; Nuccio and Paonita, 2001; Paonita et al., 2002, 2013; Granieri et al., 2006). The geochemical and isotopic compositions of these gas emissions underwent large fluctuations during the last century reflecting potential volcanic unrest. There was an important period of anomalous degassing during 1988–1993, which saw intensification of the output rate of magmatic gases and expansion of the fumarole field that was coupled to the temperature of the fumarolic fluids increasing to 690 °C (Italiano et al., 1998). Similar events, although minor in extent, occurred in 1996, 1998, 2004-2005, and 2009 (Granieri et al., 2006; Paonita et al., 2013).

#### 3. Sample descriptions and laboratory techniques

#### 3.1. Rock samples

The analyzed products consist of eight lavas and tephra samples selected to cover the main stages of activity at Vulcano and the different evolutionary degrees of the rocks (De Astis et al., 2006). Generally, noble gas studies are performed on mafic minerals since they tend to retain the volatiles entrapped during their growth (e.g., Marty et al., 1994). We selected rock samples having highly porphyritic textures and large amounts of pyroxenes and olivines. The locations of the analyzed rocks are shown in Fig. 1, and they are described briefly as follows:

- a) The Capo Grillo formation (CG sample) belongs to the Primordial Vulcano stage of activity; it consists of porphyritic lava flows that erupted at ~110 ka, and has compositions varying from basalticandesite to shoshonite (De Astis et al., 2006).
- b) The Passo del Piano lava (PP sample) and La Sommata scoriae (SOM sample) erupted at 49 and 42 ka, respectively, and represent the infill products of the Piano Caldera. These samples are the most-basic rocks of the island, with MgO > 7 wt.% (De Astis et al., 1997; Keller, 1980).
- c) Piano Grotte dei Rossi (PGR sample) is a pyroclastic deposit generated from activity at the La Fossa caldera at ~18 ka. This deposit is characterized by a massive matrix rich in augitic clinopyroxenes larger than 1 cm, which probably derives from a crystal mush (De Astis et al., 1997; Keller, 1980).
- d) For the activity of the La Fossa cone during the last 1000 years, we selected the following three rock samples with SHO and KS

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