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# Mantle-derived fluids discharged at the Bradanic foredeep/Apulian foreland boundary: The Maschito geothermal gas emissions (southern Italy)

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## ABSTRACT

The mephitis of Maschito, known since historical times as Lago Fetente (Smelly Lake) -although the lake is now dry-, is located 20 km from the Mt. Vulture volcanic edifice (Southern Italy). It is placed along the same regional tectonic discontinuity where some maars are located, close to the boundary between the foredeep and the Apulian foreland. About 300 m<sup>2</sup> of surface is lacking in flora, while dead animals are frequently found all around it. The smelly exhalations are mainly composed of  $CO_2$  (~98%), and, in lesser amounts, of H<sub>2</sub>S, N<sub>2</sub>, CH<sub>4</sub> and other hydrocarbons. He, Ne and Ar occur in trace amounts. The CO<sub>2</sub> isotopic composition is in the range of that of the main active Italian volcanic gases. The helium isotopic ratio (4.7 Ra) fits with the values measured in Mt. Vulture volcano and particularly with the olivine and pyroxene fluid inclusions of mantle xenoliths ejected during its last volcanic activity (140,000 years). The  $^{40}$ Ar/ $^{36}$ Ar isotopic ratio of ~320 supports some minor non-atmospheric contributions. The C/ $^{3}$ He ratio  $(2.9 \times 10^9)$  is in the typical range of magma released fluids, while  $\delta^{13}C_{(CH_4)}$  and  $\delta D_{(CH_4)}$  values fall in the field of thermogenic methane.

The amount of CO<sub>2</sub> released is about 3200 tons/year. The flux of mantle-derived helium  $(>7 \times 10^{10} \text{ atoms m}^{-2} \text{ s}^{-1})$  is at least three orders of magnitude higher than that of a stable continental crust. This study strongly supports the possibility that Maschito manifestations are fed by a geothermal system, which is powered by a degassing melt, bearing in mind that the Maschito gas emissions fall along the same fault system of the Monticchio maars, which formed during Mt. Vulture volcano's last activity. © 2014 Elsevier Ltd. All rights reserved.

### 1. Introduction

Several non-volcanic gaseous manifestations have occurred along the Apennines from north to south (e.g., Italiano et al., 2001; Minissale, 2004; Caracausi et al., 2013), which geologically represent the accretionary prism of the westward subduction of the Adriatic plate (Doglioni et al., 1996). These gases are generally CO<sub>2</sub>dominated and are localized in the southern sector of the chain (Italiano et al., 2000).

The geothermal gradient displays a regular increase from east  $(20 \text{ °C } \text{km}^{-1})$  to west  $(35 \text{ °C } \text{km}^{-1})$  over quite a long strip of land that crosses the southern Apennines (Mongelli et al., 1996). Nevertheless, two small positive anomalies in the geothermal

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gradient have been recognized: the first one is at Mt. Vulture volcano (more than 40 °C km<sup>-1</sup>), the second one is at the intersection of the main faults of the 1980 Irpinia earthquake (more than 100 °C km<sup>-1</sup>). Geochemical and geophysical data coherently indicate accumulations of mantle-derived melts in the crust below the southern Apennines and their degassing through the main lithospheric faults (Italiano et al., 2000).

Recently, Caracausi et al. (2008, 2013) highlighted that active degassing of mantle-derived He occurs in the region of Mt. Vulture and along the Vulture line (D'Orazio et al., 2007), which crosses the southern Apennines from east to west, reinforcing the hypothesis of an advective ascent of mantle fluids (and/or melts) through deep tectonic discontinuities.

The Maschito Mephitis, known since historical times as lake Fetente (Smelling lake), is located 20 km from the Mt. Vulture volcanic edifice (southern Italy). Despite the name suggests the presence of a lake, no water is actually present. Instead, there is a surface of about 300 m<sup>2</sup>, characterized by smelly exhalations and









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lacking in flora (Fig. 1), where dead animals are frequently found all around it. It is located along a regional tectonic discontinuity connected to Mt. Vulture and close to the boundary between the foredeep and the Apulian foreland.

In this paper we report the results of the geochemical investigations we carried out on this exhaling area with the aim of clarifying the characteristics and origin of the gases released and their meaning in the tectonic framework of the region.

## 2. Sampling and analytical methods

Gases were sampled four times between 2005 and 2011. Chemical and isotopic analyses of fluids were performed at Istituto Nazionale di Geofisica e Vulcanologia (INGV-Palermo). Gases were analysed by double detector (TCD-FID) Perkin Elmer Autosystem XL gas chromatograph using Ar as carrier gas and on a 4-m column (Carbosieve SII) and double detector (TCD and FID). The detection limits were 500 ppm vol. for O<sub>2</sub> and 1 ppm vol. for CH<sub>4</sub>. The analytical error was about  $\pm 3\%$  for all species. The abundances of dissolved He were measured in a split-flight-tube mass spectrometer (Helix SFT) equipped with a purification line for separating noble gases from the gaseous mixture (Nuccio et al., 2008). The <sup>3</sup>He/<sup>4</sup>He were measured in a split-flight-tube mass spectrometer (GVI Helix SFT). Ion beams of <sup>3</sup>He and <sup>4</sup>He were simultaneously detected by a double collector system that yielded isotopic ratio precision within  $\pm 0.5\%$ . Purified atmospheric helium was used as a running standard. <sup>4</sup>He/<sup>20</sup>Ne ratios were measured with a quadrupole mass spectrometer. Argon isotopes were analysed in a multicollector mass spectrometer (Argus). The analytical errors of the He- and Ar-isotope analyses were less than 3% and 7%respectively.

The carbon isotope composition of carbon dioxide was measured by using a Thermo Delta XP IRMS (analytical error is  $\pm 0.15\%$ ) coupled with TRACE GC gas-chromatograph, separated

using a 30 m Q-plot column (i.d. 0.32 mm).  $\delta^{13}\text{C}$  values are per mil vs. V-PDB.

The carbon and hydrogen isotope analyses of methane were executed by a Delta Plus XP CF-IRMS (Thermo, Bremen, Germany) coupled with a TRACE 2000 GC equipped with a Poraplot-Q (Superchrom) capillary column (i.d. 30 m × 0.32 mm) and using a flux of 0.8 cc min<sup>-1</sup> of pure helium (5.6 grade) as gas carrier. GC III combustion interfaces were used to produce carbon dioxide from methane. High-temperature conversions (GC-TC interface) provide on-line methane conversion to hydrogen gas suitable for isotope analyses. The analytical errors on  $\delta^{13}$ C and  $\delta$ D are  $\pm 1\%$  and  $\pm 2\%$  respectively.

Gas-chromatographic analyses of light hydrocarbons were performed by means of a Shimadzu 2010 equipped with Poraplot Q column (length 27.5 m, internal diameter 0.32 mm), FID detector and He as carrier. Analytic error is  $\pm$ 5%.

The soil CO<sub>2</sub> measurements were carried out with the portable flux-meter (West Systems), based on the accumulation chamber method (Chiodini et al., 1998), equipped with a detector LI-COR infrared sensor for CO<sub>2</sub>. Measurements were performed at nodes of an almost regular grid of 16 nodes over an investigated surface of 266 m<sup>2</sup> Geographic coordinates of nodes were gained by using a hand held GPS receiver.

The CO<sub>2</sub> flux was computed by applying the surface and volume calculation modules of Golden Software Surfer (release 9) to the isoflux contour map, generated by the software with the kriging algorithm. The estimated overall error is within  $\pm 20\%$ .

#### 3. Results and discussion

#### 3.1. Geochemistry of fluids

Tables 1 and 2 report He, Ar, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>. CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>10</sub> abundances and  ${}^{3}\text{He}/{}^{4}\text{He}$ ,  ${}^{20}\text{Ne}/{}^{4}\text{Ne}$ ,  ${}^{40}\text{Ar}/{}^{36}\text{Ar}$  ratios and



Figure 1. The red lines are a system of faults linking the Maschito area to the Monticchio maar lakes of Mt. Vulture volcano. In the right box: The exhaling area of Lago Fetente (Smelly Lake), characterized by absence of vegetation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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