

**MT. VULTURE VOLCANO (ITALY): A GEOCHEMICAL CONTRIBUTION TO THE ORIGIN OF FLUIDS AND TO A BETTER DEFINITION OF ITS GEODYNAMIC SETTING**

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INTRODUCTION

Mt. Vulture is located in the most external part of the Apennine orogene (Southern Italy), almost at the edge of the Apulian foreland. It is a complex strato-volcano with several eccentric eruption centres mostly situated in the peripheral areas. The volcanic products cover an area of about 150 km<sup>2</sup> and are the result of both explosive and effusive activity which occurred from the Middle Pleistocene to the Upper Pleistocene (Serri et al., 2001). Compared to the other volcanoes of central-southern Italy (Roman Comagmatic Province in this work called RCP, Aeolian Archipelago) that are more or less scattered along the Tyrrhenian margin of the Italian peninsula, it is the only volcano that is located to the east of the Apennine chain. The latter was generated as a consequence of the westward subduction of the Ionian-Adria plate and the opening of the Tyrrhenian back-arc basin (Doglioni et al., 1999). Previous investigations were carried on the He, Sr and C isotopes of the Italian volcanics in order to investigate the characteristics of the mantle (Marty et al., 1994; Di Liberto, 2003; Martelli et al., 2004). Although several studies have been carried out in the last two decades, Mt. Vulture is relatively poorly known and its geodynamic significance is still a puzzle.

The study of the fluid inclusions in phenocrysts of mafic volcanics, may furnish extremely significant information for the characterization of the magma evolution at depth and for the recognition of processes that have affected the mantle, as they represent the fluid phase present in the magma at the moment of crystallization. In particular, by combining appropriate geochemical parameters episodes of partial melting, contaminations by addition of subducted crustal material or metasomatic fluids, etc., can be interpreted (see Hilton et al., 2001 for review).

The aim of this study is to provide a contribution to a better definition of the magmatism of the Mt. Vulture volcano and to its geodynamic meaning, by means of the He isotopes (<sup>3</sup>He/<sup>4</sup>He in water and gases and in the fluid inclusions of both olivines and pyroxenes) and C isotopes ( $\delta^{13}\text{C}_{\text{CO}_2}$  in free gases and  $\delta^{13}\text{C}_{\text{TDC}}$  in the waters), Sr isotopes (<sup>87</sup>Sr/<sup>86</sup>Sr in the whole-rock and in the pyroxenes), together with the distribution of the trace elements in the sampled volcanics.

We sampled lavas and pyroclastics having different ages, in order to obtain a general overview of the He isotopic composition during the evolution of Mount Vulture magmatism. However we focused our attention on the last volcanic event, dating back 130 Ka (Monticchio lakes Unit -6°UVS). Twenty-five groundwater samples were also collected with the aim of gaining information about the state of mantle fluid outgassing in the area and the water/rock interaction. The sampling sites were located almost uniformly over the studied area and were selected on the basis of peculiar hydrogeochemical features, fluid flow values and their distribution in relation to the tectonic lineaments and structures.

## RESULTS AND DISCUSSION

### *Fluids*

The geochemical characters of the Mt. Vulture groundwaters suggest that the process of water-rock interaction is mainly controlled by the addition of CO<sub>2</sub>. The C-He isotopic data suggest a common magmatic origin for CO<sub>2</sub> and He. The sampled groundwaters and bubbling gas contain mantle-derived He, variably diluted by air. The pure mantle-endmember is inferred to have a <sup>3</sup>He/<sup>4</sup>He ratio of ~ 6.0 Ra. This component is associated with CO<sub>2</sub> having a δ<sup>13</sup>C<sub>CO2</sub> values of about -4.2 ‰, vs. PDB, which is typical of the Mediterranean mantle-derived carbon.

The dissolution of CO<sub>2</sub> in water causes a substantial increase in its acidity and promotes the alteration of the rocks. There is a good correlation among alkalinity, electric conductivity and Na<sup>+</sup>, Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> concentrations. The waters, having chemical compositions between alkaline-earth-bicarbonate and alkaline-bicarbonate, represent the final result of this process. During their ascent to the surface, magmatic gases interact in different ways with the aquifers, changing their concentrations as a result of the preferential dissolution of CO<sub>2</sub>. Most of the CO<sub>2</sub>-rich springs of the investigated area are located on the west side of Mt. Vulture, near to the Valle dei Grigi-Fosso del Corbo tectonic structure and on the south-east side. Therefore these tectonic structures, that affect both the sedimentary pre-volcanic terrains and volcanic deposits, act as a preferential channel for the uprising CO<sub>2</sub>-rich gases.

### *Gas budget of mantle origin*

The budget of equivalent total CO<sub>2</sub> (expressed in mol/yr) has been estimated for Mt. Vulture aquifers taking into account both the HCO<sub>3</sub><sup>-</sup> and the CO<sub>2</sub> contents and the water outflows. The selected springs and wells gave us a representative set of chemical and isotopic data.

δ<sup>13</sup>C<sub>TDC</sub> values clearly suggest the presence of two carbon sources. The first one is biogenic CO<sub>2</sub>, while the second one is has deep inorganic origin. According to Chiodini et al. (2004), a mean value of 0.0022 mol/l can be assumed as being a representative value of biogenic CO<sub>2</sub> for all the recharge waters of the Apennines, which gives an estimate of organic CO<sub>2</sub> of 7.60x10<sup>6</sup> mol/yr for the investigated groundwaters of the Mt. Vulture area. Therefore, taking into account that the atmospheric contribution of bicarbonate is negligible, we obtained the

amount of deep inorganic CO<sub>2</sub> of about 2.77x10<sup>8</sup> mol/yr by subtracting that amount from the measured total budget of CO<sub>2</sub> (2.84x10<sup>8</sup> mol/yr).

The budget of <sup>3</sup>He has been calculated taking into account the <sup>3</sup>He/<sup>4</sup>He ratio, the He/CO<sub>2</sub> ratio, the CO<sub>2</sub> contents and the water outflows. The estimated total amount of deep CO<sub>2</sub> (0.21 ÷ 0.31 Mton/yr) and of mantle helium (3.1x10<sup>-5</sup> ÷ 4.2x10<sup>-5</sup> mol/day) suggest that Mt. Vulture is an area of still active mantle outgassing.

### *Rocks*

Almost all the lavas are tephrites-basanites, while a few are basalts or K-trachybasalts. The Mg# confirms that the sampled rocks are rather primitive, with the exception of only one sample which displays characters of an evolved/differentiated rock. The pattern of incompatible elements display enrichment in LFSE (like Rb, Ba, and Th) and depletion in HFSE (like Nb, P, and Ti). The Vulture magmas are enriched in Nb and LREE (such as La and Ce) with respect to the most primitive shoshonitic magmas of the RCP (Martelli et al., 2004), and they show lower LFSE/HFSE and Th/Nb ratios and higher P than the RCP. As already evidenced by De Fino et al. (1986), these differences cannot be generated by crystal fractionation and must be considered as having been inherited from the parental magma. The Zr/Nb and Y/Nb ratios are similar to that of OIB magmas suggesting a more enriched mantle source in a within-plate component than that of the basic rocks in the southern RCP. This conclusion is also supported by Th/Yb and Ta/Yb ratios and Th/Zr vs. Nb/Zr diagram, where the Vulture samples fall in an intermediate position between the field of arc basalts and that of intraplate basalts. These data suggest that the Vulture mantle source has been enriched in anorogenic alkaline components (such as HFSE and LREE) and subsequently affected by subduction-related metasomatism with enrichment in LFSE.

### *Fluid inclusions*

The measured <sup>3</sup>He/<sup>4</sup>He ratio in fluid inclusions of the pyroxene and olivine phenocrysts of the Vulture volcanics range from 4.5 to 6.03 Ra. In most of the pyroxene the He isotope value are lower than those in olivines while the He contents are higher than in the olivines. Measured values are probably to be referred to a lower closure temperatures and also to a less dense structure of pyroxenes with respect to olivines.

The fact that the highest <sup>3</sup>He/<sup>4</sup>He ratios measured in olivine, pyroxene and free gases, all coincide at ~ 6.0 Ra strongly suggests that this value results from a common source, which can only be represented by the mantle of the area. Among the rocks, the highest <sup>3</sup>He/<sup>4</sup>He ratios result from the most recent outcrop. These samples belong to a surge deposit and are part of the formation of the Monticchio lakes Unit. This formation is of exceptional interest, not only for its carbonate-melilite composition, but also for the presence of peculiar concentric-structured lapilli, cored with mega crystals or ultramafic nodules originating in the mantle, and of discrete peridotite nodules. These lapilli deposits indicate a direct mantle provenance, and imply that this magma ascended in a very short time (Stoppa e Woolley, 1997). The <sup>3</sup>He/<sup>4</sup>He

value (~6 Ra) is enough primitive to be in the range of both the HIMU-type mantle ( $^3\text{He}/^4\text{He} = 6.8 \pm 0.9 \text{ Ra}$ ) and SCLM ( $^3\text{He}/^4\text{He} = 6.1 \pm 0.9 \text{ Ra}$ ). The He isotope values lower than 6.0 Ra are the result of variable contamination that occurred after the melt formation. The mechanism of contamination of radiogenic helium is probably to be referred to pre-eruptive contamination by crustal fluids containing radiogenic helium. The addition of radiogenic  $^4\text{He}$  necessary to decrease the  $^3\text{He}/^4\text{He}$  ratio from 6.7÷7.0 Ra (the mantle end-member in the Italian region, Martelli et al., 2004) to ~6.0 Ra (the assumed value of the Mt Vulture mantle) may have arisen: a) through the direct addition of He to the mantle beneath Mt Vulture or b) through the addition of U and Th and subsequent radiogenic decay to  $^4\text{He}$ . As discussed by Di Liberto (2003), these processes are compatible with the He concentration in the sub continental lithosphere mantle (SCLM) or HIMU mantle.

Analogously to that observed in the RCP (Martelli et al., 2004), the investigated samples display an appreciable correlation between He and Sr isotopes. A limited number of samples display particularly high Sr isotope values (as high as 0.7070) in coincidence with low  $^3\text{He}/^4\text{He}$  ratios. This is indicative of contamination processes that have affected both the Sr and He isotopic signature. Considering that the Sr isotope ratios in the clinopyroxenes of Mt. Vulture peridotites are more primitive (0.7042÷0.7058), we can assume that they are representative of the Vulture mantle. According to that assumption, the mantle is enriched in radiogenic Sr than HIMU ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7027$ ) and is close to SCLM ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7019 \div 0.7044$ ), displaying lower values than the RCP rocks (0.7056÷0.7105; Martelli et al., 2004). On the basis He-Sr systematics, the Vulture magmatism is less contaminated than the RCP one.

#### A CONTRIBUTION TO THE GEODYNAMIC CHARACTERIZATION OF MT VULTURE MANTLE SOURCE

The Puglia region and the Bradanic foredeep underwent uplift since the middle Pleistocene. Doglioni et al. (1994) interpreted this characteristic as being due to the arrival of the thicker southern Adriatic continental lithosphere at the subduction, that produced a slowing of the down-going process, and generated a differential slab retreat of the subduction. In addition, this tectonic regime has determined the formation of extensional tectonics and strikeslip faulting detached at the base of the lithosphere, occurring both in the foreland and in the belt.

The Ofanto graben, located to the south of the Gargano promontory, is probably related to these extensional lithospheric structures, generating a “vertical slab window” in the down going lithosphere roughly beneath Mt. Vulture. The slab window may have facilitated mantle decompression and its subsequent melting, allowing to the ascent of the Vulture magmas through that “window”. This could explain the ambiguous character between intraplate and subduction volcanism of the Mt Vulture magmatism. In fact, the intraplate character may result by the mantle flooring the Adriatic lithosphere, while the subduction-related character may result by fluids released by the subducting slab and carried by the eastward asthenospheric flow through the “vertical slab window”. Furthermore, the He isotope

signature of Mt. Vulture mantle-source ( $\sim 6$  Ra) falls in the same range of that of Mt. Etna ( $6.4 \pm 0.9$  Ra; Marty et al., 1994) and both mantle sources display ambiguous characters of intraplate and subduction-related magmatism.

We suggest that in the general geodynamic framework of the Central Mediterranean Sea the Mt. Vulture magmatism displays distinct characters with respect to almost all the other Italian volcanoes and represents the counterpart of the Etnean one (Doglioni et al., 2001), although the different dip of contiguous slabs in the first one is caused by the different thickness of the downgoing lithosphere, instead of the different characters of the subducting slabs (continental/oceanic) in the latter.

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