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Mantle CO_2 degassing at Mt. Vulture volcano (Italy): Relationship between CO_2 outgassing of volcanoes and the time of their last eruption

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A B S T R A C T

Mantle volatiles are mainly lost from the Earth to the atmosphere through subaerial and submarine volcanism. Recent studies have shown that degassing of mantle volatiles also occurs from inactive volcanic areas and in tectonically active areas. A new challenge in Earth science is to quantify the mantle-derived flux of volatiles (e.g., CO_2) which is important for understanding such diverse issues as the evolution of the atmosphere, the relationships between magma degassing and volcanic activity, gas pressure and seismogenic processes, and the hazards posed by volcanic lakes. Here we present a detailed study of mantle-derived CO_2 budget from Mt. Vulture volcano in the Apennines, Italy, whose latest eruption occurred 141 ± 11 kyr ago.

The relationship between $\delta^{13}C_{CO2}$ and total dissolved carbon at Mt. Vulture volcano indicates that the emitted CO_2 is a mixture of a biogenic end-member with an average $\delta^{13}C_{CO2}$ of about $-17‰$ and a mantle-derived CO_2 end-member with $\delta^{13}C_{CO2}$ values from $-3‰$ to $+2‰$. These values of mantle-derived $\delta^{13}C_{CO2}$ are in the range of those for gas emitted from active volcanoes in the Mediterranean. We calculated the contribution of individual components (CO_2 in groundwater, in lakes and from main pools) to the total CO_2 budget in the area. We used new measurements of water flow, combined with literature data, to calculate the CO_2 flux associated with groundwater, and measured the gas flux from the main pools on the volcanic edifice. Finally, we calculated the CO_2 flow in the lakes based on the gradient concentration and eddy diffusivity. The total mantle-derived CO_2 budget in the area is 4.85×10^8 mol yr^{-1}, which is more than double previous estimates. This is higher than those observed in younger volcanic systems elsewhere, thereby supporting the existence of actively degassing mantle melts below Mt. Vulture volcano.

A structural map highlights the tectonic control on CO_2 flow across the Mt. Vulture volcanic edifice. Indeed, the tectonic discontinuities that controlled the magma upwelling during the most recent volcanic activity are still the main active degassing structures.

The new estimate of CO_2 budget in the Mt. Vulture area, together with literature data on CO_2 budget from historically active and inactive Italian volcanoes, suggests a power-law functional relationship between the age of the most recent volcanic eruption and both total discharged CO_2 ($R^2 = 0.73$) and volcano size-normalized CO_2 flux ($R^2 = 0.66$). This relation is also valid by using data from worldwide volcanoes highlighting that deep degassing can occur over very long time too. In turn, the highlighted relation provides also an important tool to better evaluate the state of activity of a volcano, whose last activity occurred far in time.

Finally, our study highlights that in the southern Apennines, an active degassing of mantle-derived volatiles (i.e., He, CO_2) occurs indiscriminately from west to east. This is in contrast to the central–northern Apennine, which is characterized by a crustal radiogenic volatile contribution, which increases eastward, coupled to a decrease in deep CO_2 flux. This difference between the two regions is probably

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due to lithospheric tears which control the upwelling of mantle melts, their degassing and the transport of volatiles through the crust.

1. Introduction

The way in which CO_2 outgasses is crucial to understanding the compositional evolution of the atmosphere through geological time, life on Earth and climate changes. However, CO_2 outgassing from the Earth remains poorly constrained, which hampers our understanding of the geological carbon cycle (Berner and Lagasa, 1989; Burton et al., 2013). Since industrialization, anthropogenic CO_2 emissions have added significantly to natural emissions, resulting in a sharp increase in CO_2 concentration in the atmosphere. Indeed, CO_2 concentration increased from 190 to 280 ppmv over the past 400,000 years, and reached ~400 ppmv during the past 100 years (Burton et al., 2013 and references therein; Monastersky, 2013). Volcanic emissions of CO_2 contribute to the "greenhouse" effect but are poorly constrained (Burton et al., 2013, and references therein), in spite of the increasing number of investigations on this topic. Mörner and Etiope (2002) estimated that subaerial volcanic emissions of CO_2 are almost equal to other inorganic natural non-volcanic CO_2 emissions. However, we could reasonably expect that estimates of their total contribution will increase according to both the technical improvement of measurements and the extension of investigated areas. In fact, CO_2 emitted from volcanic lakes has only recently been considered in the computation of the total CO_2 discharged from volcanic systems (Perez et al., 2011). The contribution of volcanic lakes to the global CO_2 budget has been evaluated at ~94 $Mt\,yr^{-1}$, compared with 271 $Mt\,yr^{-1}$ released from volcanic plume passive degassing, which is the largest contributor to the estimated global CO_2 flux (Burton et al., 2013). Such recent assessments confirm the underestimation of the CO_2 flux from volcanically and tectonically active regions. Indeed, a recent review on deep carbon emission from volcanoes (Burton et al., 2013) showed that our knowledge of the different components (soil degassing, CO_2 dissolved in groundwater, CO_2 from vents and pools) contributing to the total CO_2 flux is still fragmentary. New efforts in quantifying natural CO_2 emissions are needed, given the occurrence of sudden and fatal gas release events in places such as Mammoth Mountain (USA), Hakkoda (Japan), Mefite D'Ansanto (Italy), Lake Nyos and Monoun (Cameroon), and the Dien Volcanic complex (Indonesia) (Allard et al., 1989; Chiodini et al., 2010; Giggenbach et al., 1991; Hernández et al., 2003; Sorey et al., 1998).

The global volcanic emissions of CO_2 have been estimated mainly from measurements taken at active volcanoes (e.g., Allard et al., 1991; Burton et al., 2013; Gerlach, 1991; Marty and Tolstikhin, 1998). Recent studies have shown that soil-diffuse degassing and magmatic CO_2 dissolved in groundwater make a significant contribution to the total magmatic CO_2 budget from both active and quiescent volcanoes (e.g., Caliro et al., 2005; Chiodini et al., 2004; Gambardella et al., 2004; Inguaggiato et al., 2012; Rose and Davisson, 1996; Sorey et al., 1998). In a study of central–southern Italy, Gambardella et al. (2004) calculated the budget of dissolved CO_2 from Italian quaternary volcanoes and highlighted that they are still degassing a large amount of CO_2, even though they show no signs of recent surface activity. Moreover, Chiodini et al. (2004) discussed a relation between CO_2 degassing and seismogenesis in Italy, highlighting that CO_2 degassing drastically decrease in the Apennine, in correspondence of a narrow band where the seismicity is mainly concentrated. This is due to the accumulation of gas in crustal traps ant the overpressurized CO_2 reservoirs induce seismicity in the area (Chiodini et al., 2004).

In this study, we investigated the CO_2 budget released at Mt. Vulture in the southern Apennines of Italy, a quaternary volcano with both intraplate and subduction affinities (De Astis et al., 2006). This volcano is the eastern-most occurrence of the Quaternary Italian volcanism, and is the only volcano to the east of the Apennine mountain belt. Its most recent eruptive period occurred about 141 kyr ago, giving rise to some maar craters. Two of these craters are marked out by carbonatitic ejecta and are now occupied by the Monticchio lakes (Lago Piccolo and Lago Grande di Monticchio; LPM and LGM, respectively). The volcanic products yield $^3He/^4He$ values in phenocryst fluid inclusions up to ~6.0 Ra, and Sr isotopes consistent with an origin in a mantle minimally affected by contamination from the subducted Adriatic slab (Caracausi et al., 2013a). Similar $^3He/^4He$ values, measured in fluids from around Mt. Vulture, indicate that the deep volcanic system is still degassing (Caracausi et al., 2009, 2013b; Chiodini et al., 2000a). The two maar lakes act as collectors of mantle-derived He and CO_2 (Caracausi et al., 2013b and references therein) and in the last few centuries they have shown evidence of several sudden releases of mantle-derived fluids, which had accumulated in the crust and/or volatiles which had outgassed from magma (Caracausi et al., 2009 and references therein). Hence geochemical evidences support that an active outgassing of mantle-derived volatiles from magmatic intrusion at depth occurs in the region of the Mt. Vulture volcano (Caracausi et al., 2013a, 2013b). This is strongly supported by recent geophysical investigations that highlighted: 1) the presence of magmatic intrusions between 5 and 20 km at depth under the Mt. Vulture volcano, probably linked to the past activity of the volcano (Cella and Fedi, 2012; Florio et al., 2009); 2) the partial melting of mantle due to asthenospheric upwelling is occurring beneath the southern Apennines, just in correspondence of MT. Vulture volcano (Ökeler et al., 2009).

Previous studies on CO_2 dissolved in groundwater at Mt. Vulture evaluated a budget of 0.0083 $Mt\,yr^{-1}$, which is among the highest in Italy (Gambardella et al., 2004). Here we report the results of a new estimate of CO_2 budget in the Mt. Vulture area, based on assessments of three components: 1) CO_2 dissolved in groundwater, 2) CO_2 budget into the two maar lakes located on the SW flank of the volcano, and 3) CO_2 emitted from the main pools on the volcanic edifice. The results are then discussed and compared with estimates of the CO_2 budgets of other active and inactive worldwide volcanoes reported in the literature.

2. Geological and hydrogeological framework

Mt. Vulture is a Pleistocene composite volcano located at the easternmost border of the Apennine compressive front (Fig. 1), at the western margin of the Apulia foreland and ~100 km east of the Campanian Province. Volcanic activity started at 742 ± 11 kyr and subsequently a long-lasting quiescence interval, the volcanic activity resumed along active fault systems. The latter continued until 141 ± 11 kyr (Büettner et al., 2006 and references therein). It is an alkaline stratovolcano composed mainly of pyroclastic deposits and lava flows of tephritic-phonolite, phonofoidite, foidite, melilitite and carbonatites (Beccaluva et al., 2002). Carbonatitic products were emitted mainly during the most recent volcanic activity, highlighting the CO_2-rich nature of the emitted magmas (e.g., Jones et al., 2000 and references therein). Mt. Vulture shows