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Role of non-mantle CO₂ in the dynamics of volcano degassing:

The Mount Vesuvius example

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ABSTRACT

Mount Vesuvius, quiescent since 1944, is a dangerous volcano currently characterized by elevated CO₂ emissions of debated origin. We show that such emissions are most likely the surface manifestation of the deep intrusion of alkali-basaltic magma into the sedimentary carbonate basement, accompanied by sidewall assimilation and CO₂ volatilization. During the last eruptive period (1631–1944), the carbonate-sourced CO₂ made up 4.7–5.3 wt% of the vented magma. On a yearly basis, the resulting CO₂ production rate is comparable to CO₂ emissions currently measured in the volcanic area. The chemical and isotopic composition of the fumaroles supports the predominance of this crust-derived CO₂ in volatile emissions at Mount Vesuvius.

INTRODUCTION

Volatile abundances in magmas are widely considered to be inherited from melting conditions in the mantle and subsequently modified by degassing processes during magma rising. However, crustal assimilation may dramatically affect volatiles dissolved in magma at a low concentration level (<1wt%), such as C-S-Cl (Behrens and Gaillard, 2006), whenever small

amount of carbonates, sulfates, or salt rich-sediments are assimilated. Nevertheless, in the recent literature the addition of volatiles of crustal origin during magma transfer toward the surface has been suggested only in a few instances (Goff et al., 2001; Obenholzner et al., 2003; Werner and Brantley, 2003). In this paper, we present a novel approach to quantify the contribution of carbonate assimilation to CO₂ degassing at Mount Vesuvius, Italy. Our estimates are based on petrological constraints and are in agreement with geochemical data about current fluxes and isotopic composition of Mount Vesuvius volcanic gases.

MOUNT VESUVIUS PLUMBING SYSTEM AND GAS EMISSIONS

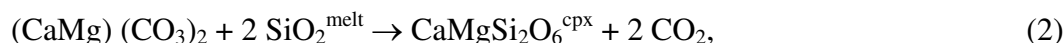
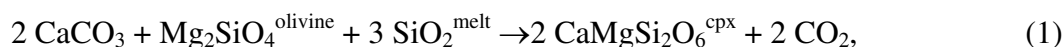
Mount Vesuvius is located on the southern margin of the Campanian Plain and is emplaced on a carbonate sedimentary sequence several kilometers thick. No sedimentary rocks are exposed in the plain; however, it is bordered by structural highs (e.g., Mount Massico, the Sorrento Peninsula) where Mesozoic carbonate rocks crop out. The sedimentary sequence comprises Upper Triassic dolomitic limestones and dolostones, Jurassic limestones, and Cretaceous-Paleogene limestones and dolostones (D'Argenio and Alvarez, 1980). The Trecase 1 geothermal well, on the southeast slopes of Mount Vesuvius, encountered dolomitic deposits at ~1890 m (1665 m below sea level [bsl]; Brocchini et al., 2001). Figure 1 summarizes the information, from geophysical surveys, about the Mount Vesuvius basement and magmatic system. Seismic tomographic studies have imaged an extended low velocity layer, with a flat top at ~8–10 km b.s.l. beneath the volcano, interpreted as the top of the present-day magma reservoir (Auger et al., 2001, and references therein). No evidence exists of any reflectors between the top of the limestone basement (2–3 km b.s.l.) and the 8–10 km discontinuity (Auger et al., 2001), suggesting that the magma is probably hosted within or at the base of the carbonate sequence.

The seismic data are consistent with a sill-shaped zone constituted by magma interspersed in a densely fractured rock, favoring exchanges between magma and host-rock (Auger et al., 2001).

Since the last eruption in 1944, Mount Vesuvius has been quiescent; only seismicity (De Natale et al., 2006) and low temperature fumarolic emissions (Chiodini et al., 2001) suggest that it is still active.

CO₂ PRODUCTION BY SEDIMENTARY CARBONATE ASSIMILATION AT MOUNT VESUVIUS

The importance of limestone assimilation in the plumbing system of Mount Vesuvius has long been recognized (Rittmann, 1933). However, recent geochemical and experimental studies suggest that Mount Vesuvius magmas underwent increasing carbonate assimilation in the past 25 k.y. (Iacono-Marziano et al., 2008), with as much as 10–15 wt% carbonate assimilation for recent volcanic rocks (Di Renzo et al., 2007). Laboratory work (Iacono-Marziano et al., 2008) has shown that magmatic assimilation of carbonates liberates CO₂ following the reactions:



where cpx is clinopyroxene. More details about the petrological implications of carbonate assimilation (after Iacono-Marziano et al., 2008) are in the GSA Data Repository. Figure 2 shows the variations in composition of primitive melt inclusions in olivine and clinopyroxene from the 1794–1944 Mount Vesuvius eruptive period (Fulignati et al., 2004; Marianelli et al., 2005), and of melt inclusions in clinopyroxene of high temperature skarn xenoliths of the 1944 eruption (Fulignati et al., 2004). The experimental results (Fig. 2; after Iacono-Marziano et al., 2008) show that such variations are consistent with the effect of carbonate assimilation by basaltic magmas in the upper crust (see the Data Repository). We provide quantitative

constraints on the assimilation process by means of mass-balance calculations considering variable degrees of dolomite +/- calcite assimilation and clinopyroxene +/- olivine crystallization (see the Data Repository for explanation). These calculations permit an accurate estimation of the amount of assimilated carbonates, because (1) they use the most suited composition of the uncontaminated magma, and (2) the compositions of the assimilated rocks can be fitted together with the mineral and fluid proportions (see the Data Repository). A shoshonite with $\text{SiO}_2 \sim 51 \text{ wt\%}$ and $\text{MgO} \sim 8.5 \text{ wt\%}$ (Fig. 2) has been assumed as the noncontaminated, or at least less contaminated, composition. Di Renzo et al. (2007) came to the same conclusions on the basis of the shoshonite Sr isotopic ratio, which is one of the lowest measured at Mount Vesuvius. The best-fit of melt inclusion array (curves in Fig. 2) is obtained by computing progressing carbonate assimilation from 0 to $\sim 22 \text{ wt\%}$ of which dolomite composed 60%–85% (Table DR1). Melt inclusions record variable degrees of carbonate assimilation probably because they sample melt aliquots at variable distances from the carbonate host rock. Field evidence show that carbonate assimilation affects the magma composition in an inhomogeneous way (Barnes et al., 2005), as also suggested by the strongly heterogeneous Sr isotopic composition of Mount Vesuvius eruptive products belonging to a single eruptive period (Di Renzo et al., 2007 and references therein). However, the average amount of assimilation can be estimated for the most recent eruptive period, on the basis of the bulk rock composition of the erupted lavas and pyroclasts. Between 1631 and 1944, tephritic to tephriphonolitic magmas have been erupted (Joron et al., 1987); we restrict our calculations to the more mafic terms because the assimilation process is significantly more efficient in hotter and Mg-rich magmas (Barnes et al., 2005; Iacono-Marziano et al., 2008). The compositions of the most primitive tephritic-

phonotephritic rocks (gray square in Fig. 2; after Joron et al., 1987) require 9.8–11.2 wt% of assimilation, of which dolomite composed 82–84% (tephrite average in Table DR1).

Figure 1 illustrates the role of carbonate assimilation in the dynamic of magma degassing at Mount Vesuvius. The rising basaltic magma batches are likely to be horizontally channeled at the carbonate-crystalline basement discontinuity (De Natale et al., 2006). The Upper Triassic dolomitic formations (>1200m) at the base of the Mesozoic sedimentary series (D'Argenio and Alvarez, 1980) represent the first layers in which the magma most extensively assimilates carbonate rocks, upon which clinopyroxene crystallizes and CO₂ is liberated, according to reactions 1 and 2. An average of 9.8–11.2 wt% of carbonate assimilation liberates 4.7–5.3 wt% CO₂ (Fig. 2). Under the relatively low crustal pressure conditions at which carbonate assimilation is likely to occur (<300 MPa), CO₂ solubility does not exceed 0.3–0.4 wt% CO₂ (Blank and Brooker, 1994). CO₂ contents dissolved in primitive melt inclusions of the last Mount Vesuvius eruption (1944) range between 0.09 and 0.30 wt% (Fig. 2; after Marianelli et al., 2005). Most of the 4.7–5.3 wt% CO₂ deriving from carbonate assimilation is therefore likely to be present as a separate gas phase, with only minor CO₂ dissolved in the melt. At 200 MPa and 1150–1200°C, considering a density of CO₂ of ~0.5 g/cm³ (Bottinga and Richet, 1981) and an average magma density of 2.7 g/cm³, we calculate that the mafic Mount Vesuvius magma is likely to contain ca. 25–30 vol.% of bubbles following 9.8–11.2 wt% of carbonate assimilation at a depth of ~7.5 km. CO₂-rich bubbles tend to escape from the system because the magma and the surrounding rocks are significantly more dense. Provided that the host rocks are sufficiently permeable, most of the CO₂ produced at depth will therefore ascend toward the surface.

Currently, at least 301 t/day of deep CO₂ are degassed in the Mount Vesuvius volcanic area: 151 t/day are diffusely degassed from the crater area and 150 t/day are dissolved in the

groundwaters of the volcano flank (Fron dini et al., 2004; Caliro et al., 2005). The tensile faults in the Mesozoic basement, typically oriented northwest-southeast and northeast-southwest, act as tectonic controls on CO₂ emissions, facilitating and to channelling the rising CO₂ (Federico et al., 2002).

QUANTIFICATION OF NONMANTLE CO₂ EMISSIONS AT MOUNT VESUVIUS

We first use helium and carbon abundances and isotopic compositions in the gases of the fumaroles to infer the proportion of mantle CO₂ at Mount Vesuvius. The He (³He/⁴He = 2.51–3.98 Ra, where Ra is the atmospheric ratio = 1.38 × 10⁻⁶; Tedesco et al., 1998) and C (δ¹³C = 0.06–0.34‰ Vienna Pee dee belemnite, VPDB; Chiodini et al., 2001) isotopic compositions of the CO₂-rich gas emitted by the crater fumaroles are similar to those of groundwaters and magmatic volatiles analyzed in CO₂-rich inclusions of recent volcanic products (Tedesco et al., 1998; Federico et al., 2002; Martelli et al., 2004), indicating a common source. The carbon isotopic composition clearly deviates from the typical mantle range (δ¹³C = -4 to -7 ‰; Pineau et al., 2004) and from the mantle volatile end member of Pantelleria Island, southern Italy (δ¹³C = -4.2 to -5.8 ‰; Parello et al., 2000), and most likely indicates a dominant contribution from marine carbonate (Chiodini et al., 2001). The He isotopic composition also strongly deviates from characteristic mantle signatures (~7–9 Ra; Tedesco et al., 1998 and references therein) and suggests a “dilution” by more radiogenic materials. The C isotopic composition of Mount Vesuvius fumaroles can be used to estimate the contribution of sedimentary sources to volcanic emissions, using an approach similar to that of Werner and Brantley (2003), who calculated between 40 and 50% of crustal contribution at the Yellowstone area, western United States. The carbonate contribution (% carb) is here estimated as:

$$\% \text{ carb} =$$

$$100 * (\delta^{13}\text{C fumarole} - \delta^{13}\text{C mantle}) / (\delta^{13}\text{C carbonate} - \delta^{13}\text{C mantle}), \quad (3)$$

where $\delta^{13}\text{C mantle}$ is the isotopic compositions of the mantle end member reported above, and $\delta^{13}\text{C carbonate}$ is the C isotopic composition of the carbonate rocks of the Campanian platform (between -2 and $+4$ ‰ VPDB; Parente et al., 2007). The resulting carbonate contribution is between 52 and 100%. A more accurate estimation of the sedimentary contribution is possible using the Sano and Marty (1995) approach. CO_2 concentrations in the fumaroles of Mount Vesuvius crater are 75,900–156,800 $\mu\text{mol/mol}$, and He concentrations are 0.22–0.64 $\mu\text{mol/mol}$ (Chiodini et al., 2001). The $\text{CO}_2/{}^3\text{He}$ ratio is therefore $4.5\text{--}9.9 \times 10^{10}$ (using He isotopic ratios of Tedesco et al., 1998). Considering $\text{CO}_2/{}^3\text{He}$ ratios of $\sim 2 \times 10^9$ for the mantle source (Sano and Marty, 1995) and $1 \times 10^{12}\text{--}10^{13}$ for the carbonate rocks (the variations of this parameter being insignificant in the calculations), we estimate carbonate contributions to volcanic emissions of 96–98%. Although these calculations lack precision, due to the uncertainties in the concentration and isotopic composition of the source and, to a lesser extent, of the contaminant, they strongly suggest that carbonate assimilation plays a major role in volcanic emissions at Mount Vesuvius.

Although the estimation of the amount of CO_2 currently produced at Mount Vesuvius by carbonate assimilation is unfeasible on the basis of the petrological constraints detailed above (due to the lack of lava emissions since 1944), present day measured emissions can be compared to carbonate-derived CO_2 estimated for the last eruptive period. During this period (1631–1944), Mount Vesuvius was characterized by semipersistent activity in open conduit conditions: 20 cycles of mainly effusive activity were distinguished, separated by short rest periods (generally not exceeding a few years) and closed by powerful explosive eruptions (Civetta and Santacroce, 1992; Scandone et al., 2008). Erupted lavas and pyroclasts are characterized by relatively primitive compositions and are supposed to have been erupted after a nearly direct ascent from

the deep part of the magma plumbing system (Scaillet et al., 2008). The magma feeding rate is therefore assumed to equal the eruption rate (Rosi et al., 1987), which has been estimated at $1.05\text{--}4.31 \times 10^6 \text{ m}^3/\text{yr}$ (Rosi et al., 1987; Civetta and Santacroce, 1992; after Scandone et al., 2008). Combining this magma feeding rate (MFR) with the estimated amounts of carbonate assimilation (wt% carb), following the equation:

$$\text{CO}_2 \text{ (t/day)} = \frac{\text{MFR}(\text{m}^3/\text{yr}) \times \text{magma density (kg/m}^3) \times \text{wt\% carb} \times \text{MW CO}_2}{10^5 * 365 * \text{MW CaCO}_3} \quad (4)$$

where MW is molecular weight, we calculate a rate of CO_2 production of 335–1566 t/day for the recent eruptive period. This estimation is comparable to present-day measured emissions in the Mount Vesuvius area (301 t/day; Frondini et al., 2004; Caliro et al., 2005), which represent a minimum estimation of the current CO_2 production rate at depth.

A pure magmatic contribution to CO_2 degassing is barely quantifiable at Mount Vesuvius, because good estimations of CO_2 concentration in the mantle source are not available. The CO_2 contents in primitive melt inclusions that did not undergo assimilation represent the contribution of magmatic CO_2 dissolved in the magma. The maximum CO_2 content in the most primitive melt inclusions of the period 1794–1944 (considered representative of the uncontaminated or less contaminated magma) is ~0.3 wt% (Marianelli et al., 2005), which represents 6-7% of what we estimate to be produced by carbonate assimilation. Primitive magmas may have been volatile saturated at the depth at which these inclusions were trapped (~8 km; Marianelli et al., 2005); however, there are no constraints on the amount of the mantle CO_2 that could have been in the gas phase. Available data on fluid inclusions identified in Mount Vesuvius products concern metamorphic and metasomatized sedimentary nodules and cumulate

ejecta (Gilg et al., 2001, and references therein), which most likely derive from the interaction between the magma and the carbonate rocks (Gilg et al., 2001).

Several lines of evidence hence suggest that carbonate assimilation, which is thought to be responsible for the secular chemical variations of Mount Vesuvius eruptive product since 25 ka, may currently account for the elevated CO₂ emissions measured in Mount Vesuvius volcanic area, prevailing over the contribution of mantle-derived CO₂.

CONCLUSIONS

The carbonate assimilation process presented in this study represents a CO₂ degassing mechanism alternative to those classically considered to drive magmatic degassing, i.e., crystallization at depth and decompression related to magma ascent.

Like Mount Vesuvius, several other volcanic centers, either quiescent or active, recognized to be emplaced over carbonate sedimentary successions and showing skarn xenoliths in their eruptive products, are characterized by elevated rates of CO₂ degassing (high ratios of emitted gas to emitted magma), e.g., Alban Hills and Mount Etna in central-southern Italy (Michaud, 1995; Iacono-Marziano et al., 2007), Popocatepetl in Mexico, Yellowstone in the United States, Merapi in Indonesia, and Mount Erebus in Antarctica (Goff et al., 2001; Werner and Brantley, 2003; Chadwick et al., 2007). For some of these volcanoes, magma-carbonate interactions have been proposed to contribute to their degassing dynamics to some extent (Goff et al., 2001; Obenholzner et al., 2003; Werner and Brantley, 2003). Further studies are therefore needed to assess the total contribution of CO₂ of nonmantle origin to global magmatic degassing.

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FIGURE CAPTIONS

Figure 1 Simplified (not to scale) mechanism of carbonate assimilation and CO₂ release at Mount Vesuvius. Rising primary magma (magma feeding rates from Rosi et al., 1987; Civetta and Santacroce, 1992; Scandone et al., 2008) is channeled at the metamorphic basement-carbonate rocks discontinuity, forming sill-shaped body (Auger et al., 2001; De Natale et al., 2006). Primary magma reacts with carbonate rocks, crystallizing clinopyroxene (cpx) and liberating CO₂ according to the reactions 1 and 2 in text. Arrows indicate CO₂ migration through rock's most permeable zones, dissolving in the aquifer (Caliro et al., 2005), and finally generating diffuse degassing at the surface concentrated above the tensile faults of the sedimentary basement (Federico et al., 2002). Geometry of sedimentary and metamorphic basement is from geophysical surveys. Top of carbonate sequence is dissected by series of regional normal faults and generally deepens toward Bay of Naples and center of Campanian

Plain (Berrino et al., 1998). Inversion of gravity data suggests that the thickness of the carbonate basement is ~11 km (Berrino et al., 1998 and references therein).

Figure 2 Quantification of carbonate assimilation from chemical trends in Mount Vesuvius melt inclusions (MI). Filled diamonds: primitive MI of A.D. 1794–1944 eruptive period ($\text{MgO} > 5\text{wt}\%$, Marianelli et al., 2005; Fulignati et al., 2004). Open diamonds: MI compositions in high-temperature skarn xenoliths from 1944 eruption ($\text{MgO} > 3\text{wt}\%$, Fulignati et al., 2004). Open circles: residual liquids of interaction experiments at 1150 °C and 200 MPa (Iacono-Marziano et al., 2008). Thick lines: mass balance calculations (this study) simulating chemical changes in the melt composition in response to carbonate assimilation + crystallization following reactions 1 and 2 in text; crosses show calculated melt compositions (Table DR1; see footnote 1 for explanation) for 0, 6, 14 and 22 wt% carbonate assimilation. As much as 22 wt% of carbonate assimilation is required to reproduce composition of the MI found in high-temperature skarn minerals ($\text{SiO}_2 \sim 43.3\text{ wt}\%$), while ~14 wt% of assimilation is needed for most extreme compositions of MI trapped in phenocrysts ($\text{SiO}_2 \sim 46.2\text{ wt}\%$). Gray field represents average whole-rock composition of 1631–1944 lavas (Joron et al., 1987), which is reproduced by 9.8–11.2 wt% carbonate assimilation.

¹GSA Data Repository item 2009083, petrological variations due to carbonate assimilation, and Table DR1 (details of mass balance calculations), is available online at www.geosociety.org/pubs/ft2009.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

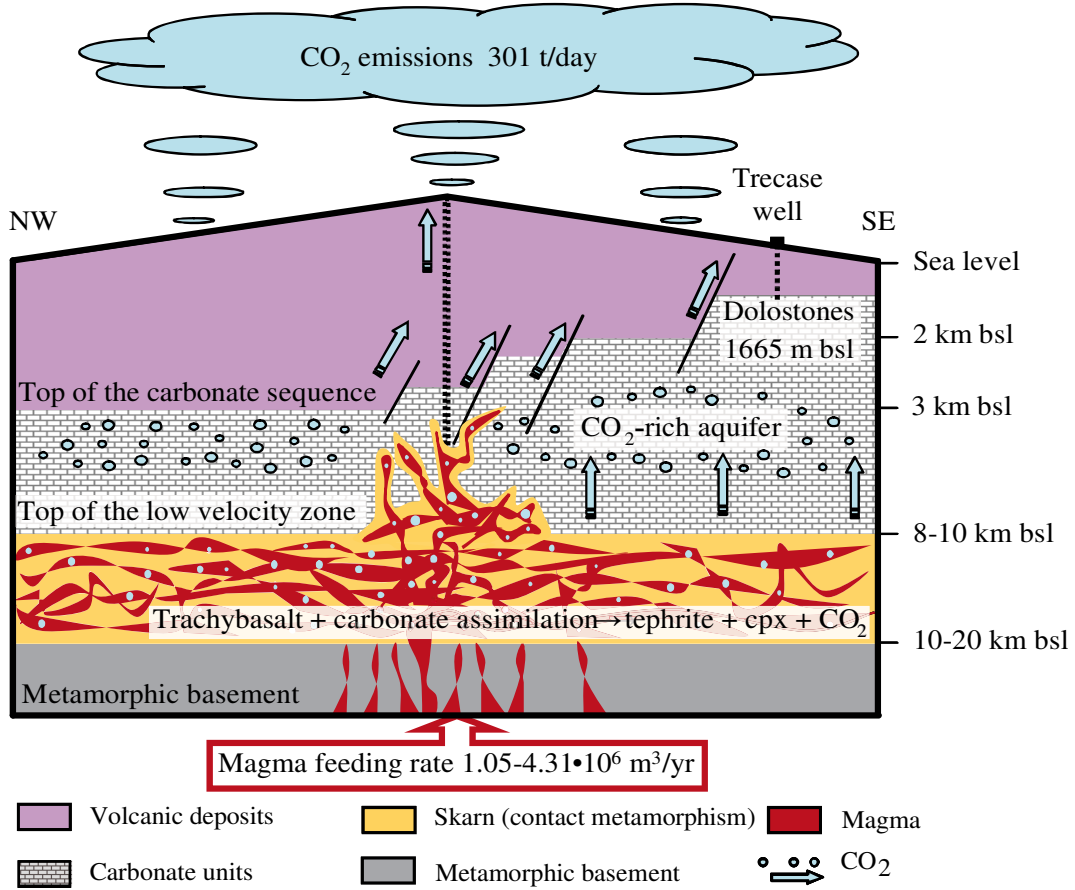


Figure 1

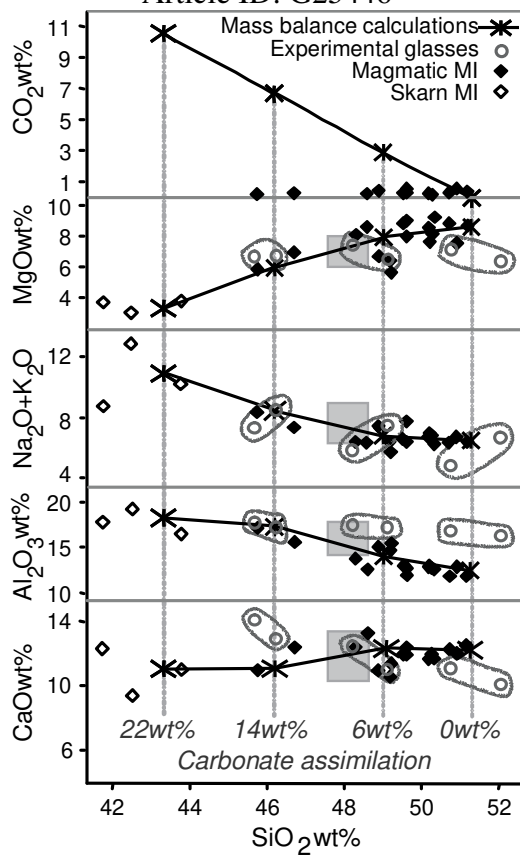


Figure 2