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Notes

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ABSTRACT

It is generally accepted, but not experimentally proven, that a quantitative prediction of volcanic eruptions is possible from the evaluation of volcanic gas data. By discussing the results of two years of real-time observation of H₂O, CO₂, and SO₂ in volcanic gases from Mount Etna volcano, we unambiguously demonstrate that increasing CO₂/SO₂ ratios can allow detection of the pre-eruptive degassing of rising magmas. Quantitative modeling by the use of a saturation model allows us to relate the pre-eruptive increases of the CO₂/SO₂ ratio to the refilling of Etna's shallow conduits with CO₂-rich deep-reservoir magmas, leading to pressurization and triggering of eruption. The advent of real-time observations of H₂O, CO₂, and SO₂, combined with well-constrained models of degassing, represents a step forward in eruption forecasting.

Keywords: Mount Etna, volcanoes, degassing, volatiles, gas plumes, volcanogenic processes.

INTRODUCTION

Upon their migration from the source region toward the Earth's surface, magmas release volatile species into the gas phase in response to decreasing solubilities in the silicate melt (Carroll and Holloway, 1994). This exsolved gas phase feeds persistent degassing at quietest volcanoes, and is the fuel for magma fragmentation during explosive eruptions (Cashman et al., 2000). The composition of volatiles degassed during magma ascent is primarily dependent on the original volatile content of the silicate melt and on volatile solubilities, governing partitioning between liquid and gas phases (Oppenheimer, 2003). Because pressure is the key control on solubilities, the composition of volcanic gas reaching the surface provides constraints upon the dynamics of magma supply and ascent, thus potentially contributing to volcanic hazard assessment (Giggenbach, 1996). However, in contrast with the routine sensing of volcanic SO₂ by ultraviolet spectroscopy (Andres and Kasgnoc, 1998), the most abundant volcanic gases, CO₂ and H₂O, are also the most difficult to measure, because they have significant background atmospheric abundances (Brantley and Koepenick, 1995; Burton et al., 2000). Furthermore, most conventional techniques for measur-

ing volcanic gases are not developed well enough to allow real-time continuous observations (thus precluding the intrusion of fast-rising magmas to be detected), and the few known examples (e.g., Duffell et al., 2003) represent ex-post interpretations of volcanic gas measurements.

The real-time evaluation of volcanic gas data is particularly desirable at Mount Etna, a basaltic volcano in southern Italy (Bonaccorso et al., 2004) that has become increasingly active during the past 30 yr; the magma emission rate and eruption frequency are ~4 times larger than in the past centuries (Allard et al., 2006). This increasing activity has been related to the ascent and emission of unusually primitive gas-rich basaltic magmas (Spilliaert et al., 2006), which are thought to accumulate in a shallow (~3–5 km below sea level, bsl) reservoir (Fig. 1A; De Gori et al., 2005), causing pressurization and finally triggering failure of the volcano's flank, and thus eruption. Quantitatively evaluating these pre-eruptive pressurization events is of prime importance for volcanic hazard management (Patanè et al., 2003).

Mount Etna erupted again between July and December 2006, with an explosive and effusive eruptive event from its south-east summit crater (SEC) (INGV-Sezione di Catania, 2006). In the months before and during the eruption, we routinely measured the composition of volcanic

gases emitted by the central summit craters by using a multicomponent gas analyzer system (Multi-Gas); these real-time measurements allowed us to acquire the first systematic set of simultaneous H₂O, CO₂, and SO₂ observations in a volcanic gas plume. Here we focus on the interpretation of the volcanic gas CO₂/SO₂ ratio, which, in light of the contrasting solubility properties of the two volatiles (Papale, 1999; Moretti and Ottonello, 2005), is considered to be a key parameter in volcano monitoring. We show that a pre-eruptive increase of the CO₂/SO₂ ratio in the volcanic gas phase is a precursor to the ascent of gas-rich magmas later involved in the eruption. Combining our measurements with results from a multicomponent gas-melt saturation model (Moretti et al., 2003), we attempt a quantitative interpretation of the acquired data set, and provide decisive evidence for CO₂/SO₂ (and H₂O/CO₂) ratios being useful tracers of the refilling of the volcano's plumbing systems, and thus helpful in predicting volcanic eruptions.

RESULTS

Figure 2A shows the temporal evolution of the CO₂/SO₂ molar ratio in Etna's central crater plume (see the GSA Data Repository¹) since January 2005; real time measured by the use of the recently proposed Multi-Gas technique (Aiuppa et al., 2005a; Shinohara, 2005). The Multi-Gas integrates an infrared spectrometer for CO₂ and H₂O determination (detection of H₂O vapor was only possible under favorable conditions, i.e., when the plume was not condensing; Shinohara et al., 2006), and a specific electrochemical sensor for SO₂ measurement,

¹GSA Data Repository item 2007276, Table DR1 (complete data set of plume composition), and Table DR2 (brief chronicle of the 2006 eruption), is available online at www.geosociety.org/pubs/ft2007.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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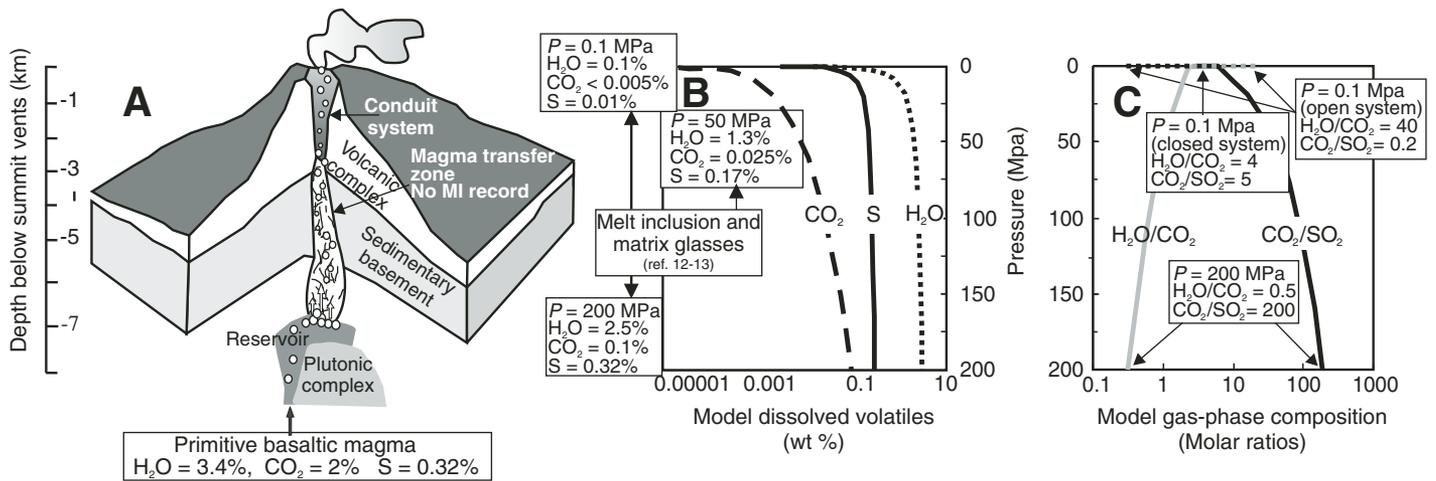


Figure 1. A: Schematic cross section of Etna's plumbing system in the 0–8 km below summit vents depth range (modified from De Gori et al., 2005). A deep (3–5 km below sea level) magma reservoir is on the western margin of a large plutonic complex. Pressurization of this ponding zone with volatile-rich magmas is the cause of periodic lateral dike intrusion on the volcano's flanks. **B:** Change in dissolved volatile contents in the melt (0.1–200 MPa), calculated with an equilibrium saturation model. Model melt compositions at 200–50 MPa and 0.1 MPa are in agreement with volatile contents in melt inclusions trapped at comparable pressures and matrix glasses, respectively (Métrich et al., 2004). **C:** Model-predicted equilibrium CO_2/SO_2 and $\text{H}_2\text{O}/\text{CO}_2$ molar ratios in the magmatic gas phase degassed from Etnean magmas. The model-predicted gas composition ranges from CO_2 rich at reservoir conditions to H_2O and SO_2 rich at pressure, $P = 0.1$ MPa. Solid lines refer to closed-system degassing conditions, while dashed lines are calculated assuming Rayleigh-type open system degassing at 0.1 MPa. Model CO_2/SO_2 ratios at 0.1 MPa range from ~5 (closed system) to ~0.2 (open system).

and allows the determination of the volcanic gas CO_2/SO_2 ratio with an accuracy of $\pm 20\%$ (at 1σ) (Aiuppa et al., 2006). The Multi-Gas operated in situ (e.g., on the rim of Etna's central vent and a few hundred meters from the emission vent) in a series of discrete bimonthly surveys from December 2005 to May 2006. From June 2006, measurements were intensified with the installation on Etna's central craters of the permanent Multi-Gas device, the first of its kind on an active volcano. This captured the bulk composition of the central crater plume, and performed four daily measurement cycles (each 30 min long) with a 9 s acquisition step.

Figure 2 shows that CO_2/SO_2 ratios were determined to be ~9 in the January–April 2005 period, with the 2004–2005 effusive event still in progress (although the poor sampling frequency might have partially hindered the detection of short-term variations). After the end of the 2004–2005 eruption, a gradual decrease of CO_2/SO_2 ratios was observed, reaching a minimum (0.7) in mid-April 2006. Because CO_2 has at the same P - T - X conditions, a much lower solubility in silicate melts than sulfur, this steady decline of CO_2/SO_2 ratios probably reflected an increasing contribution to the sustained summit plume emissions from cooling and crystallizing residual magma in the conduit system, which had undergone extensive volatile degassing during the 2004–2005 event (Aiuppa et al., 2006). By the same argument, the subsequent increase of CO_2/SO_2 ratios, starting from May 2006 (Fig. 2A), implies a replenishment of the volcano plumbing system with CO_2 -rich

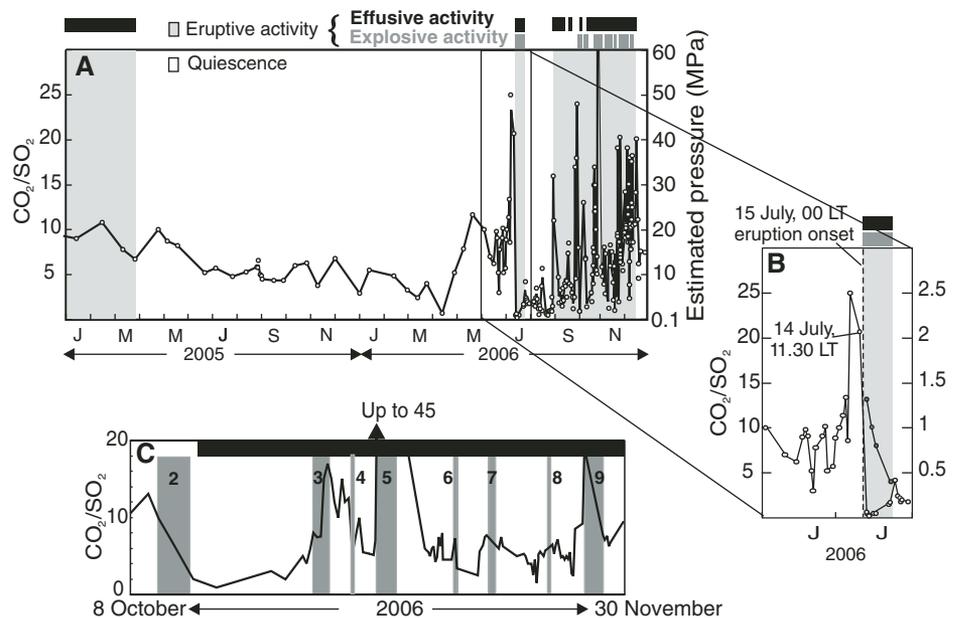


Figure 2. A: Time evolution of CO_2/SO_2 molar ratios in Etna central crater's plume. Right axis shows estimated pressures (in MPa) evaluated by combining volcanic gas data with model results. Timing of 2004–2005 and 2006 eruptions are also shown. **B:** Detail of June–July 2006 period. Gray dots refer to composition of plume released at eruptive vent (right scale). LT—local time. **C:** Detail of the October–November 2006 period. Dark gray bars indicate timing of Strombolian events 2–9 that occurred at south-east summit crater (SEC).

deep-rising magmas. The improved acquisition frequency guaranteed by the permanent device since June 2006 allowed us to detect the emission of CO_2 -rich volcanic gases as a short-term chemical indicator of the imminent eruption, with a remarkable ~50-fold increase of the

CO_2/SO_2 ratio observed in the days before the eruption (the CO_2/SO_2 ratio was ~25 on July 10 and ~21 on July 14, just a few hours before opening of a fracture field on the SEC eastern flank; Fig. 2B). Measurements carried out on July 2006 after the eruption onset showed a

CO₂-poor composition (CO₂/SO₂ < 1) for volcanic gases emitted at both the summit craters and the eruptive vent (Fig. 2B). This rapid drop of the CO₂/SO₂ ratio in the central crater's plume after July 14 suggests that there was no syneruptive supply of volatile-rich magmas from depth, consistent with the rapid termination of lava effusion on July 24, after only 10 days of eruptive activity. After a period of quiescence, during which CO₂-poor volcanic gases were emitted from the volcano summit, a new sudden increase of CO₂/SO₂ ratios occurred on August 31, paralleling the resumption of effusive activity on the same fracture field (Fig. 2A). Explosive activity at SEC also resumed in early October, when a cyclic phase of periodic terminal eruptions started (more than 10 main paroxysmal events were observed during October–December). Nearly all paroxysmal events were associated with an increase of the CO₂/SO₂ ratio from the central crater's plume (Fig. 2C); CO₂/SO₂ ratios increased systematically in the hours before the onset of explosive activity, paralleling an increase in seismic tremor amplitude, peaking during eruption climax, and then smoothly decreasing as Strombolian activity gradually ceased (Fig. 2C). The time scale of the precursor increase of the CO₂/SO₂ ratio in October–December 2007 was generally much shorter (hours) than in May–July 2007 (days); this suggests that each SEC explosive event in the most recent period was likely due to the supply of fast-ascending CO₂-rich magmas to an already emplaced shallow magmatic reservoir. The CO₂/SO₂ ratio decreased to lower values (≤7) only after exhaustion of eruptive activity on December 15.

DISCUSSION

Our two years of uninterrupted observations provide evidence for a pre-eruptive increase of the volcanic gas CO₂/SO₂ ratio being a possible indicator of incoming eruptions at Etna (and likely other basaltic volcanoes). In order to quantitatively interpret our volcanic gas observations, and support our arguments further, we make use of a multicomponent equilibrium saturation model (Moretti et al., 2003; Moretti and Papale, 2004) to calculate the theoretical compositions of both dissolved volatiles in the melt (Fig. 1B) and the coexisting magmatic gas phase (Fig. 1C). The model was initialized at a set of *P-T-X*-redox conditions relevant to the system being investigated, as detailed in the following. The pressure range was 0.1–200 MPa, as within Etna's shallow plumbing system (Fig. 1); temperature was taken as 1100 °C, representing a good compromise between the temperature of lavas and crystallization temperatures of the Mg-rich olivines hosting melt inclusions (1120–1150 °C; Métrich and Clacchiatti, 1996); melt volatile-free composition was evaluated

by averaging compositional data for post-1974 Etna's trachybasalt (Métrich et al., 2004); and redox conditions were fixed at the nickel-nickel oxide buffer (NNO; Métrich and Clacchiatti, 1996). This average redox condition holds for the investigated pressure range, within which the constant ferrous to ferric iron ratio buffer (Moretti and Papale, 2004) would yield comparable oxygen fugacities (0.39 units below NNO at 200 MPa, and 0.2 above it at 0.1 MPa for a FeO/Fe₂O₃ mass ratio of 4). Total water and sulfur contents (H₂O^{TOT}: 3.4 wt%; S^{TOT}: 0.32 wt%, respectively) were derived from average volatile contents in primitive glass inclusions (Métrich et al., 2004). Due to the early exsolution of CO₂ at subcrustal conditions (Kamenetsky and Clacchiatti, 1996), the highest ever measured CO₂ content in glass inclusions (0.4 wt%; Métrich et al., 2004) most likely underestimates CO₂^{TOT}. This was evaluated at 2 wt% by scaling a C/S volcanic gas molar ratio of ~5 (representing the time-averaged ratio of the April 2005 to May 2006 quiescent phase, but also consistent with previous determinations of Allard et al., 1991) to the above-estimated S^{TOT}. Note that extending such an approach to the use of measured H₂O/SO₂ ratios in Etna's volcanic gases (Shinohara et al., 2006) would yield an H₂O^{TOT} of 3.4 wt%, in agreement with the maximum dissolved water content in glass inclusions. Our estimates for total volatile abundances of the parental magma are also in agreement with those given by Scaillet and Pichavant (2005). Model runs were carried out in both closed-system and open-system (Rayleigh type) conditions. In the closed-system case, total (melt + gas) volatile contents are conserved as the chemical compositions of coexisting melt and gas change on decreasing pressures (in the 200–0.1 MPa range). In the open-system case, isobaric (at 0.1 and 20 MPa, respectively) continuous gas separation is assumed to occur, giving rise to declining total volatile contents. Because pressure is constant in the Rayleigh-type simulation, degassing results from crystallization of volatile-free crystals, which in turn leads to volatile oversaturation in the residual melt (Villemant and Boudon, 1998).

Model results demonstrate that the gas phase at equilibrium with the melt within the Etna's 3–5 km bsl reservoir will be CO₂ rich (CO₂/H₂O = 2, CO₂/SO₂ = 200; Fig. 1C); while H₂O and SO₂ will dominate the gas phase exsolved in the shallow conduit system (CO₂/H₂O ≪ 1 and CO₂/SO₂ ≤ 5; Fig. 1C), H₂S being a minor sulfur species at atmospheric conditions (Aiuppa et al., 2005b). More important, the fairly good agreement between our field-measured volcanic gas data and model compositions, as shown in Figure 3, allows us to attempt a quantitative interpretation of the time evolution of Etna's plumbing system over 2005–2006.

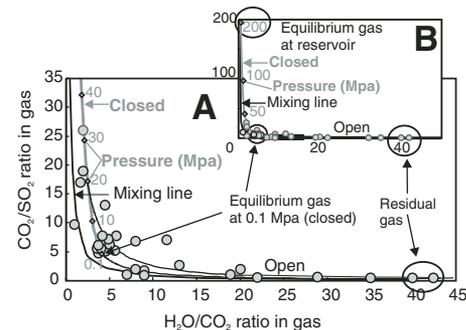


Figure 3. A: Pressure-dependent model evolution lines of the magmatic gas phase contrasted with Etna's volcanic gas plume measurements (circles) in H₂O/CO₂ vs. CO₂/SO₂ scatter plot. All gas measurements where H₂O was also available are shown. Gray line is model trend calculated in closed system conditions. Black curve labeled "mixing line" simulates addition of subsequent amounts of CO₂-rich reservoir equilibrium gas to CO₂-depleted residual gas filling the upper conduit system (composition is fixed by our April 2006 volcanic gas composition). Residual gas composition is in agreement with model compositions calculated assuming Rayleigh-type open system degassing at 0.1 MPa and 20 MPa (lower and upper, respectively, black curves labeled "open"). B: Same as A, showing calculated model compositions up to 200 MPa.

Our measurements and calculations indicate that the CO₂/SO₂ ratios in Etna's plume of ~5, observed in the July 2005–January 2006 period (Fig. 2A), fit very well with the composition of the equilibrium gas phase produced by closed-system bulk degassing at 0.1 MPa (Figs. 1C and 3). This suggests that a slowly convecting magma filled the Etna's shallow plumbing system in that period, and fed persistent plume degassing close to the surface gas-melt separation. The lower (<5) CO₂/SO₂ ratios observed in February–April 2006, combined with high (>4) H₂O/CO₂ ratios, cannot be interpreted as closed-system degassing. These compositions are instead consistent with shallow (0.1–20 MPa) open-system Rayleigh-type degassing of previously degassed magma (Fig. 3). Such gas is produced by crystallization-driven gas distillation from a stagnant and unreplenished magma body (Villemant and Boudon, 1998). Our observations thus rule out any supply of gas-rich magmas ascending from the reservoir in that period, and support the idea that residual degassing of resident magma in the conduits was the prevalent source of this CO₂-depleted residual gas. In contrast, resumption of fresh magma supply to the summit plumbing system since May–July 2006 is clearly documented by the observed pre-eruptive increases of the CO₂/SO₂ plume ratio. These require an additional source of CO₂ for the emitted gases, and testify to the ascent and degassing of

CO₂-rich deep-reservoir magma batches as the trigger mechanism of Etna's most recent eruptive activity. The pre-eruptive peaks of the CO₂/SO₂ plume ratio are factors of 5–50 times higher than those observed during quiescent degassing, and up to 4 times higher than those in syn-eruptive volcanic gases emitted during lava fountains at the SEC in 2000 (CO₂/SO₂ ~10; Allard et al., 2005), but still substantially lower than those predicted for the gas phase at equilibrium with melt at reservoir conditions (Fig. 3). We evaluate that the pre-eruptive CO₂/SO₂ plume ratios of 25–45 correspond to the composition of a magmatic gas phase in equilibrium with the melt at ~30–55 MPa (Fig. 2), and interpret this pressure range as representative of the depth (~1.1–2 km; calculated assuming magmatic pressure and a bulk magma density of 2700 kg·m⁻³) at which magmatic gases separate (and thus last equilibrate) from the ascending reservoir magma. Note, however, that the estimated pressures (depths) have validity, provided no mixing takes place in the conduit between the deep ascending CO₂-rich gas and the CO₂-poor residual gas. The addition of 10–20 wt% of CO₂-rich residual gas bubbles to CO₂-depleted residual gases (having the compositions given in Fig. 3) would also be consistent with our observed plume compositions.

CONCLUSIONS

Our pre-eruptive observations provide evidence that real-time volcanic gas measurements of H₂O, CO₂, and SO₂ can be used as useful eruption predictors on Etna. The new capability to perform such measurements (for the first time at an active volcano) will provide immediate benefit in the evaluation of volcanic hazard, and is expected to play a pivotal role at Mount Etna, a volcano that dominates a densely populated area and that in the future may produce more frequent, voluminous, and potentially hazardous eruptions. The interpretation of volcanic gas data with theoretical models of volcanic degassing makes possible quantitative evaluation of unexplored aspects of magmatic processes.

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