

Hydrogen in the gas plume of an open-vent volcano, Mount Etna, Italy

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[1] We report here on the first hydrogen determinations in the volcanic gas plume of Mount Etna, in Italy, which we obtained during periodic field surveys on the volcano's summit area with an upgraded MultiGAS. Using a specific (EZT3HYT) electrochemical sensor, we resolved H₂ concentrations in the plume of 1–3 ppm above ambient (background) atmosphere and derived H₂-SO₂ and H₂-H₂O plume molar ratios of 0.002–0.044 (mean 0.013) and 0.0001–0.0042 (mean 0.0018), respectively. Taking the above H₂-SO₂ ratios in combination with a time-averaged SO₂ flux of 1600 Gg yr⁻¹, we evaluate that Etna contributes a time-averaged H₂ flux of ~0.65 Gg yr⁻¹, suggesting that the volcanogenic contribution to the global atmospheric H₂ budget (70,000–100,000 Gg yr⁻¹) is marginal. We also use our observed H₂-H₂O ratios to propose that Etna's passive plume composition is (at least partially) representative of a quenched (temperatures between 750°C and 950°C) equilibrium in the gas-magma system, at redox conditions close to the nickel-nickel oxide (NNO) mineral buffer. The positive dependence between H₂-SO₂, H₂-H₂O, and CO₂-SO₂ ratios suggests that H₂ is likely supplied (at least in part) by deeply rising CO₂-rich gas bubbles, fluxing through a CO₂-depleted shallow conduit magma.

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1. Introduction

[2] Of the intensive parameters governing the evolution of a magmatic system, the magma redox state plays a key role in determining iron (and dissolved sulfur) speciation, thus contributing in controlling magma crystallization sequence and differentiation, and volatile partitioning between gas and melt [Fudali, 1965; Sato, 1978; Carmichael and Ghiorso, 1986; Moretti and Papale, 2004]. Since both hydrogen and sulfur may form different species in magmatic gases, studying the composition of volatiles discharged by active volcanoes offers indirect, but still highly valuable, insights into the redox properties of magmatic systems [e.g., Gerlach, 1982]. As such, the redox conditions of magmatic gases have long been targeted by research, particularly since when it became established [Sato and Wright, 1966; Sato and Moore, 1973] that O₂ fugacity (*f*O₂) in gases is buffered by oxidation-

reduction reactions among ferromagnesian minerals in the surrounding silicate (rock, melt) matrix.

[3] Hydrogen (H₂) is an additional proxy for magmatic gas oxidizing-reducing conditions, since it is intimately interconnected to *f*O₂ via the water dissociation reaction [e.g., Giggenbach, 1987]. In addition, given its low weight and low solubility in groundwater and hydrothermal fluids (all concurring to determine an overall high mobility), H₂ is a potentially excellent tracer of processes operating deep in magmatic systems. As such, attempts have been made to measure H₂ in a variety of volcanic fluids [Sato, 1988], including hot spring waters [Hirabayashi *et al.*, 1986], soil gases [Sato and McGee, 1981; Giammanco *et al.*, 1998; Hernández *et al.*, 2000; Melián *et al.*, 2007], and high-temperature magmatic gases (see Giggenbach [1996] and Oppenheimer [2003] for recent reviews). Unfortunately however, volcanic gas plumes (we refer here to a volcanic gas plume as the atmospheric dispersion of hot magmatic gases) have not been targeted for their H₂ content until very recently [Shinohara *et al.*, 2011]. Yet, one may expect that gas plume H₂ compositions are more strictly related to magma degassing dynamics (and, particularly, magma redox conditions) than any diffuse (soil) or peripheral (hot spring) manifestation: in the latter, H₂ behavior may potentially be also controlled by nonmagmatic processes, particularly reactions of groundwaters with host rocks. The potential of gas plume H₂ observations was first invoked by Sato and McGee [1981]: the authors, in their measurements taken during the 1980 Mount St. Helens eruption, observed that, while soil H₂ increases apparently lagged behind eruptive

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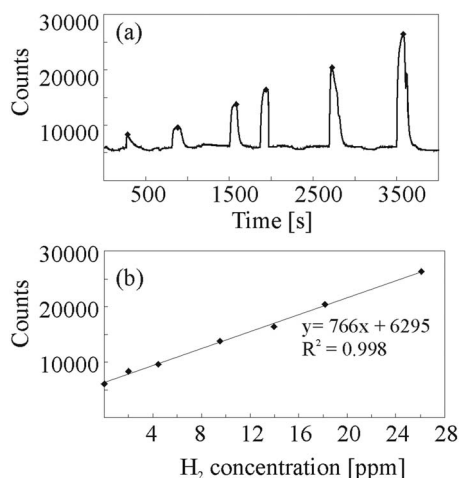


Figure 1. Calibration of the EZT3HYT hydrogen sensor in the laboratory. (a) A subset of gas mixture (with increasing H₂ concentrations) is sequentially sent to the sensor using the onboard MultiGAS pump; the sensor output (counts) is measured at a 0.3 Hz rate. (b) Peak sensor output (counts; diamonds in Figure 1a) versus standard H₂ concentrations. A linear response is observed in the 0–26 ppm range.

(and/or seismic) events by hours, large increases in atmospheric H₂ (interpreted by the authors as due to site fumigation by the volcano’s summit plume) were observed days prior to eruptions. This earlier suggestion, while highly attractive, has however not been pursued further by researchers.

[4] H₂ is potentially accessible to volcanic gas plume observations because, while being a relatively minor element in the troposphere (~0.53 ppm [Novelli *et al.*, 1999]), is generally present at much higher (0.1–2 mol %) levels in high-temperature magmatic gas emissions [Oppenheimer, 2003]. In addition, H₂ has relatively inert atmospheric behavior over the typical time scales of volcanic gas release and atmospheric transport (e.g., oxidation is slow below several hundreds of degrees, and the residence time in the atmosphere is ~2 years [Ehhalt and Rohrer, 2009]); which suggests that, as magmatic gases mix and cool in the atmosphere, plume H₂-H₂O ratios will likely remain quenched close to the source magma H₂-H₂O ratio (at least in noncondensing plumes). In spite of all the argumentations above, however, the absence of ad hoc techniques has long prevented H₂ sensing in volcanic plumes.

[5] Here, we report on the first H₂ measurements in the open-vent volcanic gas plume emissions of Etna volcano, Italy. We use our novel H₂ measures with simultaneous determinations of major plume constituents (H₂O, CO₂, and SO₂) to derive novel constraints on degassing mechanisms, and particularly on the underlying redox conditions of the source magmas. We also combine our measurements with SO₂ flux inventories (from UV spectroscopy) to provide the first assessment of Etna’s H₂ atmospheric source strength.

2. Technique

[6] H₂ measurements in the Etna’s volcanic gas plume were performed using a portable Multicomponent Gas Analyzer System (MultiGAS). The custom INGV-type

MultiGAS has been described in several recent papers [see, e.g., Aiuppa *et al.*, 2010a], and the basic version allows real-time measurement of CO₂ and H₂O (via a Licor LI-840 NDIR closed-path spectrometer) and SO₂ (using a 3ST/F electrochemical sensor by City Technology Ltd.) concentrations in a volcanic gas plume. In this study, we used an updated MultiGAS configuration, also integrating a relatively cheap (~450€) electrochemical sensor (EZT3HYT “Easy Cal” by City Technology Ltd.) for H₂ detection. This sensor, while not 100% specific to H₂, has limited cross-sensitivity to other gas plume components (see below).

[7] Broadly speaking, electrochemical sensors are devices allowing detection of the concentration of a given gas, after measurement of the current flow produced by an oxidation-reduction reaction catalyzed by noble metal electrodes immersed in an electrolyte (normally an aqueous solution of strong inorganic acids). When a chemically reactive reduced gas, such as H₂, passes through the diffusion barrier in the electrolyte, it is oxidized, and the resulting potential difference between the two electrodes causes a current to flow. Oxygen is an essential ingredient in this reaction, and sustains the current flow between electrodes. In an oxygen free (nitrogen) matrix, the hydrogen EZT3HYT sensor has a nominal range of 0–200 ppm H₂, and an accuracy of 2 ppm (laboratory tests with a 200 ppm H₂ standard (in nitrogen) produced an output signal of quasi-saturation). In contrast, in an oxygen-bearing gas matrix, the sensor resolution increases significantly: by dilution of the 200 ppm H₂ standard with an atmospheric gas standard (450 ppm CO₂, 21% O₂ in nitrogen), we obtained calibration gas mixtures having H₂ concentrations of 26.09, 18.18, 13.95, 9.52, 4.44, and 1.98 ppm (dilution factors of 7.6, 11, 14.3, 21, 45, and 101, respectively). The resulting response of the EZT3HYT sensor is shown in Figure 1, demonstrating high linearity ($R^2 > 0.99$) and improved resolution ($\sigma \pm 0.29$). Tests in the laboratory with standard gases also demonstrated that the sensor has no cross-sensitivity to common plume gases such as CO₂, SO₂, HCl and H₂S. While a nominal sensor’s cross-sensitivity to CO of <20% is reported by City Technology Ltd., our laboratory tests demonstrated a cross-interference of only ~5%. Even the worst-case scenario interference (20%), however, would negligibly affect our H₂ determinations: from our measured SO₂ concentrations, and taking a representative CO-SO₂ ratios in quiescent gas emissions from Etna of ~0.01 [Allard, 1986], we obtain that interfering CO may contribute to 1%–5% of measured H₂ at most.

[8] During 2009–2010, we repeatedly deployed the portable MultiGAS at the rims of Etna’s Bocca Nuova, Voragine, Southeast, and Northeast craters (Figure 2). Attention was paid to avoid gas contribution from low-*T* fumaroles on the craters’ rims, so that the sampled plume was primarily (or even exclusively) sourced from gas vents deep in the craters’ floor. During the field surveys, this near-vent gas plume was pumped through the MultiGAS, the sensor readouts were captured at 0.3 Hz by an onboard data logger. Postprocessing of the acquired data (see section 3) resulted in the data set reported in Table 1. In the September 2009 campaign, the INGV-type MultiGAS was used concurrently with a GSJ-type MultiGAS (operated by H.S.), whose configuration is detailed by Shinohara *et al.* [2011]. In spite of the different sensors and configurations used, the

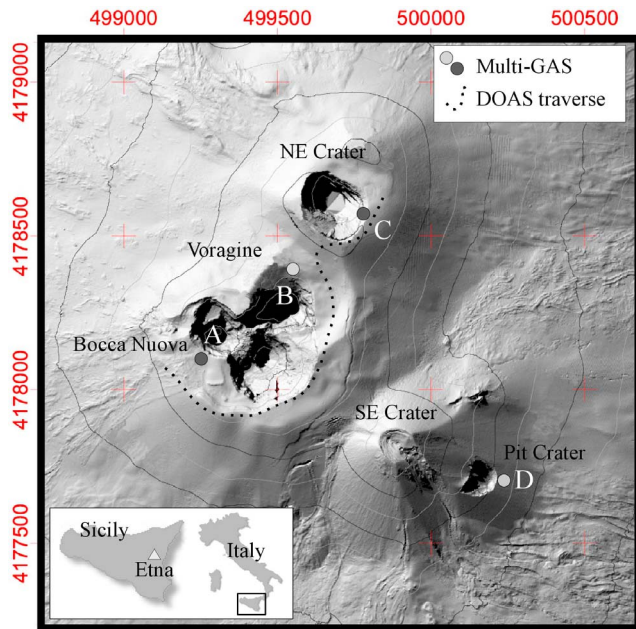


Figure 2. Map of the summit area of Mount Etna (modified from *Neri et al.* [2008]), showing the location of the MultiGAS measurement sites and the track (dotted line) of the walking traverse used to derive SO_2 fluxes for individual craters in June 2010.

simultaneously obtained H_2 data are reasonably consistent (Table 1).

3. Results

[9] An example of MultiGAS acquisition, shown in Figure 3a, demonstrates the highly correlated SO_2 and H_2 signals observed during each survey. In view of the very low (~ 20 ppb) SO_2 concentration in the troposphere, Figure 3 is strongly supportive of the dominantly volcanic origin of our measured H_2 . Background H_2 concentrations in the ambient atmosphere were obtained by taking out-of-plume measurements upwind of the vents prior to and after each acquisition. These values were subtracted from each data set to obtain background corrected (excess) H_2 concentrations typically of 1–3 ppm (Figure 3). The parallel variations of SO_2 and H_2 concentrations are also indicative for that H_2 - SO_2 ratios are independent of plume density, implying that H_2 is relatively unreactive upon atmospheric transport (as already suggested for S species [see, e.g., *Aiuppa et al.*, 2005]).

[10] Using H_2 versus SO_2 scatterplots analogous to that shown in Figure 3b, we derived, for each survey and for each crater, the characteristic plume H_2 - SO_2 ratios (from the gradient of the best fit regression lines). These ranged from 0.002 to 0.044 (mean 0.013; Table 1), and were positively correlated to CO_2 - SO_2 ratios (from 0.1 to 8.3) (Figure 4a). In spite of our relatively limited interval of observations, we observed both large (up to a factor ~ 8) temporal variations of H_2 - SO_2 ratios at each vent, and large (up to a factor ~ 10) vent-to-vent variations during individual surveys. While compositions of the different vents resulted to overlap overall, the Northeast crater was apparently characterized by somewhat higher H_2 - SO_2 ratios (>0.017), at least in 2009–2010 (Figure 4a).

Table 1. MultiGAS-Derived Molar Ratios in Etna's Near-Vent Volcanic Gas Plumes of Bocca Nuova, Voragine, Southeast, and Northeast Summit Craters^a

Date	Vent	H_2 - SO_2	CO_2 - SO_2	H_2 - H_2O	SO_2 - H_2S
3 Sep 2009	BN	0.018 (0.02 ^b)	1.1	0.0018 ^b	120 ^b
3 Sep 2009	VOR	0.002 (0.003 ^b)	1.2	0.0001 ^b	200 ^b
3 Sep 2009	NEC	n.d.	1.2	n.d.	n.d.
4 Sep 2009	BN	0.017 (0.02 ^b)	0.8	0.0015 ^b	100 ^b
4 Sep 2009	VOR	0.003 ^b	0.9	0.0001 ^b	215 ^b
4 Sep 2009	NEC	0.002 ^b	2.0	n.d.	n.d.
5 Sep 2009	BN	n.d.	0.8	n.d.	n.d.
5 Sep 2009	NEC	0.002 ^b	2.0	n.d.	n.d.
5 Sep 2009	VOR	0.011 (0.003 ^b)	1.1	0.0001 ^b	200 ^b
5 Sep 2009	BN	0.012	0.9	n.d.	n.d.
9 Nov 2009	VOR	0.020	2.2	0.00203	n.d.
9 Nov 2009	BN	0.017	2.7	0.00407	100
8 Apr 2010	BN	0.003	0.1	0.000729	n.d.
22 Apr 2010	BN	0.023	3.7	n.d.	n.d.
22 Apr 2010	NEC	0.017	3.0	n.d.	n.d.
23 Jun 2010	BN	0.016	4.0	0.00251	n.d.
23 Jun 2010	NEC	0.026	6.8	n.d.	n.d.
23 Jun 2010	NEC	0.028	4.9	0.00418	n.d.
23 Jun 2010	VOR	0.004	0.9	n.d.	n.d.
23 Jun 2010	VOR	0.005	0.7	0.00283	n.d.
24 Jun 2010	NEC	0.044	8.3	n.d.	n.d.
24 Jun 2010	VOR	0.006	2.3	n.d.	n.d.
24 Jun 2010	BN	0.019	3.0	n.d.	n.d.
24 Jun 2010	BN	0.011	2.4	0.0019	n.d.
24 Jun 2010	PIT SE	0.004	0.6	n.d.	n.d.

^aAll data are obtained with the INGV-type configuration described in the main text, except as noted otherwise. Abbreviations are as follows: BN, Bocca Nuova; NEC, Northeast; PIT SE, Southeast; VOR, Voragine; n.d., no data.

^bDerived using the GSJ MultiGAS described by *Shinohara et al.* [2011].

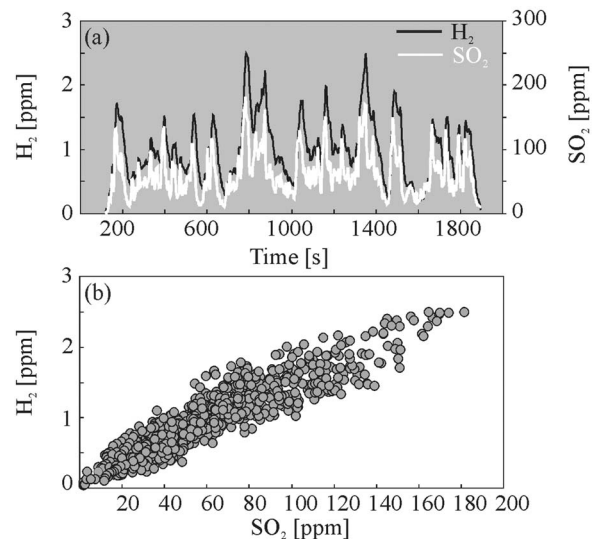


Figure 3. An example of MultiGAS acquisition (data from the 9 November 2009 survey). (a) SO_2 and H_2 plume concentrations, measured at 0.3 Hz for ~ 2000 s at Bocca Nuova crater (for H_2 , we report excess concentrations after subtraction of an ambient air contribution of ~ 0.5 ppm). (b) H_2 versus SO_2 scatter drawn from the same data set, from which plume the H_2 - SO_2 ratio was derived (as the gradient of the best fit regression line).

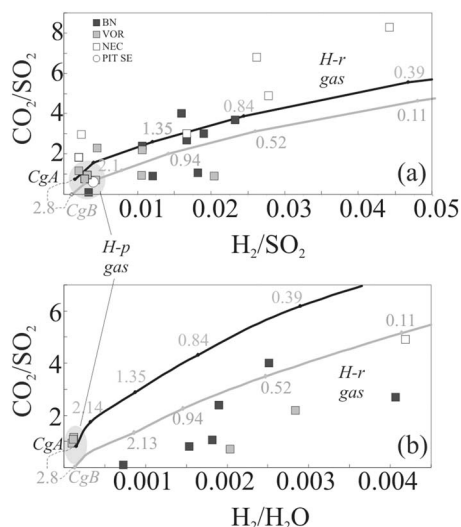


Figure 4. Scatterplot of simultaneously acquired (a) H_2 - SO_2 and CO_2 - SO_2 ratios and (b) H_2 - H_2O and CO_2 - SO_2 ratios. Data for all different vents and surveys are drawn (from data reported in Table 1). The diagram suggests that Etna's magmatic fluids range in composition from CO_2 - H_2 -rich (H-r gas) to SO_2 -rich and H_2 -poor (H-p gas) gases. The natural data are compared with the model lines calculated from (isenthalpic) mixing between deep reservoir gas and two shallow gas components (conduit gas A, CgA, and conduit gas B, CgB; see Table 2; solid and shaded lines, respectively; numbers on the two curves are equilibrium oxygen fugacities of the gas phase at the mixture temperature, given as ΔNNO). The overall (qualitative) agreement between measured and modeled compositions suggests that H-p gases are derived from degassing of a volatile-poor shallow conduit magma and have suffered H_2 - H_2O reequilibration upon cooling and atmospheric discharge, and H-p gases are (at least partially) supplied by CO_2 - H_2 -rich gas bubbles, in ascent from the deep Etna reservoir.

[11] Volcanic H_2O detection was precluded in most cases by the large and erratic variations of ambient atmosphere H_2O concentrations. When volcanic H_2O was detected in tandem with other gas species (see Aiuppa et al. [2010a] for details on H_2O retrieval), however, we obtained H_2 - H_2O plume ratios of 0.0001 to 0.0042 (mean 0.0018). These derived H_2 - H_2O ratios also display a positive dependence on CO_2 - SO_2 ratios (Figure 4b).

4. Discussion

[12] In the context of the present study, we use below our H_2 observations to derive first constraints on Etna's H_2 atmospheric source strength, and to explore novel aspects of H_2 behavior upon magmatic degassing. These, while specific to Etna's plumbing system, are likely to be relevant to open-vent basaltic volcanism in general.

4.1. Etna's H_2 Atmospheric Flux and the Volcanic Contribution to the Global H_2 Budget

[13] Our measurements contribute to a better evaluation of H_2 emissions from active volcanism. While it has long been known that volcanoes are important atmospheric sources of

“reduced” chemical species such as CO [Wardell et al., 2004] and H_2S [Aiuppa et al., 2005], the volcanic contribution to the global H_2 atmospheric budget is poorly known: the only available estimate is from Warneck [1988], who reported a global H_2 volcanic flux of $\sim 200 \text{ Gg yr}^{-1}$. If our mean H_2 - SO_2 ratio of 0.013 (molar) is used in tandem with time-averaged SO_2 flux from Etna of 1600 Gg yr^{-1} (or 4500 t d^{-1} [Allard, 1997]), we obtain a first-order assessment of the volcano's H_2 flux of 0.65 Gg yr^{-1} (range 0.1 – 2 Gg yr^{-1}). This estimate may likely be an upper limit, however, since Allard's [1997] estimate pertains to the 70s to 90s period, well before the volcano experienced a substantial reduction of its gas emissions following the large 2001 eruption (INGV-CT; monitoring reports available at <http://www.ct.ingv.it/>). On 23 and 24 June 2010, for example, we used the walking traverse technique of Aiuppa et al. [2008] to derive single-vent SO_2 fluxes from Northeast (216 – 240 t d^{-1}), Bocca Nuova (415 – 560 t d^{-1}), and Voragine (423 – 560 t d^{-1}), thus obtaining a cumulative SO_2 flux of only 1054 – 1352 t d^{-1} (consistent with the relatively low SO_2 fluxes measured by the INGV-Catania network of scanning spectrometers in early summer 2010; from reports available at <http://www.ct.ingv.it/>). With these numbers, and using the contemporaneously obtained H_2 - SO_2 ratios for each crater (reported in Table 1), we finally derived total H_2 fluxes of 0.17 (23 June) to 0.3 (24 June) Gg yr^{-1} . Our observations finally suggest that Etna's H_2 emissions are low (with respect to other natural contributions) and that, if we were to accept that Etna's contributions correspond to 10% of global volcanogenic gas emissions at most [Oppenheimer, 2003], the global H_2 volcanic flux would be estimated at only $\sim 10 \text{ Gg yr}^{-1}$. This accounts for a very marginal fraction of the H_2 yearly tropospheric flux of $70,000$ – $100,000 \text{ Gg}$, which is primarily contributed by photochemical oxidation of methane and hydrocarbons in general, as well as by biogenic and combustion processes (human activities contribute for about one quarter of the total atmospheric flux) (see Ehhalt and Rohrer [2009] for a recent review). We stress, however, that extrapolating Etna's H_2 contribution (estimated in this work) to global volcanism in the proportion of Etna's contribution to global SO_2 emissions assumes a uniform Etna-type H_2 - SO_2 ratio at all volcanoes, which is unlikely (H_2 - SO_2 ratio at a given volcano will depend on temperature but mostly on the relative abundances of water and sulfur in the magma). Therefore, the global volcanic H_2 flux quoted here ($\sim 10 \text{ Gg yr}^{-1}$) should only be viewed as an order of magnitude assessment, rather than a truly significant figure.

4.2. Insights Into the Redox Properties of the Source of Degassing

[14] The observations presented here open the way to exploration of novel aspects of magmatic degassing at Mount Etna, and more specifically to verify the hypothesis of whether or not the quiescent plume's composition reflects (and thus allow derivation of) the redox properties of the degassing magmas.

[15] At equilibrium, H_2 - H_2O ratios in high-temperature volcanic fluids will depend on temperature (T) and oxygen fugacity ($f\text{O}_2$), according to [Giggenbach, 1996]:

$$\log \frac{\text{H}_2}{\text{H}_2\text{O}} = \log K_{(1,T)} - 0.5 \cdot \log f\text{O}_2, \quad (1)$$

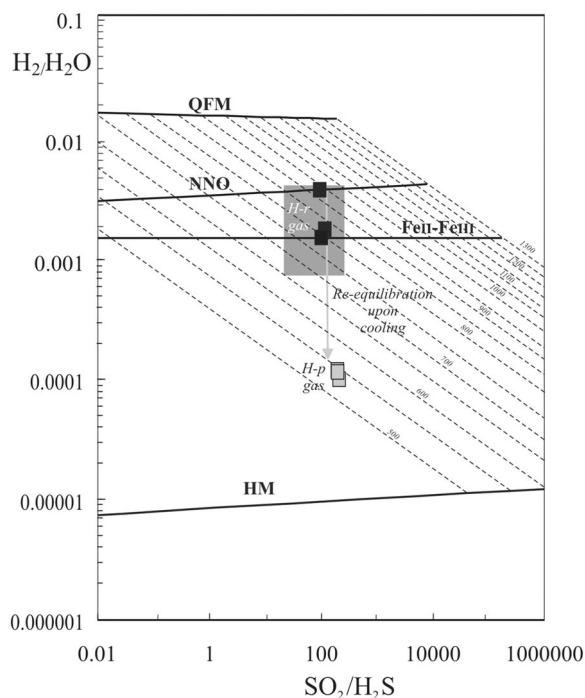
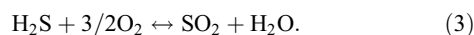


Figure 5. Equilibrium $\text{SO}_2\text{-H}_2\text{S}$ and $\text{H}_2\text{-H}_2\text{O}$ ratios in magmatic gases, calculated at 0.1 MPa pressure from relations (2) and (5) in a range of temperatures (isotherms are shown) and redox conditions. The model lines labeled QFM, NNO, HM, and $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ have been obtained by substituting into relations (1) and (3) the $f\text{O}_2$ -temperature dependences fixed by the rock buffers (quartz-fayalite-magnetite, nickel-nickel oxide, hematite-magnetite, and Fe (II)-Fe(III), respectively). The shaded area marks the typical compositional range of Etna's magmatic gases (see text), with the exception of three samples from Voragine crater, in which H_2 -poor (H-p gas) composition is ascribed to re-equilibration of the $\text{H}_2\text{-H}_2\text{O}$ redox couple upon cooling of the gas phase down to $\sim 550^\circ\text{C}$. $\text{SO}_2\text{-H}_2\text{S}$ is apparently quenched at the magmatic values over the same cooling path, consistent with its slow kinetics [Giggenbach, 1987].

where $K_{(1,T)}$ is the temperature-dependent equilibrium constant of the water dissociation reaction. Using the thermodynamic data of Stull *et al.* [1969], this reduces to

$$\log \frac{\text{H}_2}{\text{H}_2\text{O}} = -\frac{12707}{T} + 2.548 - 0.5 \cdot \log f\text{O}_2. \quad (2)$$

In the attempt to concurrently derive both T and redox conditions, we also consider the equilibrium reaction between S species:



This reaction determines the well-behaved highly positive temperature dependence of the equilibrium $\text{SO}_2\text{-H}_2\text{S}$ ratio according to

$$\log \frac{\text{SO}_2}{\text{H}_2\text{S}} = \log K_{(3,T)} + \left[\frac{3}{2} \cdot \log f\text{O}_2 \right] - \log f_{\text{H}_2\text{O}} \quad (4)$$

($f_{\text{H}_2\text{O}}$ being water fugacity), or, using thermodynamic data from Stull *et al.* [1969]:

$$\log \frac{\text{SO}_2}{\text{H}_2\text{S}} = \frac{27377}{T} - 3.986 + \left[\frac{3}{2} \cdot \log f\text{O}_2 \right] - \log f_{\text{H}_2\text{O}}. \quad (5)$$

As for $f\text{O}_2$, we substitute in relations (2) and (5) the temperature dependences of the most common rock buffers pertinent to basaltic volcanism (quartz-fayalite-magnetite, QFM; nickel-nickel oxide, NNO; and Fe(II)-Fe(III) [Huebner and Sato, 1970; Carmichael and Ghiorso, 1986; Giggenbach, 1996]); and finally obtain, using relations (2) and (5) in tandem, the couples of equilibrium $\text{H}_2\text{-H}_2\text{O}$ and $\text{SO}_2\text{-H}_2\text{S}$ gas ratios, at each T and for each rock redox buffer (at 0.1 MPa pressure) (Figure 5). In Figure 5, these are compared with the plume-measured $\text{H}_2\text{-H}_2\text{O}$ and $\text{SO}_2\text{-H}_2\text{S}$ ratios (Table 1). Our newly derived $\text{SO}_2\text{-H}_2\text{S}$ ratios (from Table 1) range 100–215, and therefore result a factor 5–10 higher than previously determined (~ 20 [Aiuppa *et al.*, 2005, 2007a]). In Figure 5, we therefore assume a $\text{SO}_2\text{-H}_2\text{S}$ range of 20–200 as representative of high-temperature Etna's gas emissions.

[16] Comparison between the model-derived compositions and natural data suggests that most of our observed plume compositions (at least those falling in the gray shaded box of Figure 5) closely match those representative of quenched (high-temperature) gas melt equilibria for redox conditions at, or slightly (approximately one log unit at most) above, the NNO buffer (Figure 5). Magma redox conditions close to NNO have indeed been supposed at Etna based on direct $f\text{O}_2$ measurements in fumaroles [Sato and Moore, 1973], and by S speciation data in plume [Aiuppa *et al.*, 2005] and magmas, with the latter recording $f\text{O}_2$ values averaging at ~ 0.35 log units above NNO [Métrich and Clocchiatti, 1996]. From this, we take the final conclusion that $\text{H}_2\text{-H}_2\text{O}$ ratios, in otherwise “cold” and “air-diluted” volcanic gas plumes, apparently preserve the original (magma-buffered) high- T and reduced conditions of the sourcing magma. Our estimated equilibrium temperature (750°C – 950°C) range is somewhat below the accepted magma temperature at Etna ($\sim 1050^\circ\text{C}$), implying some extent of reequilibration upon cooling and atmospheric discharge.

[17] By contrast, we observe that three samples from Voragine crater display far lower $\text{H}_2\text{-H}_2\text{O}$ ratios (~ 0.0001) than the main data cluster (shaded box). These samples thus point to the existence of a gas component significantly more oxidized (H_2 -poor) and colder (equilibrium T of $\sim 550^\circ\text{C}$) than the source magma itself. It is worth noting that periodic field surveys with an infrared camera (performed by INGV-Catania; reports available at <http://www.ct.ingv.it/>) systematically failed in detecting high-temperature anomalies inside the Voragine's crater bottom; thus suggesting that low-temperature fumaroles, rather than open-vent magma degassing, were sustaining plume emissions at that crater. Therefore, we propose that the low H_2 content of the Voragine gas must reflect substantial reequilibration of the $\text{H}_2\text{-H}_2\text{O}$ ratio upon cooling of the gas phase in the fumarole conduits, while the slow-reacting $\text{SO}_2\text{-H}_2\text{S}$ redox couple remained essentially quenched at the magmatic value [Giggenbach, 1987] (Figure 5).

Table 2. Magmatic Gas Phase Compositions Calculated Using the *Moretti and Papale* [2004] Saturation Model^a

	Reservoir Gas	Conduit Gas A	Conduit Gas B
T , °C	1100	550	550
P , Mpa	140	0.1	0.1
Redox,	$\Delta\text{NNO} =$	$\Delta\text{NNO} =$	$\Delta\text{NNO} =$
$\log f\text{O}_2$	0 (-8.89)	+2.8 (-18) ^c	+2.8 (-18) ^c
$X\text{H}_2\text{O}$	0.408	0.87	0.89
$X\text{H}_2$	0.00178 ^b	0.0001 ^b	0.0001 ^b
$X\text{CO}_2$	0.57	0.055	0.00003
$X\text{SO}_2$	0.0044	0.068	0.108
$X\text{H}_2\text{S}$	0.0117	0.0004	0.00057
$\text{H}_2\text{-H}_2\text{O}$	0.076 ^b	0.00013 ^b	0.00013 ^b
$\text{H}_2\text{-SO}_2$	7.0	0.0017	0.0011
$\text{CO}_2\text{-SO}_2$	130	0.8	0.0003
$\text{SO}_2\text{-H}_2\text{S}$	0.4	192	188

^aThe reservoir gas composition was calculated as the magmatic gas phase at equilibrium with Etna's basalt in magma reservoir at 140 MPa pressure [Spilliaert *et al.*, 2006]. The conduit gas compositions were derived for thermodynamic equilibrium with the basaltic magma at 0.1 MPa, following either closed-system (conduit A) or open-system (conduit B) degassing (upon decompression) of the reservoir magma (more specifically, in case A, closed-system behavior was maintained in the 140–1 MPa pressure range, followed by open-stem degassing between 1 and 0.1 MPa). In both cases A and B, the decompression path was computed for initial nickel-nickel oxide redox conditions and magma cooling from 1140°C to 1100°C. In a second step, the obtained 0.1 MPa conduit gases (both A and B) were cooled down to 550°C, with all the gas ratios (including the $\text{SO}_2\text{-H}_2\text{S}$ ratio) kept fixed (e.g., quenched) at the original (1100°C) values, except $\text{H}_2\text{-H}_2\text{O}$. This was allowed to equilibrate at the new temperature and was calculated from relation (2).

^bCalculated from equation (2) using temperatures and $f\text{O}_2$ values given in the same column. Our computations actually violate mass balances for H_2 in the system, an approximation viable in light of the fact that $\text{H}_2\text{O} \gg \text{H}_2$.

^cCalculated from equilibrium (5) at 550°C and using the quenched equilibrium $\text{SO}_2\text{-H}_2\text{S}$ ratios at 1100°C (192 and 188 for cases A and B, respectively).

[18] Our argumentations above suggest that $\text{H}_2\text{-H}_2\text{O}$ ratios in plume reflect to some extent the cooling history of the magmatic gas phase upon atmospheric release. When the magmatic gas phase is directly injected in the atmosphere at high temperature, as at open vents (Bocca Nuova, Northeast craters), and then rapidly cooled, the $\text{H}_2\text{-H}_2\text{O}$ and $\text{SO}_2\text{-H}_2\text{S}$ gas ratios are quenched to reflect redox properties of the source magmas (hydrogen-rich gas; H-r gas). When degassing is fed instead by low-temperature fumaroles in a cooled and crystallizing magma (filling a closed vent on the crater floor, as at Voragine), plume $\text{H}_2\text{-H}_2\text{O}$ ratios will likely be unrepresentative (far lower) than the magmatic conditions (hydrogen-poor gas; H-p gas).

4.3. Modeling H_2 Source Mechanisms

[19] Inspection of Figure 4 indicates that a trend of increasing $\text{CO}_2\text{-SO}_2$ ratios parallels the transition from low $\text{H}_2\text{-H}_2\text{O}$ (and $\text{H}_2\text{-SO}_2$) H-p gas, to more magmatic (high $\text{H}_2\text{-H}_2\text{O}$ and $\text{H}_2\text{-SO}_2$) H-r gas. This supports the conclusion that H_2 shares some common degassing behavior with CO_2 .

[20] Previous research has shown that Etna's shallow magmas, filling the upper volcano's conduit system, are highly CO_2 depleted [Métrich *et al.*, 2004; Collins *et al.*, 2009], to the point that degassing of their residual dissolved volatiles may only sustain a CO_2 -poor ($\text{CO}_2\text{-SO}_2 \ll 1$) conduit gas phase [Aiuppa *et al.*, 2007b]. On the other hand, the recurrent CO_2 -rich signature of Etna's plume emissions [Allard *et al.*, 1991; Aiuppa *et al.*, 2007b, 2010b] requires the

additional contribution of CO_2 -rich bubbles, likely supplied by the Etna's deep magma reservoir(s) [Spilliaert *et al.*, 2006]. According to Shinohara *et al.* [2008], a mixture of deep-rising CO_2 -rich reservoir gases, and CO_2 -poor conduit gases, finally fuels Etna's passive gas emissions.

[21] Data trends shown in Figure 4 now suggest that conduit CO_2 -poor gases are of the H-p gas type, while deeply rising high $\text{CO}_2\text{-SO}_2$ gases are typically more H_2 -rich (H-r gases). We therefore hypothesize that a two-component mixing process, similar to that envisaged by Shinohara *et al.* [2008], can explain our spread of H_2 compositions (Figure 4). By analogy with Aiuppa *et al.* [2007b], we used the multi-component equilibrium saturation model of Moretti and Papale [2004] to calculate the theoretical compositions of magmatic gases at both deep reservoir and shallow conduit conditions. The reservoir gas composition (Table 2) was calculated as the magmatic gas phase at equilibrium with Etna's basalt at 1100°C, 140 MPa pressure (the derived pressure for the upper margin of Etna's deep reservoir [Spilliaert *et al.*, 2006]) and redox conditions at NNO buffer (total magmatic CO_2 , H_2O and S contents as by Aiuppa *et al.* [2007b]). The $\text{H}_2\text{-H}_2\text{O}$ gas ratio was calculated using equation (2), which implies our computations do not make use of any solubility model for H_2 (assumed as a completely mobile and free component). While our computations violate hydrogen mass balance in the system, we consider our approximation acceptable given that $\text{H}_2\text{O} \gg \text{H}_2$. The conduit gas composition was derived instead as the gas phase in equilibrium (at 0.1 MPa pressure) with a basaltic magma formed after either closed-system (conduit A) or open-system (conduit B) degassing upon decompression (from 140 to 0.1 MPa) of the reservoir magma (Table 2). We assume that, in the most extreme scenario, the conduit gas will rapidly cool down to 550°C prior to emission (Figure 5). If this was to occur, the $\text{SO}_2\text{-H}_2\text{S}$ ratio would essentially remain quenched [Giggenbach, 1987] at the magmatic ($T = 1100^\circ\text{C}$) value of ~ 200 , while the $\text{H}_2\text{-H}_2\text{O}$ would reequilibrate at the lower-temperature conditions (as for H-p gas in Figure 5). In the conduit gas calculations, we therefore calculated the $\text{H}_2\text{-H}_2\text{O}$ gas ratio from equation (2), using $T = 550^\circ\text{C}$ and $f\text{O}_2$ calculated from relation (5) (at $T = 550^\circ\text{C}$, and for magmatic $\text{SO}_2\text{-H}_2\text{S}$ ratios of 192 and 188 for conduit A and conduit B cases, respectively; Table 2). Finally, isenthalpic mixing between reservoir gas and either conduit A gas or conduit B gas was used to draw the mixing lines shown in Figures 4a and 4b.

[22] Results show that our model-derived conduit gas compositions are in reasonable agreement with our measured H-p gas compositions from Voragine (Figure 4); demonstrating the plausibility of the model assumptions, and further supporting earlier conclusions (Figure 5) of the shallow (near-surface), cold (550°C), and oxidized (conduit gases have equilibrium redox conditions at $\text{NNO} + 2.8$; Table 2) environment of final equilibration of H-p gas. Figures 4 and 5 also demonstrate that our model mixing curves between reservoir gas and conduit gases (solid and shaded lines for conduit gas A and B, respectively) reproduce, at least qualitatively, the chemical evolution toward CO_2 - and H_2 -rich (H-r) gas. Thus, while a more rigorous knowledge of the model input parameters (e.g., pressure, redox conditions, and total volatile contents in reservoir) would probably be required to obtain a better fit between modeled and measured compositions, we conclude that mixing between deep reservoir and conduit gas

is a viable mechanism to account for H₂ content and degassing behavior in Etna's emissions. This deep gas contribution to the mixture may vary both in space (e.g., from crater to crater, being the highest at open vents, where the effect of cooling and reequilibration would be more marginal) and time (depending on the structural and magmatic processes governing exsolution, separation and ascent of gas bubbles from the reservoir); therefore proving quantitative explanation for the spread of H₂ compositions in our data set.

5. Conclusions

[23] We have shown that a commercially available electrochemical sensor has sensibility, resolution, and cross sensitivity suitable for resolving volcanic H₂ above the ambient tropospheric contents (~0.5 ppm) in volcanic gas plumes. As such, the MultiGAS technique opens promising opportunities to investigate H₂ behavior in volcanic environments (a still open matter). Our measurements on Etna volcano allow us to derive a first-order assessment of the H₂ flux from Etna (0.65 Gg yr⁻¹), and to propose a simple degassing mechanism accounting for H₂ content and behavior in the plume. We finally propose that H₂ in Etna's plume emissions is contributed to by both residual degassing of a shallow (and volatile-depleted) conduit magma, and ascent of deep-reservoir (CO₂-H₂-rich) gas bubbles. This "deep" H₂ contribution, if confirmed by additional observations, may prompt future applications in volcano monitoring.

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