



Rapid oxidation of mercury (Hg) at volcanic vents: Insights from high temperature thermodynamic models of Mt Etna's emissions

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ABSTRACT

A major uncertainty regarding the environmental impacts of volcanic Hg is the extent to which Hg is deposited locally or transported globally. An important control on dispersion and deposition is the oxidation state of Hg compounds: Hg(0) is an inert, insoluble gas, while Hg(II) occurs as reactive gases or in particles, which deposit rapidly and proximally, near the volcanic vent. Using a new high temperature thermodynamic model, we show that although Hg in Etna's magmatic gases is almost entirely Hg(0) (i.e., gaseous elemental mercury), significant quantities of Hg(II) are likely formed at Etna's vents as gaseous HgCl₂, when magmatic gases are cooled and oxidised by atmospheric gases. These results contrast with an earlier model study and allow us to explain recent measurements of Hg speciation at the crater rim of Etna without invoking rapid (<1 min) low temperature oxidation processes. We further model Hg speciation for a series of additional magmatic gas compositions. Compared to Etna, Hg(II) production (i.e., Hg(II)/Hg_{tot}) is enhanced in more HCl-rich magmatic gases, but is independent of the Hg, HBr and HI content of the magmatic gases. Hg(II) production is not strongly influenced by the initial oxidation state of magmatic gases above NNO, although production is hindered in more reduced magmatic gases. The model and results are widely applicable to other open-vent volcanoes and may be used to improve the accuracy of chemical kinetic models for low temperature Hg speciation in volcanic plumes.

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1. Introduction

Active volcanoes are a major source of Hg to the atmosphere (Pyle and Mather, 2003; Bagnato et al., 2010). An estimated ~75–100 Mg yr⁻¹ is released by quiescent degassing at volcanoes such as Mt Etna, Sicily (Bagnato et al., 2007) and Masaya, Nicaragua (Witt et al., 2008). Other natural sources of Hg to the atmosphere include evasion from soils, vegetation, agriculture and the oceans (Schroeder and Munthe, 1998), yielding a total natural Hg flux of ~4400–5200 Mg yr⁻¹, much of which is recycled Hg from earlier anthropogenic emissions (Mason, 2009; Pirrone et al., 2009). The anthropogenic Hg flux is of the same order (2200–4000 Mg yr⁻¹; Selin, 2009; Pirrone et al., 2009); the most significant of these flux sources is coal combustion, but metal production, waste incineration and artisanal gold mining are also important (Mason, 2009). The total atmospheric burden of Hg has more than doubled from ~1600 to 1800 Mg in pre-anthropogenic times (Mason et al., 1994; Lamborg et al., 2002) to ~5000 Mg at the present day (Selin et al., 2008) due to these industrial activities. This significant

increase in atmospheric Hg is reflected in archives such as lake sediments, peat bogs and ice records which show a 2- to 4-fold increase in the past 150 years (Lindberg et al., 2007; Farmer et al., 2009). These archives also reflect the importance of volcanic explosions (e.g., Shotyk et al., 2005; Hobara et al., 2009; Guevara et al., 2010); ice-core data suggest that large events such as Tambora, 1815, or Krakatau, 1883, can result in deposition rates of Hg similar to those of global anthropogenic processes (Schuster et al., 2002).

Mercury exists in the atmosphere predominantly as gaseous elemental mercury (GEM = Hg(g)). GEM has a long atmospheric lifetime (0.5–2 years, Lindqvist and Rodhe, 1985; Slemr et al., 1985) due to its low solubility in water, which inhibits removal by wet deposition, and its gaseous nature, which inhibits sedimentation. In contrast, most other trace metals are largely present in the particulate form and are deposited after only a few days (Galloway et al., 1982; Schroeder and Munthe, 1998). The long atmospheric lifetime of GEM promotes long-range global transport, explaining the elevated concentrations of Hg found in remote regions of the world (Fitzgerald et al., 1998; Morel et al., 1998). A major loss process for GEM is oxidation to more soluble Hg(II) forms such as reactive gaseous Hg (RGM = HgCl₂(g), HgBr₂(g), Hg(OH)₂(g), etc.) and particulate Hg (Hg_p). These compounds are quickly removed by dry and wet

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deposition processes and have atmospheric lifetimes of days to weeks. RGM and Hg_p make up only a few percent of total atmospheric Hg, although these proportions may be higher close to emission sources (Schroeder and Munthe, 1998). Once deposited into waters, soils and sediments, biological and chemical processes can convert Hg into toxic methylated forms (Ullrich et al., 2001) which are lipid soluble and bioaccumulate and biomagnify in the food chain (Bloom, 1992; Jonnalagadda and Rao, 1993; Lindberg, 1996; Morel et al., 1998).

The focus of this paper is the fate of the primary mercury emissions from open volcanic vents. Most modern measurements have concentrated on determining the flux and speciation of mercury as it is emitted from the vent (e.g. Bagnato et al., 2007; Witt et al., 2008). Recent crater rim measurements show total Hg concentrations of >100 ng m⁻³, which correspond to ~100× the local atmospheric background (e.g., Bagnato et al., 2007, 2009, 2010). Such measurements indicate that RGM + Hg_p comprise ~1–2% of Hg_{tot} at Etna, Sicily (Bagnato et al., 2007) and La Soufrière, Guadeloupe (Bagnato et al., 2009), 2–8% of Hg_{tot} at Masaya, Nicaragua (Witt et al., 2008) and a poorly quantified amount (<20%) of Hg_{tot} at Kīlauea, Hawaii (Mather et al., 2010). Early studies have reported much higher RGM + Hg_p, including >60% of Hg_{tot} at Etna (DeDeurwaerder et al., 1982) and 80% of Hg_{tot} at Erebus, Antarctica (McMurtry et al., 1979). The process and extent of Hg deposition has yet to be studied in any detail and remains a key unknown, although is likely influenced by the initial Hg speciation (i.e., Hg_{tot} = GEM + RGM + Hg_p) (von Glasow, 2010).

To assess the potential for local Hg deposition we made thermodynamic model calculations to investigate the controls on Hg speciation in the high-temperature mixtures of magmatic and atmospheric gases formed at Etna's vents. This assessment is based solely on high-temperature thermodynamic considerations, i.e., the extent to which Hg(0) is oxidised to Hg(II), and extends an earlier high temperature Hg speciation model for Etna's emissions (Bagnato et al., 2007). We further model Hg speciation for a series of additional magmatic gas compositions to investigate how Hg(II) formation is affected by the oxidation state of magmatic gases, along with the abundances of Hg and the halogens (e.g., HCl, HBr and HI). We also consider the potential effects of the magmatic gas temperature on Hg speciation. These results will be widely applicable to other open-vent volcanoes.

1.1. Mt Etna (Sicily)

Mt Etna is a ~3300 m high basaltic stratovolcano located in NE Sicily. Lavas are mostly of hawaiite composition with a gradual shift recently towards more K-rich trachybasalts (Allard, 1997). The volcanic activity at Etna is characterised by quiescent degassing, punctuated by occasional Strombolian eruptions and lava flows from the four summit craters (Bocca Nuova, Voragine, North-East crater and South-East crater) and sporadic flank eruptions ranging from passive lava flows to violent fire-fountains which produce significant quantities of ash (Allard et al., 2006). Within the spectrum of eruptive activity there are differences through time with respect to the number, length and vigour of eruptive episodes.

The composition of Etna's emissions is well constrained in terms of the most abundant gases (e.g., H₂O, SO₂, CO₂, H₂S, HF, HCl, HBr, HI; Aiuppa et al., 2004, 2005a, 2005b, 2008). The relatively detailed understanding of the degassing regime makes Etna an important "laboratory" volcano for investigating metal emissions from volcanoes. These emissions at Etna have been investigated using a wide range of techniques, including bulk- and micro-analyses of the aerosol (e.g., Toutain et al., 1995; Varekamp et al., 1986; Gauthier and Le Cloarec, 1998; Aiuppa et al., 2003; Bagnato et al., 2007) and eruptive products (e.g., Ferlito et al., 2008; Collins et al., 2009). It is thought that the separation of gas from melt plays an important role in influencing both the compositions of volcanic aerosol and of the residual melts (e.g. Aiuppa et al., 2004; Spilliaert et al., 2006). Other studies have focused on

Etna's influence on metals in groundwater (e.g., Giammanco et al., 1998; Aiuppa et al., 2000), rainwater (e.g., Aiuppa et al., 2006), and biological systems (e.g., Barghigiani et al., 1988; Notcutt and Davies, 1989; Monna et al., 1999; Watt et al., 2007; Martin et al., 2009a; Quayle et al., 2010). Few studies of Etna's metal emissions report data on Hg despite the flux (5.4 Mg yr⁻¹; Bagnato et al., 2007) being comparable to that of other "trace" metals (e.g., As, Cd, Tl; Table 1). Recent measurements at the crater rim of Etna indicate that Hg(II)/Hg_{tot} ~ 10⁻², with mean GEM + RGM = 277 ng m⁻³ and mean Hg_p = 3.6 ng m⁻³ (Bagnato et al., 2007), while background GEM + RGM = 3 ng m⁻³.

Low temperature kinetic modelling of Etna's emissions (von Glasow, 2010) suggests that, within 15 min of emission, Hg(0) (i.e., GEM) may be oxidised completely to Hg(II) (i.e., RGM + Hg_p) by Br and Cl radicals. The source of these Br and Cl radicals is thought to be high temperature chemistry occurring as magmatic and atmospheric gases mix and react at Etna's vents (Bagnato et al., 2007). Unfortunately, no downwind Hg speciation measurements are available to confirm this model result so the environmental behaviour of Hg remains uncertain. An additional complicating factor is that diffuse degassing of Hg in CO₂-rich fluids potentially occurs on Etna's flanks (Varekamp and Buseck, 1986).

2. Thermodynamic model for Hg speciation

Thermodynamic models have been used in a number of recent studies to model the compositional changes occurring as hot magmatic gases mix and react with cold atmospheric gases at volcanic vents (e.g., Gerlach, 2004; Martin et al., 2006; Bagnato et al., 2007; Bobrowski et al., 2007; Martin et al., 2009b). The assumption in these models is that magmatic and atmospheric gases equilibrate instantaneously at the vent until a temperature (typically >500 °C) is reached where the composition becomes frozen (i.e., the quenching temperature). While there remain uncertainties about the validity of the equilibrium assumption (e.g., Aiuppa et al., 2007; Martin et al., 2009b), thermodynamic models enable parametric dependences to be investigated in the absence of chemical kinetic schemes. The model used here runs within commercial software (HSC Chemistry v5.1) and is based upon the high-T thermodynamic model of Martin et al. (2006), which includes 110 gas-phase species of C, O, S, H, Cl, F, Br, I and N. To the existing model we incorporate Hg, HgH, HgO, HgS, HgF, HgCl, HgBr, HgI, HgF₂, HgCl₂, HgBr₂, HgI₂, HgSO₄, HgSO₄.HgO, HgSO₄.2HgO and Hg₂SO₄. All compounds are included as both gas and condensed phases except for HgH (gas phase only) and the Hg sulphates (condensed phases only). The full species list is given in Appendix A. The software iterates to find the molecular composition (i.e., a mixing ratio for each species) with the lowest Gibbs free energy

Table 1
Mass ratios of As, Cd, Tl and Hg to SO₂ in Etna's emissions.

	Mass ratio	Reference
As/SO ₂	2 × 10 ⁻⁶	Bocca Nuova Crater 2001; Aiuppa et al., 2003 ^a
	3 × 10 ⁻⁶	Monti Carcarazzi vent 2001; Aiuppa et al., 2003 ^a
Cd/SO ₂	1 × 10 ⁻⁶	Bocca Nuova Crater 2001; Aiuppa et al., 2003 ^a
	2 × 10 ⁻⁶	Monti Carcarazzi vent 2001; Aiuppa et al., 2003 ^a
	8.3 × 10 ⁻⁶	Summit vents 1992–1995; Gauthier and Le Cloarec, 1998
	4.0 × 10 ⁻⁵	Effusive vents 1992; Gauthier and Le Cloarec, 1998
Tl/SO ₂	4 × 10 ⁻⁶	Bocca Nuova Crater 2001; Aiuppa et al., 2003 ^a
	7 × 10 ⁻⁶	Monti Carcarazzi vent 2001; Aiuppa et al., 2003 ^a
	2.3 × 10 ⁻⁵	Summit vents 1992–1995; Gauthier and Le Cloarec, 1998
Hg/SO ₂	4.1 × 10 ⁻⁴	Effusive vents 1992; Gauthier and Le Cloarec, 1998
	8.8 × 10 ⁻⁶	Summit vents 2004–2007; Bagnato et al., 2007
	6.0 × 10 ⁻⁶	Bocca Nuova Crater 1980; DeDeurwaerder et al., 1982
	1.0 × 10 ⁻⁵	Summit fumaroles 1981; Varekamp and Buseck, 1986
	8.9 × 10 ⁻⁵	Summit vents 1976; Buat-Menard and Arnold, 1978

^a In Aiuppa et al. (2003), mass ratios were given relative to particulate S. To convert, we assume all particulate S is SO₄²⁻, and SO₄²⁻/SO₂ ~ 0.01 (e.g., Allen et al., 2006).

at a specific temperature, pressure and atomic composition. This molecular composition is the equilibrium composition.

The composition of magmatic gases was defined in terms of H₂O, CO₂, SO₂, HCl, HF, HBr, HI, H₂S, H₂ and Hg (composition A; Table 2). The composition of atmospheric gases was defined as 78% N₂, 21% O₂ and 1% Ar, and the degree of mixing was parameterised by V_A/V_M, representing the volume ratio of atmospheric to magmatic gases in the mixture (Martin et al., 2006). Condensed Hg phases were assumed to form an ideal solution with a pre-existing aerosol. The vapour pressure of a component (i.e., GEM, RGM) above an ideal solution only depends on the concentration of the component (i.e., Hg_p) within the ideal solution. The composition of the pre-existing aerosol is therefore irrelevant and only the total molar amount of pre-existing aerosol needs to be specified. This simplified model does not account for the thermodynamic Kelvin effect, which would tend to favour gaseous Hg relative to our model results (e.g., Seinfeld and Pandis, 1998). All calculations were made at a pressure of 1 atm.

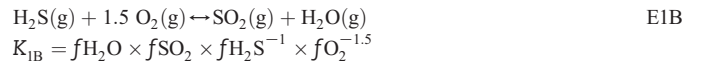
The thermodynamic model extends the model of Bagnato et al. (2007) and shares similarities. However, there are several important differences between our model and the model of Bagnato et al. (2007)

- (1) Iodine chemistry was not included within the model of Bagnato et al. (2007). We include iodine chemistry within the model since, although HI is a minor component of Etna's emissions, iodine is potentially an important control on Hg speciation due to the strong affinity of Hg for soft, highly polarisable elements such as iodine. The input composition reflects HCl/HBr~1000 and HCl/HI~1.4 × 10⁵ (Aiuppa et al., 2005a).
- (2) Neither H₂S nor H₂ were included within the model of Bagnato et al. (2007) because measurements at Etna suggest that H₂S does not re-equilibrate completely with atmospheric gases after emission (Aiuppa et al., 2005b, 2007) and because there are no measurements available for H₂ in Etna's emissions. These reduced gases fix the oxidation state of the mixture, and their absence would imply (within the model) a more highly oxidised version of Etna's emissions so we include both H₂S and H₂ in the input composition. The input composition reflects SO₂/H₂S~20 (Aiuppa et al., 2005b) and equilibrium H₂/H₂O at 1100 °C, at the oxygen fugacity of Etna's magma, log(*f*O₂) = *NNO* + 0.3 (e.g., Allard et al., 2005).
- (3) The model of Bagnato et al. (2007) had aerosols occupying the entire volume of the system resulting in an over-estimation of aerosols formed at high temperature. We consider a single mixed aerosol phase occupying only a small volume relative to

the total volume. While uncertainties and limitations remain with the modelling of aerosols, our approach better reflects the true phase nature.

- (4) The model of Bagnato et al. (2007) used the thermodynamic database supplied with HSC Chemistry v2.1, while we use a much revised version of the thermodynamic database (supplied with HSC Chemistry v5.1). This revised version includes updated thermodynamic properties for species present in v2.1, along with many additional species.

A series of additional magmatic gas compositions (compositions B–F; Table 2) were generated by adjustment of Etna's magmatic gas composition (composition A). These compositions remain plausible for magmatic gases but do not reflect any individual volcano. This approach allows the influence of each parameter to be investigated by comparison with the results for Etna's magmatic gas composition. Relative to composition A, composition B has 10× increased Hg, composition C has 10× increased HI and HBr, and composition D has 2× increased HCl. Composition E and F are, respectively, more oxidised (i.e., log(*f*O₂) = *NNO* + 0.8) and more reduced (i.e., log(*f*O₂) = *NNO* – 0.2) than composition A; both compositions were generated by scaling H₂ (proportional to *f*O₂^{–0.5}; E1A) and H₂S (proportional to *f*O₂^{–1.5}; E1B). Equilibrium constants (*K*) are expressed here in terms of fugacities (e.g., *f*O₂ in bar); equivalent relationships apply for mixing ratios (e.g., [H₂O] in mol mol^{–1}).



3. Results and discussion

3.1. Model calculations for Etna's magmatic gases

For a given magmatic gas composition (Table 2) and magmatic gas temperature (1100 °C), the variables influencing Hg speciation in high temperature mixtures of magmatic and atmospheric gases are the mixture temperature, its oxidation state, and the aerosol volume. These influences convolve during air mixing (represented by increasing V_A/V_M), which decreases the mixture temperature and increases its oxidation state. Less directly, the aerosol volume would also increase during air mixing due to condensation of metal salts at high-temperature (e.g., NaCl; Toutain et al., 1995) and aqueous aerosol at low-temperature (e.g., Allen et al., 2006; Martin et al., 2008). Therefore, we need model only a specific path through parameter space (i.e., a V_A/V_M, *T*-path). This path was calculated with a simple thermal mixing model (i.e., Δ*H* = 0), assuming that magmatic gases have a 30% higher specific heat capacity than atmospheric gases over the temperature range.

Several "end member" model initialisations were chosen to assess the different influences on Hg speciation in Etna's emissions:

Model 1 – Thermal equilibration of magmatic gases (1100 °C) with atmospheric gases (25 °C) down to 600 °C. The atmospheric gases cool and dilute the magmatic gases but do not react with the magmatic gases.

Model 2 – Chemical equilibration of magmatic gas (1100 °C) with atmospheric gas (25 °C) down to 600 °C. The atmospheric gases cool, dilute and react with the magmatic gases.

Model 3 – as for Model 2, with a pre-existing aerosol (molar ratio of aerosol/SO₂~0.01). This model assumes that the crater rim aerosol (e.g., Allen et al., 2006; Martin et al., 2008) is entirely formed at high temperature.

Table 2

Magmatic gas compositions used within the high temperature thermodynamic model. The differences between Etna's magmatic gas composition (composition A) and the additional magmatic gas compositions (B–E) are denoted using bold text.

Species	A ^a	B ^b	C ^b	D ^b	E ^b	F ^b
Hg(g)	2.9 × 10 ^{–7}	2.9 × 10^{–6}	2.9 × 10 ^{–7}	2.9 × 10 ^{–7}	2.9 × 10 ^{–7}	2.9 × 10 ^{–7}
H ₂ O(g)	0.86	0.86	0.86	0.86	0.86	0.86
SO ₂ (g)	0.029	0.029	0.029	0.029	0.029	0.029
CO ₂ (g)	0.096	0.096	0.096	0.096	0.096	0.096
HCl(g)	0.014	0.014	0.014	0.028	0.014	0.014
HF(g)	0.003	0.003	0.003	0.003	0.003	0.003
HBr(g)	1.4 × 10 ^{–5}	1.4 × 10 ^{–5}	1.4 × 10^{–4}	1.4 × 10 ^{–5}	1.4 × 10 ^{–5}	1.4 × 10 ^{–5}
HI(g)	1.0 × 10 ^{–7}	1.0 × 10 ^{–7}	1.0 × 10^{–6}	1.0 × 10 ^{–7}	1.0 × 10 ^{–7}	1.0 × 10 ^{–7}
H ₂ S(g)	0.0015	0.0015	0.0015	0.0015	2.7 × 10^{–4}	8.4 × 10^{–3}
H ₂ (g)	0.005	0.005	0.005	0.005	2.8 × 10^{–3}	8.9 × 10^{–3}

^a Etna's magmatic gas composition. The amounts of H₂O(g), SO₂(g), CO₂(g), HCl(g), HF(g) and Hg(g) are as used by Bagnato et al. (2007). Additionally, our input composition reflects HCl/HBr~1000 (Aiuppa et al., 2005a), HCl/HI~1.4 × 10⁵ (Aiuppa et al., 2005a, 2005b), SO₂/H₂S~20 (Aiuppa et al., 2005b) and equilibrium H₂/H₂O at 1100 °C and log(*f*O₂) = *NNO* + 0.3 (e.g., Allard et al., 2005).

^b Additional magmatic gas compositions. Compared to A, B is 10× Hg(g), C is 10× HBr(g) and HI(g) and D is 2× HCl(g). Compositions E (log(*f*O₂) = *NNO* + 0.8) and F (log(*f*O₂) = *NNO* – 0.2) have different oxidation states than composition A.

In Model 1 (Fig. 1; only the 8 most abundant species are shown), GEM (i.e., Hg(g)) is the most stable (i.e., most abundant) form of Hg over the entire temperature range. RGM/Hg_{tot} is low and approximately constant ($\sim 10^{-4}$), although the contributions from different species vary. At high-T, the dominant contributors are HgS(g) and HgO(g) while at lower-T the dominant contributors are HgS(g) and HgCl₂(g). HgS(g) is a particularly insoluble form of Hg(II) (Boening, 2000) so wet deposition would be inhibited in this form. The inclusion of iodine chemistry into the model does not affect RGM/Hg_{tot} significantly and the abundance of HgI₂(g) is low. However, we note that the abundance ratios between Hg(II) halides at 600 °C (e.g., HgCl₂(g)/HgI₂(g) $\sim 10^4$) is lower than the abundance ratios between the hydrogen halides (e.g., HCl/HI $\sim 10^5$). This result is explained by the increased polarisability of I relative to Cl, allowing for increasingly favourable bonding interactions with Hg (i.e., “soft–soft”) as predicted in Section 2. Despite HF being more abundant than either HBr or HI, a negligible amount of HgF₂(g) is formed, reflecting the high bond strength of HF. Within the temperature range, negligible Hg_p is formed (Hg_p/Hg_{tot} $< 10^{-30}$). The results shown here are distinct from those presented in the comparable (i.e., pure magmatic gas) model initialisation of Bagnato et al. (2007), who predict a much lower abundance of HgS(g), yet a higher and more variable RGM/Hg_{tot} ratio increasing to $> 10^{-2}$ at 600 °C. These differences reflect the absence of H₂S and H₂ from the input composition of Bagnato et al. (2007), which resulted in a more oxidised mixture. Our model results indicate that the crater rim measurements showing RGM + Hg_p comprise 1–2% of Hg_{tot} at Etna (Bagnato et al., 2007) cannot be explained on the basis of pure magmatic gases.

In Model 2, we may predict that a compositional discontinuity occurs at $V_A/V_M \sim 0.02$, equivalent to 1082 °C, due to the complete oxidation of H₂S and H₂ in the mixture (Martin et al., 2006, 2009b). Model results for the temperature range 600–1100 °C are shown (Fig. 2; for the 8 most abundant species) with the 1080–1100 °C range expanded. As expected, the model predicts a significant (100×) increase in RGM immediately below 1082 °C to RGM/Hg_{tot} $\sim 10^{-2}$, with the dominant contributors being HgO(g) and HgCl₂(g). Despite being the most abundant RGM species in Model 1, HgS(g) is found to be highly unstable below 1082 °C. The instability of HgS(g) in more oxidised mixtures (i.e., > 1082 °C) results in decreasing Hg(II) as the mixture approaches the compositional discontinuity from low V_A/V_M , since HgS(g) is the major contributor to Hg(II).

The results at temperatures close to 1000 °C are more comparable to those of Bagnato et al. (2007) (for their magmatic and atmospheric

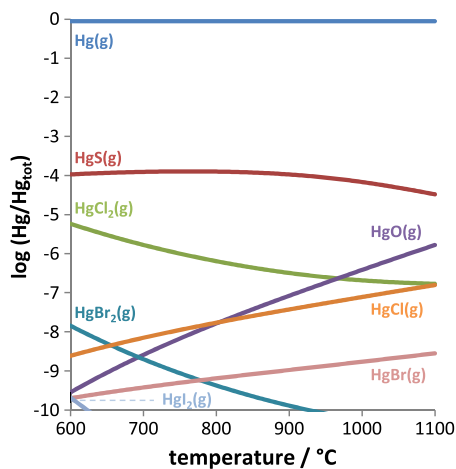


Fig. 1. Thermodynamic model results for thermal equilibration of Etna's magmatic gas (1100 °C) with atmospheric gas (25 °C) to 600 °C (Model 1). Only the 8 most abundant species are shown.

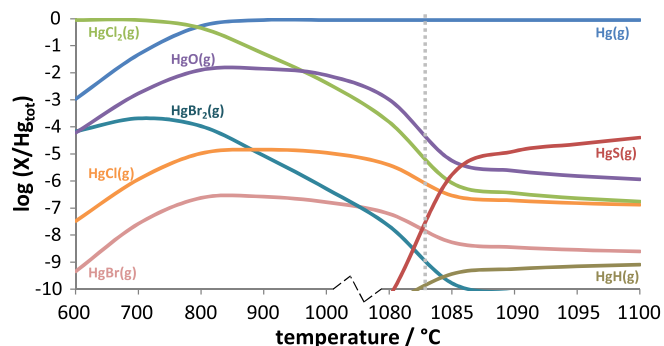


Fig. 2. Thermodynamic model results for chemical equilibration of Etna's magmatic gas (1100 °C) with atmospheric gas (25 °C) to 600 °C (Model 2). Only the 8 most abundant species are shown. The compositional discontinuity at 1082 °C is indicated by the vertical dashed line.

gas model) confirming that the main difference between the two models is the oxidation state of the magmatic gases (i.e., at 1000 °C, the addition of atmospheric oxygen is the dominant control on oxidation state rather than the initial abundances of H₂ and H₂S, and the extent of their re-equilibration). However, a critical difference is that we find HgCl₂(g) becomes increasingly abundant at lower temperatures and is the most abundant Hg species below 800 °C. This behaviour has also been shown using thermodynamic models of Hg speciation in coal-fired power station plumes (Senior et al., 2000). This difference can be explained by our use of revised thermodynamic data for HgCl₂(g) included within the more recent version of the HSC Chemistry software used here. The previously unrecognised stability of HgCl₂(g) at volcanic vents is an important finding because it explains crater rim Hg speciation at Etna (i.e., Hg(II)/Hg_{tot} ~ 1 –2%; Bagnato et al., 2007) without the need to resort to an *ad hoc* process of rapid, low temperature oxidation. The necessity for such a process is implied by the model results of Bagnato et al. (2007), which suggest that, Hg(II)/Hg_{tot} reaches a maximum of 10^{-3} at < 600 °C (in their magmatic and atmospheric gas model). For Etna, we may infer that equilibration must cease at a quenching temperature between ~ 1000 °C and 1082 °C (i.e., the temperature at which the compositional discontinuity is crossed) to obtain Hg(II)/Hg_{tot} $\sim 10^{-2}$. This result offers confidence in the proposed explanation for Hg speciation (i.e., Hg(0) oxidation in a high temperature mixture) since Hg(II)/Hg_{tot} $\sim 10^{-2}$ can be attained at reasonably high quenching temperature. In general, lower quenching temperatures become increasingly implausible (e.g., Gerlach, 2004). As for Model 1, negligible Hg_p is formed (i.e., Hg_p/Hg_{tot} $< 10^{-30}$) within the temperature range. Bagnato et al. (2007) show the formation of Hg_p in their magmatic gas and atmospheric gas model initialisation at significantly higher levels (i.e., Hg_p/Hg_{tot} $\sim 10^{-3}$). This difference reflects the more realistic treatment of aerosols within the current model (i.e., the aerosol volume is small compared to the total volume).

In Model 3, Hg speciation was modelled along the same V_A/V_M , T -path as in Model 1 and 2, but with a pre-existing aerosol at a concentration of aerosol/SO₂ = 0.01. Fig. 3 (only the six most abundant condensed phases are shown) shows Hg_p/Hg_{tot} $< 10^{-5}$, which differs from the result of Hg_p/Hg_{tot} $\sim 10^{-3}$ predicted by the model of Bagnato et al. (2007). The abundances of gas-phase species are not significantly changed from Model 2 (Fig. 2) because Hg_p is small. The aerosol/SO₂ ratio used here is an upper-limit and assumes the crater rim aerosol (Martin et al., 2008) is formed at high temperature. While this is unlikely to be the case, it is not known how the aerosol evolves as the plume cools to ambient temperatures. However, we may predict that the Hg_p/Hg_{tot} at equilibrium (at a given temperature) is proportional to the molar amount of pre-existing aerosol. This prediction is justified by “Raoult's Law”, which requires that the mole fraction of Hg_p in the aerosol is proportional to the

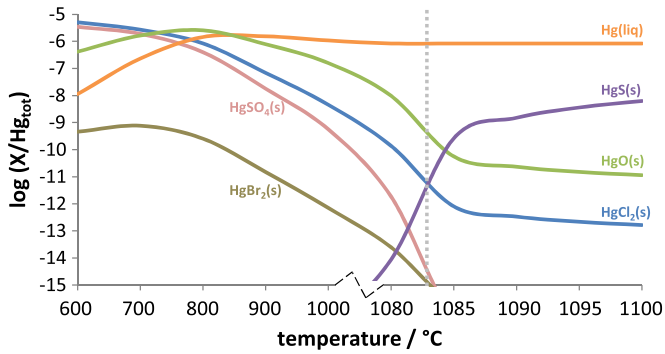


Fig. 3. Thermodynamic model results for chemical equilibration of Etna's magmatic gas (1100 °C) with atmospheric gas (25 °C) to 600 °C. The molar amount of pre-existing aerosol is set as aerosol/SO₂ = 0.01 (Model 3). Only the 6 most abundant condensed species are shown. The compositional discontinuity at 1082 °C is indicated by the vertical dashed line.

concentration of Hg_{tot} in the vapour. Thus, if the molar amount of pre-existing aerosol decreases (with negligible effect on Hg_{tot}), the molar amount of Hg_p must decrease proportionally to maintain the mole fraction of Hg_p in the aerosol. We suggest that the formation of Hg_p begins only after other phases condense (e.g., metal halides, water). Hence, even the very small Hg_p/Hg_{tot} shown is over-estimated meaning that Hg_p << RGM at high temperature. The comparable amounts of Hg_p and RGM found at the crater rim of Etna (Bagnato et al., 2007) likely reflect low temperature condensation or uptake into aqueous aerosol, converting RGM formed at the vent into Hg_p.

To summarise the thermodynamic model results, we find that when H₂S and H₂ are included in the magmatic gas composition, significant quantities of RGM (i.e., RGM/Hg_{tot} > 10⁻²) are formed at Etna's vents only if magmatic gases are oxidised by atmospheric gases; cooling alone cannot generate high levels of RGM. In contrast to the results of an earlier model (Bagnato et al., 2007), we show that RGM/Hg_{tot} increases to > 10⁻² if the mixture continues to equilibrate to lower temperatures (< 1082 °C), potentially explaining the recent crater rim measurements of Hg speciation at Etna and at other volcanoes. Hg_p/Hg_{tot} remains very small (< 10⁻⁵) at high temperature suggesting that Hg_p measured at the crater rim is due to the low-T condensation of RGM formed at the vent. This analysis explicitly assumes that the crater rim Hg speciation is influenced only by the high-T chemistry occurring at the vent.

3.2. Model calculations for other magmatic gases

To further investigate the influences of Hg speciation at volcanic vents, the Model 2 initialisation was used with the additional magmatic gas compositions (B–F) shown in Table 2. Results are shown in terms of X/Hg_{tot} for total Hg(0) and total Hg(II) (Fig. 4). At all temperatures, the results for compositions A (i.e., Etna's magmatic gas composition), B (i.e., 10× increased Hg) and C (i.e., 10× increased HI and HBr) are indistinguishable. These results reflect the minor abundance of Hg, I and Br compared to the elements which comprise the most abundant oxidised Hg species (e.g., HgCl₂, HgS, HgO). For example, any realistic change in Hg will not influence H₂ or HCl significantly so HgCl₂/Hg and total Hg(II) would remain unchanged (E2A). Also, while a change in the amount of HBr and HI in the mixture will result in an increase in HgBr₂ and HgI₂ (E2B, E2C), Fig. 2 shows that these species are minor contributors to total Hg(II).

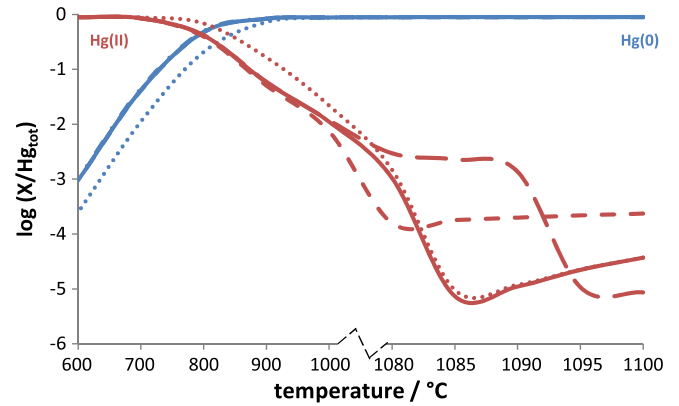
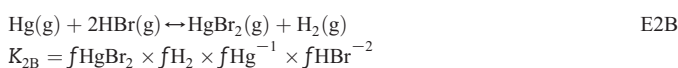
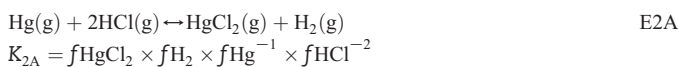
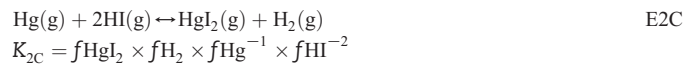


Fig. 4. Thermodynamic model results for chemical equilibration of the different magmatic gas compositions (1100 °C) with atmospheric gas (25 °C) to 600 °C. The molar amount of pre-existing aerosol is set as aerosol/SO₂ = 0.01 (Model 3). Results for compositions A, B and C are indistinguishable and shown as a solid line. Results for compositions D (dots), E (long dashes) and F (short dashes) show significant differences with results for composition A.



Differences were found between the results for composition A and D (i.e., 2× increased HCl) at temperatures between 800–1000 °C. This result reflects the significant contribution made by HgCl₂ to total Hg(II) in this temperature range. As indicated by the equilibrium constant (E2A), a 2× increase in HCl may result in a 4× increase in HgCl₂. However, at lower temperatures (< 800 °C) this reaction is limited by Hg so the results for composition A and D are more similar. At higher temperatures (> 1000 °C), HgCl₂(g) is not a significant contributor to total Hg(II) so the results for composition A and D are again similar.

Differences were found between the results for composition A and E (i.e., more oxidised; log(*f*O₂) = *NNO* + 0.8) only above ~1000 °C. Here, the compositional discontinuity occurs at V_A/V_M = 0.01, equivalent to ~1093 °C. Although an increase in Hg(II) does occur immediately below ~1093 °C, the amount of Hg(II) formed is minor (Hg(II)/Hg_{tot} < 10⁻²) at this temperature. While Hg(II)/Hg_{tot} increases to > 10⁻² below 1000 °C, this is not due to the initial *f*O₂ of the magmatic gas, but instead to the increasing V_A/V_M of the mixture. Under these conditions, the oxidation states of the mixtures derived from composition A and E are comparable and so the results are equivalent. For composition F (i.e., less oxidised; log(*f*O₂) = *NNO* - 0.2), the compositional discontinuity occurs at V_A/V_M = 0.08, equivalent to 1037 °C. While this would hinder Hg(II) production if quenching occurs above the compositional discontinuity, there is little difference in Hg(II) production at ~1000 °C. These results suggest that in oxidised magmatic gases (i.e., ≥ *NNO*), Hg(II) production is not strongly controlled by the oxidation state of the magmatic gases, provided that the compositional discontinuity is reached. In more reduced magmatic gases (i.e., < *NNO*), Hg(II) production requires re-equilibration to increased values of V_A/V_M, which becomes increasingly unfeasible due to the decreasing temperatures at which equilibrium must occur at, so Hg(II) production will be hindered relative to more oxidised magmatic gases.

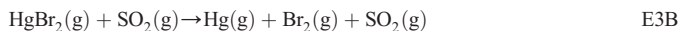
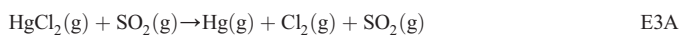
An additional influence on Hg speciation at volcanic vents is the magmatic gas temperature, since different magmatic gas temperatures would result in compositional evolution along different V_A/V_M, *T*-paths. The two extreme cases are where the quenching temperature is comparable to, or independent of the magmatic gas temperature. In the former case, where mixing is near-instantaneous at the vent, Hg(II) formation would be diminished for a higher temperature magmatic gas as the mixture would quench at higher temperature. Conversely, in the latter case, perhaps where some mixing and cooling

occurs deeper within the vent, Hg(II) formation would be enhanced as the mixture would quench at higher V_A/V_M . Previous model studies have assumed that the former case is more realistic (e.g., Gerlach, 2004; Martin et al., 2006), based on the varied quenching temperatures for different volcanic systems, which generally bear some relationship to the temperature of the magmatic gases (e.g., Gerlach, 1980; Le Guern et al., 1982; Gerlach and Casadevall, 1986).

In summary, this model comparison and discussion suggest that Hg(II) production is promoted by lower quenching temperatures and an increased mole fraction of HCl in the magmatic gases. In contrast, Hg(II) production is not sensitive to the abundances of Hg, HBr and HI. Furthermore, while Hg(II) production is hindered in reduced magmatic gases (i.e., $<NNO$), there are only relatively minor differences between increasingly oxidised magmatic gases (i.e., $\geq NNO$). If it is assumed that lower quenching temperatures result from lower magmatic gas temperatures, then we might predict that volcanoes with low temperature, HCl-rich and oxidised magmatic gases are most prone to increased Hg(II)/Hg_{tot} at the crater-rim. However, since T_q is influenced by dynamics at the vent, any measured differences in Hg(II)/Hg_{tot} (i.e., 1–2% at Etna; 2–8% at Masaya) cannot be explained purely in terms of magmatic properties (i.e., temperature, oxidation state, Cl content).

3.3. Implications for future investigation of Hg speciation in volcanic emissions

As indicated in the Introduction, we have explicitly assumed that Hg speciation at the crater rim is controlled by high temperature processes occurring at the vent. An alternative hypothesis is that the Hg speciation is controlled by rapid (i.e., <1 min) low temperature processing of GEM, and the production of RGM and Hg_p at the vent is a minor contribution. While this possibility is not indicated by the long lifetime of GEM (i.e., 0.5–2 years) in the troposphere, the unique chemistry in young volcanic plumes may accelerate this oxidation process. Indeed, a recent model study by von Glasow (2010) predicted near-complete oxidation of GEM to RGM and Hg_p within 15 min of emission from Etna due to reactions between GEM and reactive Br and Cl species. This work identified two important loss processes for RGM in the young plume (E3A–B), which suppresses the build-up of RGM until the plume had diluted significantly and SO₂ concentrations are lowered.



If these loss processes are more rapid than formation processes at the crater rim, while RGM + Hg_p comprise 1–2% of crater rim Hg_{tot} (Bagnato et al., 2007), the amount of RGM + Hg_p formed at the vent is potentially much larger (i.e., consistent with equilibration below 1000 °C within our model). In the light of the very significant uncertainties with kinetic parameters for Hg (as admitted by von Glasow, 2010), it is important to appreciate that crater rim observations of Hg speciation can be explained on the basis of high temperature chemistry alone. Therefore, crater rim measurements of Hg speciation cannot be used to validate kinetic models of Hg chemistry. Instead, we must both model and monitor the variation in Hg speciation over wider spatial and temporal scales.

4. Conclusions

A major uncertainty regarding the environmental impacts of volcanic Hg is the extent of local deposition. A likely control on deposition is the oxidation state of Hg compounds: Hg(0) is an inert, insoluble gas, while Hg(II) occurs as reactive gases and particles, which deposit rapidly and proximally. Using a new high temperature thermodynamic model, we show that although Hg in magmatic gases

is almost entirely Hg(0) (i.e., GEM), significant quantities (i.e., $>1\%$ of total Hg) of Hg(II) (i.e., RGM and Hg_p) are likely formed at Etna's vents, where magmatic gases are cooled and oxidised by atmospheric gases. The quantities of Hg(II) predicted to form explain recent measurements of Hg speciation at the crater rim of Etna, without resort to very rapid (<1 min), low-temperature oxidation processes. We further model Hg speciation for a series of additional magmatic gas compositions. Compared to Etna, Hg(II) production (i.e., Hg(II)/Hg_{tot}) is enhanced in more HCl-rich magmatic gases, but is independent of the Hg, HBr and HI content of the magmatic gases. Hg(II) production is not strongly influenced by the initial oxidation state of magmatic gases above NNO , although production is hindered in more reduced magmatic gases. The model extends the model of Bagnato et al. (2007), and uses a revised thermodynamic database, with an improved treatment of aerosols and oxidation state, and additionally considers iodine species. The model and results are widely applicable to other open-vent volcanoes and may be used to improve the accuracy of chemical kinetic models for low temperature Hg speciation in volcanic plumes.

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Appendix A

List of species considered within the high temperature thermodynamic model. Ne(g) is included as an inert species, and is used to specify the molar amount of pre-existing aerosol.

Ar(g)	COOH(g)	HgF(g)	IF(g)	O ₃ (g)	SOCl ₂ (g)
Br(g)	COS(g)	HgF ₂ (g)	IIO(g)	OBrO(g)	SOF(g)
Br ₂ (g)	CS(g)	HgH(g)	IO(g)	OCIO(g)	Ne(g)
BrBrO(g)	CS ₂ (g)	HgI(g)	IOO(g)	OIO(g)	Hg(liq)
BrCl(g)	F(g)	HgI ₂ (g)	N(g)	S(g)	Hg ₂ Br ₂ (s)
BrF(g)	H(g)	HgO(g)	N ₂ (g)	S ₂ (g)	Hg ₂ Cl ₂ (s)
BrO(g)	H ₂ (g)	HgS(g)	N ₂ O(g)	S ₂ Br ₂ (g)	Hg ₂ F ₂ (s)
BrOBr(g)	H ₂ O(g)	HI(g)	N ₂ O ₂ (g)	S ₂ Cl ₂ (g)	Hg ₂ I ₂ (s)
BrOO(g)	H ₂ O ₂ (g)	HIO(g)	N ₂ O ₃ (g)	S ₂ Cl ₂ (g)	Hg ₂ SO ₄ (s)
CH ₃ (g)	H ₂ S(g)	HNCO(g)	NBr(g)	S ₂ O(g)	HgBr ₂ (s)
CH ₄ (g)	H ₂ S ₂ (g)	HNO(g)	NH ₂ (g)	S ₃ (g)	HgCl ₂ (s)
Cl(g)	H ₂ SO ₄ (g)	HNO ₂ (g)	NH ₂ OH(g)	S ₄ (g)	HgF ₂ (s)
Cl ₂ (g)	HBr(g)	HNO ₃ (g)	NH ₃ (g)	S ₅ (g)	HgI(s)
Cl ₂ O(g)	HCl(g)	HO(g)	NO(g)	S ₆ (g)	HgI ₂ (s)
ClClO(g)	HClCO(g)	HO ₂ (g)	NO ₂ (g)	SBr ₂ (g)	HgO(s)
ClF(g)	HCN(g)	HOCl(g)	NO ₂ Cl(g)	SCl(g)	HgS(s)
ClO(g)	HCO(g)	HOCN(g)	NO ₃ (g)	SCl ₂ (g)	HgSO ₄ (s)
ClO ₂ (g)	HCOOH(g)	HS(g)	NOBr(g)	SF(g)	HgSO ₄ *2HgO(s)
ClOCl(g)	HF(g)	HSO ₃ Cl(g)	NOCl(g)	SO(g)	HgSO ₄ *HgO(s)
ClOO(g)	Hg(g)	HSO ₃ F(g)	NOF(g)	SO ₂ (g)	HgO(R)(s)
CO(g)	HgBr(g)	I(g)	NOI(g)	SO ₂ Cl ₂ (g)	HgS(A)(s)
CO ₂ (g)	HgBr ₂ (g)	I ₂ (g)	NS(g)	SO ₂ ClF(g)	

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