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Nitric acid from volcanoes

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Abstract

Atmospheric cycling of nitric acid and other nitrogen-bearing compounds is an important biogeochemical process, with significant implications for ecosystems and human health. Volcanoes are rarely considered as part of the global nitrogen cycle, but here we show that they release a previously unconsidered flux of HNO_3 vapour to the atmosphere. We report the first measurements of nitric acid vapour in the persistent plumes from four volcanoes: Masaya (Nicaragua); Etna (Italy); and Villarrica and Lascar (Chile). Mean near-source volcanic plume concentrations of HNO_3 range from 1.8 to 5.6 μmol m^{-3}, an enrichment of one to two orders of magnitude over background (0.1–1.5 μmol m^{-3}). Using mean molar HNO_3/SO_2 ratios of 0.01, 0.02, 0.05, and 0.07 for Villarrica, Masaya, Etna, and Lascar respectively, combined with SO_2 flux measurements, we calculate gaseous HNO_3 fluxes from each of these volcanic systems, and extend this to estimate the global flux from high-temperature, non-explosive volcanism to be $\sim$0.02–0.06 Tg (N) yr^{-1}. While comparatively small on the global scale, this flux could have important implications for regional fixed N budgets. The precise mechanism for the emission of this HNO_3 remains unclear but we suggest that thermal nitrogen fixation followed by rapid oxidation of the product NO is most likely. In explosive, ash-rich plumes NO may result from, or at least be supplemented by, production from volcanic lightning rather than thermal N fixation. We have calculated NO production via this route to be of the order of 0.02 Tg (N) yr^{-1}.

Keywords: fixed nitrogen; nitrogen cycle; volcanic emissions; volcanic lightning

1. Introduction

Biologically available nitrogen is essential for both animal and plant life. Despite being the major component of the Earth's atmosphere, nitrogen gas (N_2) is unavailable to most organisms and must be converted or 'fixed' to chemical forms (such as NO, NO_2, HNO_3 and NH_3) that can enter the pool of N that cycles between the atmosphere and biosphere and other Earth surface reservoirs. While there is considerable uncertainty in the total release of fixed N from natural sources (130–450 Tg yr^{-1}; Table 1), much of this uncer-

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Table 1

Global fluxes of fixed (biologically available species such as NO, NO_2, HNO_3 and NH_3) nitrogen to the atmosphere, compiled from [1]

	Release of fixed nitrogen Tg (N) yr^{-1}
Natural sources:	
Lightning	< 10
Biological fixation:	
Marine ecosystems	< 30 to > 300
Terrestrial ecosystems	90–140
Total	130–450
Anthropogenic sources:	
N fertiliser	~80
Fossil fuel combustion	20
N-fixing crops	~40
Mobilisation of N:	
Biomass burning	~20[a]
Land clearing	20
Wetland draining	10
Total	180

[a] Volatilises > 40 Tg yr^{-1} of N, with ~20 Tg yr^{-1} of that fixed.

tainty lies in estimates of the marine flux. The total flux of natural fixed N from land-based sources is ~100–150 Tg yr^{-1} [1].

Although fixed N is necessary for life, anthropogenic emissions (see Table 1) have highlighted the detrimental effects of excessive releases of fixed N on local and global scales, both for the atmosphere, the terrestrial environment and human health [1–3]. Most deposition of fixed nitrogen species such as NO_x (NO and NO_2) is via conversion to nitric acid (HNO_3) by oxidation. Due to its high water solubility HNO_3 is rapidly removed to water droplets, thereby constituting one of the major components of acid precipitation (e.g. [4]) as well as acting as a source of bioavailable nitrogen to terrestrial ecosystems.

As with all biogeochemical cycles, it is necessary to evaluate the state of the N cycle prior to human influence in order to assess the effects of anthropogenic emissions. Volcanoes are major sources of many environmentally significant gases, such as SO_2 and HCl, both via explosive and effusive eruptions and continuous 'passive' degassing (e.g. [5–10]). These emissions and their reaction products in the atmosphere often experience extended atmospheric lifetimes (as volcanic emanations are often released directly into the free troposphere [5]) and can have important atmospheric and environmental consequences on both local (e.g. [11–13]) and regional to global (e.g. [14,15]) scales. The major elemental constituents of volcanic gases include hydrogen, carbon, oxygen, sulphur and halogens, and tend to occur as characteristic molecular species [16,17]. For carbon, for example, CO_2 is the dominant volcanic gas species, with CH_4 and CO occurring in lesser amounts [16,17]. Previous studies have suggested that nitrogen in volcanic emanations exists almost exclusively as molecular nitrogen (N_2), with only minor emissions of NH_3 in lower-temperature hydrothermal emissions [16,18,19]. However, other forms of fixed nitrogen, namely NO_x, have been observed in volcanic emissions (Table 2 [20–22]). Hübler et al. [23] considered the possibility that volcanic sources of NO might perturb their measurements of total reactive oxidised nitrogen (NO_y) in the remote Pacific troposphere at the Mauna Loa Observatory. They suggested that

Table 2

Previous NO_x fluxes measured at volcanoes

Volcano	Date	Flux/kg s^{-1}			Calc. N/SO_2 molar ratio	Ref.
		NO	NO_2	NO_x		
Mt. St. Helens, USA (post-eruptive emissions)	June 18, 1980	Not observed	7		0.75	[22]
	August 19, 1980	Not observed	0.3		–	[22]
	September 1980	0.01	Not measured		0.003	[21]
Mt Redoubt, Alaska (emissions between eruptions)	January 1990			< 0.1–2.7[a]	0.01–0.09	[20]

[a] Based on an estimate of 98% NO_2 and 2% NO.

hot lava might thermally fix nitrogen leading to NO_x formation, but their investigations showed no correlation between N species and any of the well known volcanic emanations. However, inspired by the occasional observation of high concentrations of nitrate in Hawaiian cloud water, Huebert et al. [24] measured NO concentrations near the surface of molten lava on Hawaii, finding levels of NO up to >170 ppbv (>7 μmol m^{-3}) compared to <1 ppbv in ambient air. They concluded that this NO resulted from thermal fixation of atmospheric nitrogen at the elevated temperatures above the lava flow and further suggested that, over a period of hours, a significant fraction of this NO must be oxidised to NO_2 and then NO_3^-.

Despite the observations of NO_x associated with volcanic activity, there have been no previous measurements of HNO_3 in volcanic emissions [12,25]. In addition, while the fluxes of N_2 from volcanic arcs have been estimated as 6.4×10^8–2.0×10^{10} mol yr^{-1} (corrected for N_2 from air or air-saturated water) [26–28], no attempts have been made to constrain the possible fluxes of fixed nitrogen from volcanic sources. Here we report elevated HNO_3 in the near-source plumes associated with four persistently active volcanoes and discuss its possible origins. From these measurements we calculate HNO_3 fluxes from each of these systems and extend these calculations to an order of magnitude estimate of the potential global HNO_3 flux from non-explosively degassing volcanoes. We have also calculated an order of magnitude estimate of N fixed during episodes of volcanic lightning in ash-rich, explosive plumes.

2. Methodology

Samples were collected in December 2001 on the crater rim of Masaya volcano (Nicaragua) downwind of the active vent and in May 2002 from the summit region of Etna (Italy), close to the active summit pit craters. Two consecutive measurements were made ~200 m downwind from the crater rim of Lascar volcano (Chile) on 23 January 2003 and four measurements were made on the crater rim downwind of the active vent of Villarrica (Chile) on 3 and 7 February 2003 (on 3 February the plume was grounding on the crater rim, whereas on 7 February it was lofting overhead, making it harder to sample). At Masaya, samples were collected both during the day and at night, at all other field locations only during the day. At the time of measurement, Masaya was emitting gas and aerosol from a vent in the floor of the active crater, a pit some 300 m deep and 500 m in diameter. Weak incandescence indicated ‘open vent’ degassing from a magma pond situated close to the surface. Etna also displays continuous open-conduit activity at the base of several deep (100–300 m) pit craters [29], as does Villarrica in its single crater. Degassing at Lascar is through high-temperature fumaroles on and around lava dome growth inside the ~300 m deep crater [30]. At the time of sampling, the surface of the collapsed dome at the base of Lascar’s crater was believed to be covered with blocky debris (E. Calder, personal communication). At all locations background measurements were taken. At Masaya the background site was in the national park upwind of the active crater; at Etna in the nearby town of Nicolosi remote from the active summit; at Lascar in the nearby village of Talabre away from metalled roads, ~2000 m lower than the active vent; at Villarrica background measurements were taken at two locations, one in woodland and one on the exposed flank of the volcano ~2000 m lower than the summit.

Gas-phase species were collected on filters housed in multiple-stage cartridges, 37 or 47 mm in diameter, actively pumped at rates of 4–30 l min^{-1} [12]. Gas and aerosol was pumped through filters that capture particles, followed by two stages of filters to collect acidic gaseous species (Whatman 41 ashless circles impregnated with $NaHCO_3$ (10% m/v) and glycerol (10%) in 1:1 methanol/deionised water). Sampling times ranged from ~5 min to ~1 h at the near-crater sites and from 1–6 h at the background sites. After collection, exposed filters were triple-sealed in small plastic bags, and stored in a freezer to limit the risk of further reaction. Filters were extracted with 10 cm^3 distilled deionised water and

Table 3a

Volcanic plume and background concentrations of HNO_3 and SO_2 in the daytime and night-time plume at Masaya and the daytime plume of Etna

	Masaya Volcano, Nicaragua							Etna Volcano, Italy				
	Concentration/μmol m^{-3}						In plume molar ratio ($n = 41$)[a]	Concentration/μmol m^{-3}				In plume molar ratio ($n = 5$)[a,b]
	Background ($n = 6$)		In plume day ($n = 34$)		In plume night ($n = 7$)			Background (n = 2)		In plume (n = 7)		
	SO_2	HNO_3	SO_2	HNO_3	SO_2	HNO_3	HNO_3/SO_2	SO_2	HNO_3	SO_2	HNO_3	HNO_3/SO_2
Mean	0.2	0.1	140.3	2.4	172.8	2.5	0.02	0.8	0.2	624.2	2.8	0.05
Maximum	0.4	0.3	410.1	7.0	232.4	5.3	0.09	1.2	0.3	4128.0	9.2	0.14
Minimum	0.1	0.0	41.8	0.3	121.4	0.0	0.00	0.4	0.0	0.6	0.5	0.00
Standard dev.	0.1	0.1	66.2	1.8	35.6	2.2	0.02	0.4	0.1	1430.9	2.8	0.05
					HNO_3 flux[c]/kg s^{-1}		0.10			HNO_3 flux[c]/kg s^{-1}		0.50

[a] Arithmetic mean of the HNO_3/SO_2 ratios of each filter pack.

[b] The two measurements barely distinguishable from the background levels (Fig. 2) were excluded from this calculation.

[c] Based on SO_2 fluxes of 5, 10, 4 and 28 kg s^{-1} for Masaya [59], Etna [60], Villarrica (our unpublished data) and Lascar (our unpublished data), respectively.

Table 3b

Volcanic plume and background concentrations of HNO_3 and SO_2 in the daytime plumes at Villarrica and Lascar

	Villarrica Volcano, Chile					Lascar Volcano, Chile				
	Concentration/μmol m^{-3}				In plume molar ratio ($n = 4$)[a]	Concentration/μmol m^{-3}				In plume molar ratio ($n = 2$)[a]
	Background ($n = 2$)		In plume ($n = 4$)			Background ($n = 1$)		In plume ($n = 2$)		
	SO_2	HNO_3	SO_2	HNO_3	HNO_3/SO_2	SO_2	HNO_3	SO_2	HNO_3	HNO_3/SO_2
Mean	0.3	1.5	220.6	1.8	0.01	0.7	0.1	77.8	5.6	0.07
Maximum	0.4	1.6	539.1	3.5	0.02	0.7	0.1	81.1	7.9	0.10
Minimum	0.1	1.4	7.0	0.1	0.01	0.7	0.1	74.6	3.3	0.04
Standard dev.	0.1	0.1	203.0	1.5	0.01	0.0	0.0	3.2	2.3	0.03
			HNO_3 flux[b]/kg s^{-1}		0.04			HNO_3 flux[b]/kg s^{-1}		1.96

[a] Arithmetic mean of the HNO_3/SO_2 ratios of each filter pack.

[b] Based on SO_2 fluxes of 5, 10, 4 and 28 kg s^{-1} for Masaya [59], Etna [60], Villarrica (our unpublished data) and Lascar (our unpublished data), respectively.

gaseous SO_2 and HNO_3 were determined as SO_4^{2-} and NO_3^- by Dionex ion chromatography using gradient analysis, with distilled deionised water and 0.1 M NaOH as eluents. Previous studies have shown good agreement between filter pack results and other established methods of HNO_3 monitoring [31] and similar methods have been used previously in volcanic situations [12,25] to sample for gaseous HNO_3.

3. Results

The concentrations of gas-phase SO_2 (taken as an indicator of the amount of volcanic plume captured in each individual sampling run) and HNO_3 measured in the background ambient air and in the volcanic plumes at the four field sites are summarised in Table 3a,b and in Fig. 1. Both HNO_3 and SO_2 are generally elevated above background in all of the volcanic plumes. At Masaya, although there is some scatter, the mean plume HNO_3 concentrations are 2.4 μmol m^{-3} (day) and 2.5 μmol m^{-3} (night) compared to a background mean of 0.1 μmol m^{-3}, an in-plume enrichment by a factor of ~25 for both daytime and night. The mean plume SO_2 concentrations are 140.3 μmol m^{-3} (day) and 172.8 μmol m^{-3} (night) compared to a background mean of 0.2 μmol m^{-3}. The minor background levels of both species may in part reflect the proximity of the background site to the active vent at Masaya. Fig. 1b–d shows similar results for Etna, Villarrica and Lascar. In-plume concentrations of both SO_2 and HNO_3 were again elevated above background values with maximum in-plume concentrations of HNO_3 of 9.2, 3.5 and 7.9 μmol m^{-3} (compared to mean background HNO_3 concentrations of 0.2, 1.5 and 0.1 μmol m^{-3}) for Etna, Villarrica and Lascar, respectively. At these field

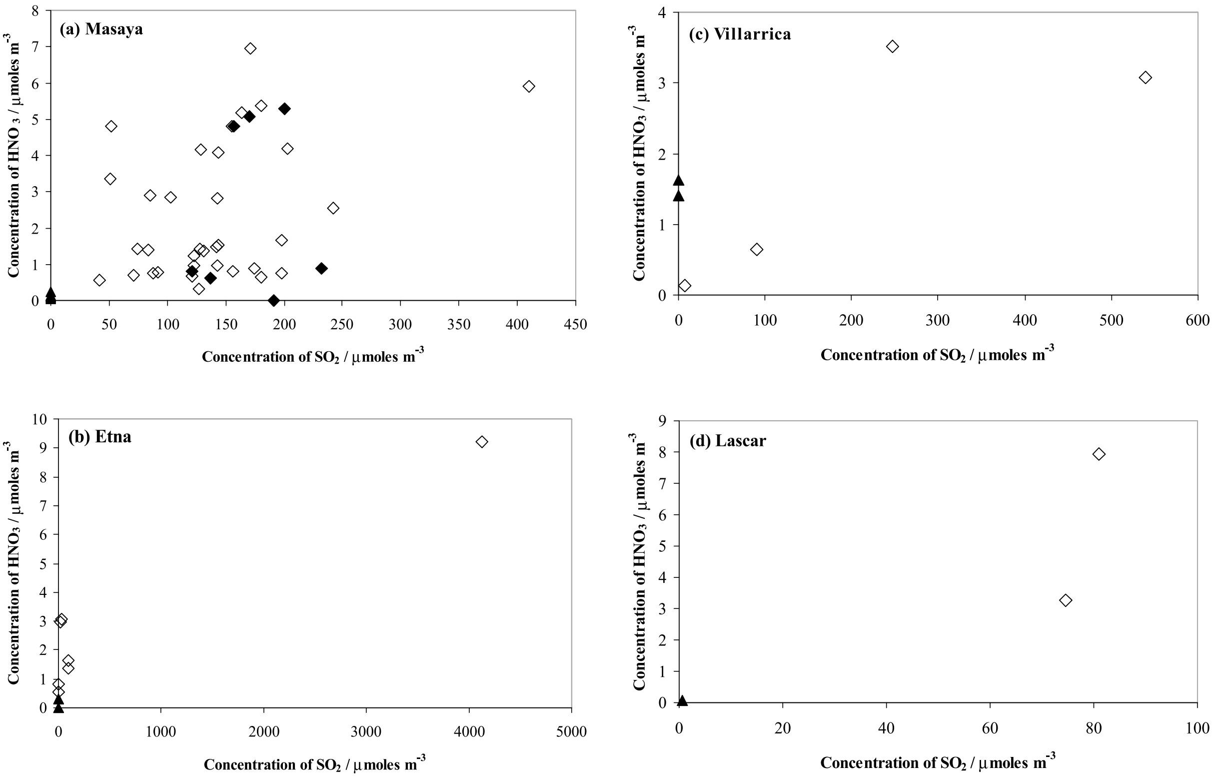

Fig. 1. Filter pack measurements of SO_2 and HNO_3 at Masaya, Etna, Villarrica and Lascar volcanoes. Open diamonds, in-plume, daytime; filled diamonds, in-plume, night-time (for Masaya only); filled triangles, background.

locations it was harder to position the sampling equipment directly in the plume so there is more variation in the concentrations of SO_2 recorded than for Masaya. In each of these cases (although there is a lot of scatter in the larger Masaya dataset) there is a general increase in HNO_3 concentration with increased SO_2 concentration, strongly suggesting that the HNO_3 observed is associated with the volcanic plumes. The decoupling (as discussed later) may result from decoupling of the SO_2 and HNO_3 production routes. At Villarrica (Fig. 1c) there is some elevated HNO_3 in the background samples (accompanied by virtually no SO_2). These samples were taken at a much lower altitude than the crater rim (~1000 m and 1439 m compared to 2847 m) and therefore the HNO_3 in these samples probably originates from the ecosystems that cover the flanks of the mountain or human activity (the towns of Pucon and Villarrica and an extensive road network are nearby). The fact that one of the crater rim samples has almost no HNO_3 or SO_2, while the other crater rim measurements have elevated levels of both (to varying degrees), suggests that the HNO_3 measured at the summit is from a different source to that measured in the background samples and that this source is the volcano. It is also hard to see much detail for the Etna data since one measurement has very much higher SO_2 and HNO_3 concentrations than the others. These complications aside, the results strongly suggest that there is HNO_3 enrichment associated with the volcanic plumes.

4. Discussion

HNO_3 has not previously been unequivocally identified in volcanic plumes. Lazrus et al. [25] analysed filter pack samples from aircraft measurements of eruption plumes downwind of three Guatemalan volcanoes (Pacaya, Fuego and Santiaguito) for HNO_3, but levels were generally low (< 0.2 μmol m^{-3} or 6 ppbv) and comparable to background measurements, or below detection limits. They concluded that measurable changes in nitric acid vapour were not observed [25]. In a later study, Allen et al. [12] did not detect HNO_3 near the summit of the Soufrière Hills Volcano, Montserrat, although low levels were detected at other locations. They concluded that oxides of nitrogen, produced at high temperatures within the Montserrat dome, only showed measurable oxidation to HNO_3 following transport away from the summit.

The observations we report demonstrate clearly, and for the first time, that HNO_3 vapour is present in the near-source plumes at some persistently active volcanoes. This necessitates consideration of how HNO_3 might originate in volcanic plumes.

4.1. Possible sources for HNO_3

We consider four possible production routes for volcanic HNO_3 vapour: primary emission of HNO_3 from the magmatic phase; revolatilisation of HNO_3 from background aerosol; boiling of nitrate-rich hydrothermal fluids, and thermal fixation of nitrogen and subsequent oxidation of NO to HNO_3.

4.1.1. Primary emission of HNO_3 from the magmatic phase

Little is known about the solubility and speciation of nitrogen in natural melts [32]. Miyazaki et al. [33] demonstrated that nitrogen dissolves as molecular N_2 in basalt under highly oxidising conditions ($fO_2 = 0.1$–0.4 atm), at 1 atm and 1300°C, with solubility close to that of Ar. The constancy of N_2/Ar ratios in oceanic basalts also suggests that N solubility is closely similar to that of Ar under typical magmatic conditions [34]. In experiments on basalts at 1250°C, with a 0.001–3 kbar confining pressure and fO_2 at the Ni–NiO buffer (NNO), Tsipenyuk et al. [35] found the solubility of nitrogen to be low (~50 ppm) and pressure-independent. At lower fO_2 (at the iron–wustite buffer) nitrogen solubility increases sharply with increasing pressure, to ~200 ppm at 3 kbar [35]. This bears out earlier observations on synthetic melts by Mulfinger [36], who suggested that under reducing conditions, the solubility of nitrogen in melts increases as nitrogen undergoes chemical solution to form nitride (N^{3-}) species. While there are no spectroscopic data to confirm either the presence of N^{3-}, or absence of NO_3^-, in natural glasses or melts, it seems most likely that under the conditions at the volcanoes under study (with fO_2 at or above NNO) molecular N_2 would be the principal form of nitrogen of magmatic origin. This suggests that emission of NO_3^- direct from a magmatic phase is unlikely.

4.1.2. Revolatilisation of HNO_3 from background aerosol

A preliminary study [37] suggested that nitrate in background aerosol that had been advected into Masaya's volcanic plume could be displaced following aerosol acidification by volcanic vapours via the following equilibrium:

$$NO_3^-(aq) + H^+_{(aq)} \Leftrightarrow HNO_{3\,(g)} \qquad (1)$$

Increased H^+ in the aerosol phase will act to move this equilibrium towards the right, and hence enrich the vapour phase in HNO_3. However, the background aerosol HNO_3 concentration measured was of the order of 0.05 μmol m^{-3} (3.0 μg m^{-3}). This low concentration suggests that revolatilisation losses are unlikely to account for our observations of mean in-plume HNO_3 vapour levels at Masaya of 2.5 μmol m^{-3}. In fact, a more comprehensive analysis of aerosol filters from Masaya does not bear out the earlier observations, and in many cases aerosol-phase NO_3^- is observed to be enriched in Masaya's plume [38].

4.1.3. Boiling of nitrate-rich hydrothermal fluids

HNO_3 is highly soluble, and may be enriched in meteoric and ground waters. Boiling of HNO_3-rich fluids associated with volcanic hydrothermal systems is a potential source of HNO_3 vapour in volcanic emanations. Further detailed investigations of the origins of gas components in the plumes of Masaya, Etna, Villarrica and Lascar (e.g. [19,39]) are required to assess whether this is a feasible source of the levels of HNO_3 observed at these high-temperature degassing systems.

4.1.4. Fixation of nitrogen to NO and subsequent oxidation to HNO_3

Prior observations of NO_x associated with volcanic activity (Table 2 and [24]) suggest that the HNO_3 emissions reported here may be produced via oxidation from NO and NO_2. NO_x production, by processes such as fossil fuel combustion, has been extensively studied. Two principal production routes have been elucidated: oxidation of nitrogen-containing compounds in fuel (fuel NO_x) and high-temperature oxidation of atmospheric molecular N_2 (thermal NO_x). Fuel NO_x production is unaffected by changes in combustion temperature, is strongly coupled to the hydrocarbon oxidation process and is dependent upon the fuel N content and oxygen availability. In contrast, thermal NO_x production is strongly temperature-dependent and decoupled from the combustion process although also promoted by high oxygen concentration [40]. NO_x emissions from volcanoes can be understood by analogy to these processes:

(1) Fuel NO_x

The high bond strength of molecular N_2 (945 kJ mol^{-1} at 298 K [41]) means that it is stable compared to the fuel C–N bonds. Thus the activation energy required for oxygen to react with fuel is considerably lower than that required to react with molecular N_2. Consequently, fuel NO_x production proceeds rapidly and is less temperature-dependent than thermal fixation, although only a fraction of the fuel N is converted to NO_x, the rest forming molecular nitrogen.

As discussed above (Section 4.1.1), physical solution of molecular N_2 in glass melts is thought to dominate at the conditions of oxygen fugacity characteristic of the molten magma in these volcanoes, while under more reducing conditions chemical solution to form nitrogen–hydrogen groups and nitrides may become important. If N is indeed incorporated into the magma, then N oxidation analogous to fuel N may be important, based on the weaker bond strength of N–Si bonds ($\sim$105 kJ mol^{-1} at 298 K [41]) compared to N_2. However, studies of fuel NO_x production suggest that its production is strongly linked to reactions involved in hydrocarbon combustion [42]. In volcanic degassing, while magmatic gases do at times combust (generally thought to be the N-free gases H_2 and CH_4, e.g. [43]), the magma itself does not, suggesting that the release of chemically bound N may not be favourable and that a full analogy to fuel NO_x production cannot be developed.

(2) Thermal NO_x

Thermal NO_x production is strongly temperature-dependent, although there is a certain degree of uncertainty at what temperature it becomes significant [44,45]. Hotspots on Lascar's dome have been measured as ~1210 K [46]. Subterranean lava pond surface temperature measurements are harder to make at the other volcanoes. Bulk magma temperatures for basaltic volcanoes such as Masaya, Etna and Villarrica are estimated to be in the range 1300–1450 K but it is likely that the surface temperatures of the magma in the magma ponds will be lower. Measurements of the surface of the lava lake of Erta'Ale volcano, Ethiopia, showed maximum temperatures of 1450 K for incandescent cracks but temperatures of ~570 K for the solid crust forming the majority of the surface [47]. However, the situation at Masaya, Etna and Villarrica is very different from that at Erta'Ale. The magma–air interface at these volcanoes is down a vent or vents and will thus be less susceptible to radiative cooling. Further, sounds audible during the sampling period at Masaya and Villarrica suggest that the lava pond surface is not calm. Waves and bubbles bursting on the surface of the magma pond could act to mix the gases at the magma–air interface further into the bulk magma and prevent the surface of the magma from forming a cooler solid crust. Gas temperatures as high as 1370 K have been previously measured from fissures on a basaltic lava flow [43]. These observations suggest that the gas temperatures experienced at the lava pond surfaces of Masaya, Etna and Villarrica will not be as far below the internal temperatures as at Erta'Ale. Although uncertainty remains, for the purposes of our discussion we will consider volcanic gases in these environments to experience temperatures in the range of ~1200–1400 K.

In order to understand the levels of NO that we might plausibly expect at these temperatures we consider the following free radical chain reaction mechanism for NO formation from air at high temperature, developed for combustion ([48] cited in [40]):

$$O_2 + M \Leftrightarrow 2O + M \tag{2}$$

$$O + N_2 \Leftrightarrow NO + N \tag{3}$$

$$N + O_2 \Leftrightarrow NO + O \tag{4}$$

(where M is a third body). Using the equilibrium approach summarised by Seinfeld [40] it is possible to calculate the NO generated at different temperatures. Fig. 2 shows the variation of NO mol fraction with temperature for three different gas compositions approximating atmospheric composition, a high-temperature gas mixture from a basaltic eruption [43] and a typical industrial flue gas composition [40]. The strong temperature dependence is clear. For the volcanic gas composition, the molar fractions of NO generated at 1200 and 1400 K are 2×10^{-4} and 6×10^{-4}, respectively. Using the ideal gas law these values correspond to concentrations of NO of ~1700 μmol m^{-3} at 1200 K and ~5400 μmol m^{-3} at 1400 K. Just after emission from the magma, Masaya's plume contains ~1.4 mol% SO_2 [49]. Our measurements of SO_2 on the crater rim (~150 μmol m^{-3}) suggest a mol% of 0.0004 (using the ideal gas law with temperature 298 K). This implies the original gas mixture is diluted by a factor of ~10^4–10^3 between emission and measurement. Assuming total conversion of NO to HNO_3 (dis-

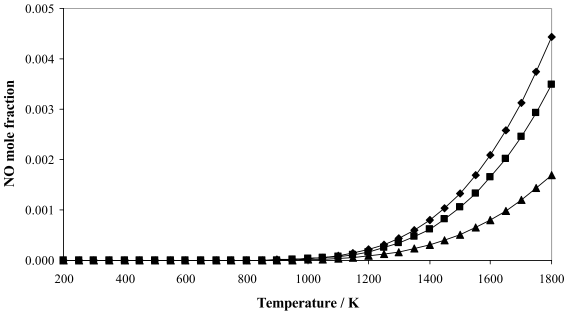

Fig. 2. Variation of molar fraction with temperature assuming equilibrium for NO based on the equilibrium calculations in Seinfeld [40]. Diamonds, atmospheric composition (mol N/mol O ~4); squares, example of high-temperature (~1370 K) basaltic volcanic gas composition calculated from Taran et al. [43] data on Klyuchevskoy volcano using Ar as a measure of atmospheric component (mol N/mol O ~8); triangles, enhanced N_2 mixture typical of industrially produced flue gases [40] (mol N/mol O ~40).

cussed below) at Masaya, HNO_3 concentrations of ~0.17–5.4 μmol m^{-3} are expected at the measurement site (assuming gases are heated to 1200–1400 K). Hence an order of magnitude calculation assuming thermal equilibrium gives a result that is the same order of magnitude as that observed (~2.5 μmol m^{-3}).

It should be highlighted that thermodynamic calculations will not give a totally accurate picture of how nitrogen fixation might work in the volcanic environment. The assumption of equilibrium gives an indication of the concentrations of NO that might be achieved at any given temperature, but assumes sufficient time for the system to come to equilibrium and a subsequent temperature drop that is sufficiently rapid to 'freeze' the high-temperature reaction products. Accurate prediction of NO levels via a kinetic model is desirable but would require the integration of the appropriate rate equations over the time–temperature history of the gases [40].

The difficulty with this explanation for the occurrence of HNO_3 is that it requires rapid conversion of NO_x to HNO_3 if it is to explain our observations. In contrast, photochemical models of the unpolluted troposphere suggest that NO_x is converted to HNO_3 on the scale of 1–2 days at mid-latitudes in the summer and about 10 days in the winter. Even field measurements of urban air in summer still suggest NO_x lifetimes of 4–8 h ([4] and references therein), suggesting that appreciable NO_x conversion, by similar processes but on a timescale between emission and measurement of only 2–3 min (from plume observations), may be unlikely. In the atmosphere, NO is oxidised to NO_2 via a number of reaction schemes [4,50], including:

$$NO + O_3 \Rightarrow NO_2 + O_2 \tag{5}$$

$$NO + OH \Rightarrow HNO_2 \tag{6}$$

$$HNO_2 + OH \Rightarrow NO_2 + H_2O \tag{7}$$

Conversion to nitric acid is then thought to proceed primarily via the following reaction [4]:

$$OH + NO_2 + M \Rightarrow HNO_3 + M \tag{8}$$

Oxidants, such as OH and O_3, are present in the ambient background air and will mix into NO_x-rich emission during transport, producing the slow NO_x removal rates discussed above [4]. In aircraft exhausts the high concentrations of OH generated during combustion can mean that reactions characterised by timescales of days under background conditions evolve in milliseconds in the jet plume [50]. Analogous processes could occur in volcanic vents with observations of near-source sulphate [37,38] and recently bromine monoxide [51], highlighting that early in their evolution volcanic plumes are highly oxidising environments. Much further work is required to elucidate the possible processes occurring in high-temperature volcanic emissions, including perhaps the application and development of models (e.g. [52]) and the use of isotopic studies [53].

From Fig. 2, it can be seen that the composition of the gas mixture as well as temperature is important in determining the position of the equilibrium, with gas mixtures enriched in N_2 having lower equilibrium concentrations of NO. At Masaya, Etna and Villarrica, where the magma–air interface is deep within a vent, the circulation of ambient air to that interface may be limited. Thus the levels of other volcanogenic gases will account for a significant proportion of the gas mixture. Further, volcanogenic N_2 emissions at these magma–air interfaces may further enrich the gas mixture in N_2 (from the atmosphere and the magma) compared to O_2 (from the atmosphere alone). This could inhibit NO production at volcanoes where the accessibility of the magma–air interface to the atmosphere is reduced. It could also explain why the HNO_3 levels at Lascar are comparable to the other higher-temperature systems: the hotspot temperatures are lower but the areas of high temperature may be more accessible to the atmospheric gas mixture. It remains possible that air also enters these systems through shallow sub-surface fractures, so reactions of air/volcanic gas mixtures within the magma itself cannot be ruled out.

The absence of HNO_3 emission at Soufrière Hills Volcano, Montserrat [12], may reflect the lower temperatures of this andesitic volcanic system. At Soufrière Hills the magmatic temperature at depth is ~1120 K [54], with hotspots on the dome of perhaps 970–1020 K. Our equilibrium calculations suggest that at a temperature of 1000 K thermal fixation of an atmospheric gas composition will only generate NO concentrations of the order of ~440 μmol m^{-3}, much lower than those predicted for the higher-temperature volcanic situations in this study. Oxidation routes from NO to HNO_3 might also operate more slowly at lower temperatures. Together, these factors could account for the lack of HNO_3 observed at the summit sites at Montserrat [12].

The low levels of HNO_3 vapour observed in volcanic ash plumes by Lazrus et al. [25] could be due to a number of factors. Their measurements were taken from an aircraft further downwind than our in-plume crater measurements. Thus, dilution or scavenging into the aqueous phase may have reduced gaseous HNO_3 levels below the detection limit. It is also possible that explosive volcanic plumes do not provide suitable conditions for thermal N fixation, with the eruption column cooling too quickly upon mixing with air for significant N_2 and O_2 to react. In some cases of explosive volcanism, however, N may be fixed by a quite different mechanism, namely volcanic lightning (e.g. [55]).

4.2. *Volcanic flux of fixed nitrogen*

Due to the relative ease with which the SO_2 flux from volcanoes can be measured it is common practice to estimate the flux of other plume components (X) by using estimates of the X/SO_2 ratio in the plume. The fluxes of HNO_3 calculated for each volcano are listed in Table 3a,b. The total flux from all four systems is 2.6 kg s^{-1} (0.02 Tg (N) yr^{-1}) with this value dominated by Lascar. Mean HNO_3/SO_2 molar ratios range from 0.01 to 0.07. This is consistent with the N/SO_2 molar ratios observed for the NO_x emissions compiled in Table 2 (ranging from 0.003 to 0.75, for emissions between and after eruptive episodes) and at the high end of the ratios we estimate (0.001 and 0.07) from the few data for explosive eruptions [25]. Our ratios, when combined with global volcanic SO_2 emission rate data, can be used to estimate the time-averaged global flux of HNO_3 from volcanoes. The small number of data points for Lascar, Villarrica and Etna, the scatter of the results and the possibly very different routes of generation for SO_2 and HNO_3 in volcanoes suggest considerable uncertainty in the calculated HNO_3/SO_2 ratios. It should hence be stressed that these estimates are intended to be at best an order of magnitude assessment. However, such difficulties are inherent in many such volcanic global flux measurements (see discussion of trace metal fluxes in Mather et al. [5] and Pyle and Mather [56]).

Assessment of recent compilations of SO_2 emissions from volcanoes ([8–10,57,58] compiled in [5]) suggest total volcanic SO_2 fluxes of 6.7–10.5 Tg S yr^{-1} of which 3.0–4.7 Tg S yr^{-1} is from continuous emissions. Our and previous measurements of volcanic plumes suggest that not all types of volcanism that release SO_2 will produce HNO_3. Therefore the estimates of total volcanogenic SO_2 must be filtered in some way. While much work remains to be done to confirm the origin of the HNO_3 observed in these high-temperature volcanic emissions, previous observations of volcanogenic NO_x suggest that fixation of N_2 is the most likely route, implying that some sort of high-temperature magma/lava–air interface may be necessary for HNO_3 production. From Andres and Kasgnoc's compilation [8], we summed the emissions from Etna, Lascar, Kilauea (continuous and sporadic), Masaya, Stromboli, Erta'Ale, Nyiragongo and Mt. Cameroon and added measurements from Carn et al. [58] of Nyamuragira, Iceland and the Galápagos and our measurements from Villarrica to give a conservative estimate of the annual flux from high-temperature volcanism of 3.7 Tg (SO_2) yr^{-1}. Using our range of molar ratios (converted to a mass ratio range of 0.02–0.07) the range of possible HNO_3 fluxes in non-explosive volcanic plumes is 0.11–0.26 Tg (HNO_3) yr^{-1}, or 0.02–0.06 Tg (N) yr^{-1}. It is worth noting that the persistent activity of the four volcanoes studied here accounts for a total SO_2 flux of ~1.5 Tg yr^{-1} (Table 3a,b [59,60]). This flux alone accounts for a significant proportion of the annual non-explosive SO_2 flux. The total emissions of HNO_3 from these volcanoes are of the order of 0.02 Tg (N) yr^{-1}, the same order of magnitude as our minimum global estimate. This lends credibility to our assertion that the global volcanic HNO_3 flux is >0.02 Tg (N) yr^{-1}. Inconclusive measurements [25] mean that the HNO_3/SO_2 ratio of explosive plumes is too uncertain for a flux estimate to be attempted.

In explosive ash-rich plumes, volcanic lightning [55] may play a role in N fixation. In order to estimate the potential flux of fixed nitrogen from such lightning we adapted the calculation method detailed in Navarro-González et al. [61] for a volcanic plume heavily diluted by the present-day atmosphere. Using a volcanic tephra flux of 10^{12} kg yr^{-1} from explosive volcanism [62], the flux of NO from volcanic lightning may be of the order of 0.02 Tg (N) yr^{-1}.

These are the first estimates of fixed N fluxes to the atmosphere from non-explosive volcanism and volcanic lightning. Although not as large as other natural global fluxes detailed in Table 1, it should be remembered that the elevated altitude of many volcanoes means that N fixed at volcanoes will enter the free troposphere where it will experience an extended atmospheric lifetime. Table 1 also reports average emissions over the entire globe. In some situations volcanic emissions can have a very obvious effect on environments on the regional scale (e.g. Masaya's low-level plume [11, 63,64]). The effects of elevated fixed N levels in such areas require further investigation. Our gaseous HNO_3 flux estimate represents a minimum value since the total NO_x emissions (precursors to HNO_3 if thermal fixation is assumed to be the production route of HNO_3) from volcanoes remain unquantified, as do thermal NO_x and HNO_3 emissions from explosive volcanism.

5. Conclusions

Elevated levels of gaseous HNO_3 have been observed in the non-eruptive plumes from Masaya, Etna, Villarrica and Lascar volcanoes. Although much further work remains to be done, previous observations of NO_x fluxes associated with volcanic activity suggest that this is the result of oxidation of NO formed via reaction of N_2 (from the atmosphere as well as magmatic sources) and O_2 (from the atmosphere). The exact mechanisms for this process, especially those associated with the relatively rapid oxidation of NO, remain uncertain. These emissions account for a previously unquantified natural flux of fixed N to the atmosphere. Based on our measurements we have estimated this to be of the order of 0.02–0.06 Tg (N) yr^{-1} from high-temperature non- to mildly explosive volcanic degassing alone. The contribution from explosive volcanism remains unclear, although NO_x emissions in highly explosive, ash-rich plumes may result from, or at least be supplemented by, production from volcanic lightning rather than thermal N fixation. We have calculated NO production via this route to be of the order of 0.02 Tg (N) yr^{-1}.

These volcanic emissions of fixed nitrogen will constitute an additional environmental perturbation during episodes of persistent degassing such as those studied here. HNO_3 deposition will contribute to acidic precipitation (although of lesser significance than that due to the major acidic volcanic species SO_2, HCl and HF) and will affect the nutrient status of surface ecosystems due to increased inputs of bioavailable nitrogen. While this may increase ecosystem productivity in the short-term, different ecosystems will react in different ways to this input and prolonged nitrate deposition followed by leaching from the soil may have a number of negative consequences both to the environment and directly to human health. Our results highlight the need for further investigation of the reaction products formed in the extreme environments surrounding volcanic vents as well as the primary species escaping from the magma, when assessing volcanic emissions.

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