Volcanic source for fixed nitrogen in the early Earth's atmosphere

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ABSTRACT

Hot volcanic vents promote the thermal fixation of atmospheric N_2 into biologically available forms. The importance of this process for the global nitrogen cycle is poorly understood. At Masaya volcano, Nicaragua, NO and NO_2 are intimately associated with volcanic aerosol, such that NO_x levels reach as much as an order of magnitude above local background. In-plume HNO_3 concentrations are elevated above background to an even greater extent (≤ 50 $\mu mol \cdot m^{-3}$). We estimate the production efficiency of fixed nitrogen at hot vents to be $\sim 3 \times 10^{-8}$ $mol \cdot J^{-1}$, implying present-day global production of $\sim 10^9$ mol of fixed N per year. Although conversion efficiency would have been lower in a preoxygenated atmosphere, we suggest that subaerial volcanoes potentially constituted an important source of fixed nitrogen in the early Earth, producing as much as $\sim 10^{11}$ $mol \cdot yr^{-1}$ of fixed N during major episodes of volcanism. These fluxes are comparable to estimated nitrogen-fixation rates in the prebiotic Earth from other major sources such as bolide impacts and thunderstorm and volcanic lightning.

Keywords: nitrogen cycle, volcanic gases, Masaya volcano (Nicaragua), atmospheric evolution.

INTRODUCTION

Nitrogen is essential for life on Earth, but atmospheric N_2 is only available to most organisms after fixation to chemical forms such as NO, NO_2 (known collectively as NO_x), and NH_3. Despite its importance, the evolution of the biogeochemical nitrogen cycle and the development of biotic fixation processes are poorly understood. Most present-day fixation is by biological or anthropogenic processes (~ 0.9–3.1×10^{13} and 1.3×10^{13} $mol \cdot yr^{-1}$ of N, respectively; Vitousek et al., 1997), but on the early Earth, prior to the evolution of nitrogen-fixing organisms (i.e., 3–2.5 Ga; Raven and Yin, 1998), abiotic processes would have been the only fixation mechanisms. Lightning is considered the main present-day abiotic fixed N source, responsible for a small fraction of current production ($<5\%$, $<7 \times 10^{11}$ $mol \cdot yr^{-1}$, Mancinelli and McKay, 1988; Vitousek et al., 1997). Thus far, lightning and bolide impacts are the major potential abiotic sources of fixed N that have been considered for the early Earth (Mancinelli and McKay, 1988; Navarro-González et al., 1998; Summers, 1999).

Volcanoes are well known for their role in the outgassing of the Earth's interior over geologic time (e.g., Kasting and Catling, 2003). Previous studies of nitrogen in volcanic emissions have focused on the small quantities of N_2 released directly from magma (e.g., Fi-scher et al., 2002). Nitrogen is only slightly soluble (at below parts-per-million levels) in high-temperature, oxidizing magmas, where it dissolves predominantly as molecular nitrogen (N_2) (Libourel et al., 2003; Miyazaki et al., 2004). Present-day volcanism sustains a return flux of $\sim 10^9$–10^{10} $mol \cdot yr^{-1}$ of N_2 to the atmosphere, mainly at subduction zones (Fischer et al., 2002; Hilton et al., 2002). However, hot magmatic vents also offer the opportunity for atmospheric nitrogen (78% of air) to be rapidly heated and to undergo thermally catalyzed reactions producing oxides of nitrogen. The potential importance of this process for the global nitrogen cycle has not yet been fully investigated.

There are few previous reports of NO_x measurements close to volcanoes. NO has been observed above Hawaiian lava flows (Huebert et al., 1999), and NO_x has been observed in dilute, ashy eruption plumes sampled by aircraft (Bandy et al., 1982; Hobbs et al., 1982, 1991). In ashy eruption plumes NO_x may have originated from volcanic lightning (Navarro-González et al., 1998; Mather et al., 2004). Recently, HNO_3, the main oxidation product of NO_x, has been discovered in young quiescent volcanic plumes (Mather et al., 2004). Here we present measurements of NO_x, NO_2, and HNO_3 in the persistent plume from Masaya volcano, Nicaragua. The data show categorically that above hot (>1200 K) magma-air interfaces associated with persistently degassing lava lakes at basaltic and andesitic volcanoes, atmospheric N_2 is first converted to NO and then rapidly oxidized to HNO_3. We extrapolate these results to suggest that high-temperature volcanism was a major, but hitherto unconsidered, source of fixed N in the early Earth.

MEASUREMENTS

We used a dust monitor and chemiluminescent analyzer to make simultaneous measurements of particles and NO_x on the crater rim of Masaya volcano, in November–December 2003. Filter packs were also deployed throughout the measurement period to sample gaseous HNO_3 and SO_2 (see Appendix). At the time of observation, gases and particles were continuously escaping from two boccas at the base of the active crater. The southern bocca emitted a constant blue or white fume, while the northern bocca exposed a vigorously degassing magma conduit, with frequent gas bursts. From visual observations, the exposed conduit surface area was conservatively estimated as ~ 10–20 m^2.

RESULTS AND DISCUSSION

Particle and NO_x concentrations from three runs are shown in Figures 1A–1D. Plume "puffs" were intermittently advected to the sampling site depending on local winds. Plume-affected air is highly enriched in fine particles (as much as ~ 50 times background) and NO_x (0.2–0.5 ppb [1 part in 10^9], as much as ~ 9 times the measured local mean back-
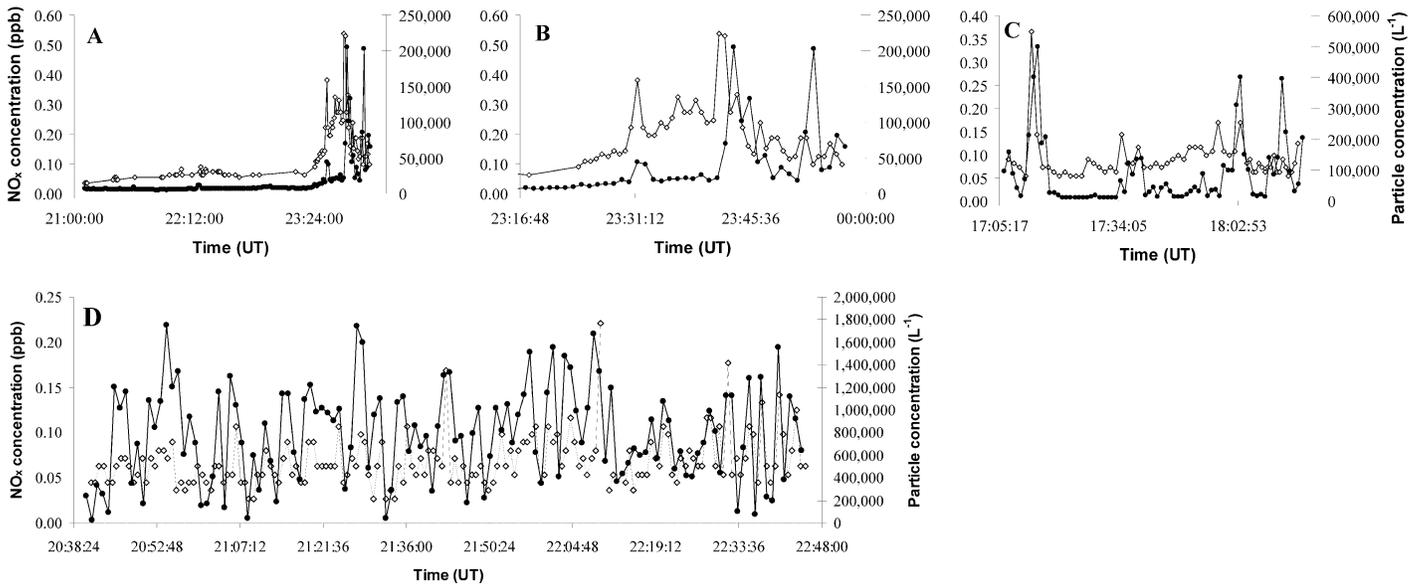
Figure 1. Time-series graphs of particle and NO$_x$ concentrations. Filled circles—particles; empty diamonds—NO$_x$. A: Results from 22 November 2003—entire run, showing clean air (until ~23:24 UT), followed by slight change in wind direction that brought plume + air mixture periodically over sampling site. B: Detail of plume measurements, 22 November. Mean "clean air" NO$_x$ concentration was 0.06 ppb, and NO$_2$ concentration was 0.02 ppb; plume + air mixture NO$_x$ concentration was 0.20 ppb, and NO$_2$ concentration was 0.09 ppb. C: Results from 26 November (morning). D: Results from 26 November (afternoon).

ground). The strong association between elevated particles and elevated NO$_x$ (Figs. 1A–1D) confirms NO$_x$ as enhanced in Masaya's plume. The mean NO$_2$ contents were 44%–57% of NO$_x$. Filter-pack measurements (Fig. 2) show that in-plume HNO$_3$ concentrations (mean, 7.2 μmol·m^{-3}; maximum, 50.3 μmol·m^{-3}) were elevated by one to two orders of magnitude above background (mean, 0.1 μmol·m^{-3}).

Our observations confirm NO$_x$ production in hot volcanic vents. At the point of measurement, plume gases have typically been diluted by ~10^3–10^4 (Mather et al., 2004), implying NO$_x$ concentrations at the vent of ~100–1000 ppb. However, measured levels of HNO$_3$ (~200 ppb) suggest NO$_x$ concentrations of ~200–2000 ppm at the vent. Simple thermodynamic modeling (Mather et al., 2004) shows that thermal fixation of O$_2$ and N$_2$ at magmatic temperatures can account for these NO$_x$ levels. Following fixation, the gas

mixture must cool rapidly to "freeze" out the reaction products, and NO$_x$ appears to be rapidly oxidized to HNO$_3$. Fast oxidation is consistent with (1) the high proportion of NO$_2$ in NO$_x$ (44%–57%) compared to the ~5% in power-station plumes (Hewitt, 2001) and the 15%–30% in lightning-affected air (Zhang et al., 2003) and (2) the observed levels of near-source sulfate in volcanic plumes of ~1% of the SO$_2$ mass (e.g., Mather et al., 2003). Faster NO$_x$ oxidation rates may explain the much greater extent of NO oxidation compared to SO$_2$ (e.g., Hewitt, 2001). Further investigation of the possible oxidation processes occurring in volcanic vents is required.

The formation rate of NO$_x$ at open vents like Masaya and over exposed hot lava flows will depend, among other things, on the volcanic heat flux. At Masaya, the opening to the lava lake is small (~10–20 m^2), suggesting a radiative and convective heat flux of ~0.1–1 MW, on the basis of observations at other lava

lakes (Harris et al., 1999). From our simultaneously measured SO$_2$ flux (2.2 kg·s^{-1}; see Appendix) and a typical Masaya gas composition with 1.4 mol% SO$_2$ and 94 mol% H$_2$O (Burton et al., 2000), the total gas flux is ~2450 mol·s^{-1}. The energy released as the magmatic gas cools from ~1400 to 1200 K (the estimated temperature below which thermal N fixation is insignificant; Logan, 1983) is ~15 MW (Harris et al., 1999). An estimated vent NO$_x$ level of 200 ppm implies a production rate of 0.5 mol·s^{-1} and NO production efficiency of ~3 × 10^{-8} mol·J^{-1} or ~2 × 10^{16} NO molecules per joule. Present-day lightning produces NO at ~1–30 × 10^{16} molecules per joule (e.g., Cook et al., 2000).

The present-day global radiant heat flux from high-temperature volcanism is ~4 × 10^{16} J·yr^{-1} (estimated by filtering Wright and Flynn's [2004] data set for high-temperature volcanism). Although for our purposes this heat flux represents only a first-order approximation (it does not include energy from gas cooling, important for low-extrusion-rate volcanoes such as Masaya, but does include heat energy radiated at <1200 K), when combined with our estimated volcanic NO$_x$ production efficiency above, this heat-flux value gives a current production rate of ~1 × 10^9 mol·yr^{-1} of fixed N, comparing well with rates of >1–4 × 10^9 mol·yr^{-1} estimated from HNO$_3$/SO$_2$ ratios and global high-temperature volcanic SO$_2$ emission rates (Mather et al., 2004). Thus, present-day volcanism fixes atmospheric nitrogen at a rate similar to the emission rate of N$_2$ from volcanoes (as much as 2 × 10^{10} mol·yr^{-1} of N$_2$; Hilton et al., 2002).

Figure 2. Filter-pack measurements of gas-phase SO$_2$ and HNO$_3$ at Masaya. Open diamonds—in plume measurements; filled triangles—background measurements. Note logarithmic scale on *y*-axis.
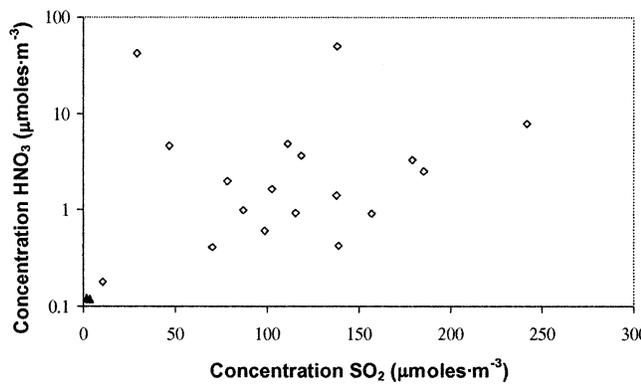
Our results categorically link high-temperature volcanic activity and the fixation of atmospheric N_2 into biologically available forms. Further, the results show that open-vent degassing volcanoes, as well as lava flows (Huebert et al., 1999), provide suitable conditions for thermal N fixation.

Volcanic fixation of nitrogen would certainly have been effective for the past 2 b.y., since the oxygenation of the atmosphere (e.g., Kasting and Catling, 2003). Fixation efficiencies, however, would have differed in the early, O_2-poor atmosphere (e.g., Yung and McElroy, 1979; Navarro-González et al., 1998). Navarro-González et al. (2001) showed that the nitrogen fixation efficiency of lightning in a CO_2-N_2 atmosphere reached a maximum (at ~10% of present-day efficiency) for CO_2 mol fractions of 40%–80%. In contrast to lightning, the composition of the gas mixture in hot volcanic environments will depend not only on the background atmospheric composition, but also on the gas mixture emitted from the hot magma. Assuming (1) magmatic gas has ~1–45 mol% CO_2 (e.g., compilation in Taran et al. [1991] for present-day, high-temperature emissions; there are no data for early Earth magmatic gases), (2) 50% dilution of magmatic gas by background atmosphere in hot volcanic environments (extent of mixing will depend on style of volcanic activity), and (3) a CO_2 level of 0.04 bar in the early Earth's atmosphere (consistent with paleosol data; Rye et al., 1995; Hessler et al., 2004) suggests gas mixtures with ~3–25 mol% CO_2 available for volcanic thermal fixation of nitrogen. For lightning, these CO_2 mixing ratios suggest N fixation efficiencies approximately one to three orders of magnitude less than in the present-day oxygenated atmosphere (Cook et al., 2000; Fig. 1 in Navarro-González et al., 2001). By analogy, we estimate possible fixation efficiencies of ~2×10^{13} to 2×10^{15} molecules of NO per joule for high-temperature volcanic processes in the prebiotic atmosphere.

The early Earth would have exhibited higher rates of volcanism (e.g., Richter, 1985) at higher magmatic temperatures (e.g., komatiite lavas; Nisbet et al., 1993). In addition, there may have been more extensive subaerial high-temperature magmatism than at present, for example, if parts of the oceanic ridges were exposed above sea level (e.g., De Wit and Hynes, 1995) or during the emplacement of flood-basalt provinces.

In Table 1 we estimate the nitrogen-fixation potential of different magma types for the prebiotic and present-day atmospheres. A present-day subaerial eruption rate of basaltic magma of ~0.2 km³·yr⁻¹ (twice the current output of Kilauea, Hawaii; Heliker et al., 2003) equates to a potential production rate of 4×10^9 mol·yr⁻¹ of fixed N, in good agreement with our other estimates of current production. Flood-basalt provinces, characterized by the eruption of prodigious lava volumes (>2×10^6 km³) over relatively short time scales (ca. 1 m.y.) at typical extrusion rates of ~2 km³·yr⁻¹ (Courtillot and Renne, 2003), would produce ~4×10^{10} mol·yr⁻¹ of fixed N with present-day atmosphere. Peak extrusion rates of these provinces probably exceeded 20 km³·yr⁻¹ (e.g., the 15 km³ Laki basalt, Iceland, was emplaced in just 8 months; Thordarson and Self, 2003), with corresponding production rates of fixed N of ~4×10^{11} mol·yr⁻¹. Similar extrusion rates of higher-temperature komatiite lava during the Archean would release thermal energy at a greater rate (Table 1) and could have led to production rates from ~2×10^9 to 2×10^{11} mol·yr⁻¹ of fixed N. These fluxes are comparable to estimated production rates in the early Earth by bolide impacts of ~10^{11} mol·yr⁻¹, by thunderstorm lightning of ~3×10^{10} mol·yr⁻¹, and by volcanic lightning of 3×10^{10} to 3×10^{11} mol·yr⁻¹ of fixed N (Mancinelli and McKay, 1988; Navarro-González et al., 1998; Summers, 1999).

Although simplified, our analysis yields a first estimate of possible volcanic nitrogen-fixation rates through Earth history. Of course, volcanic nitrogen-fixation potential will depend upon other factors such as eruption style, as well as a magma's physical properties. Although there is some uncertainty over the exact emplacement processes of large-volume basaltic lava fields, analogy with the 1783–1784 Laki eruption suggests that these eruptions are characterized by extensive fire fountaining at the vent (Thordarson and Self, 2003). Away from the vent the cooling lava crust will tend to limit nitrogen fixation other than at skylights and during lava-flow "breakout" events (Huebert et al., 1999). The lava and accompanying gases will be at their hottest at vents or fissures, and under present-day atmospheric conditions, lava fountaining would seem to offer an efficient way to mix background O_2 and N_2 into the hot environment to facilitate NO production. Because most magma degassing is thought to occur at the vents of large basaltic flows (~80%; Thordarson and Self, 2003), high-temperature fissure activity would also offer the best site (i.e., high CO_2 mixing ratio) for nitrogen fixation in a preoxygenated atmosphere. Different fixation dynamics will operate at other types of volcanic activity such as persistent open-vent degassing and lava lakes.

CONCLUSIONS

Consideration of the global nitrogen cycle and evolution of atmospheric nitrogen over geologic time should include the potential of volcanoes to fix nitrogen into water-soluble and biologically available forms. The present-day production rate of fixed nitrogen at high-temperature volcanic vents is ~10^9 mol·yr⁻¹. We suggest that in the early Earth, especially during episodes of large-volume subaerial magmatism, high-temperature volcanism could have been a major nitrogen-fixation process, with estimated production rates of ~10^9–10^{11} mol·yr⁻¹ of fixed N. Further investigation of fixation efficiencies for different gas mixtures and eruption styles would constrain these values better. Improved understanding of the oxidation processes occurring in volcanic environments would also help to elucidate the fate of volcanically fixed nitrogen in Earth's surface layers and the potential consequences of the emission of large quantities of fixed nitrogen associated with pulses of volcanism.

APPENDIX. METHODS

Particles were measured using a GRIMM dust monitor (model 1.106) with a K_2CO_3 denuder. NO_x and NO_2 were measured using a Scintrex LNC-3 NO converter coupled to a Scintrex LMA-3 chemiluminescence NO_2 analyzer (Unisearch Associates Inc.; Wendel et al., 1983). The Scintrex analyzer was calibrated (0.006–45 ppb) using a certified gas cylinder. Span checks (at 40 ppb) before and after field sampling showed that signal drift was <5%. The sample inlet was fitted with an ozone trap (Scintrex type 856005) to avoid O_3 interference (equivalent to 1% of NO_2 response). A miniature carbon vane pump pro-

TABLE 1. ESTIMATES OF THE NITROGEN FIXATION POTENTIAL FOR DIFFERENT ERUPTED MAGMAS IN THE PRESENT-DAY AND EARLY EARTH ATMOSPHERES

Magma type	Eruption temp. (K)	Magma density (kg·m⁻³)	C_m* (J·kg⁻¹·K⁻¹)	Energy available for nitrogen fixation (J·kg⁻¹)	Nitrogen fixation potential (moles of N per 1 km magma)	
					Early Earth	Present day
Andesite	1270	2600	1400	1×10^5	1×10^7 to 1×10^9	1×10^{10}
Basalt	1420	2700	1484	3×10^5	2×10^7 to 2×10^9	2×10^{10}
Komatiite	1820	2850	1658	9×10^5	1×10^8 to 1×10^{10}	1×10^{11}

Note: Calculations are based on the heat released during cooling of the melt from the eruption temperature down to ~1200 K (taken as the temperature below which thermal fixation of N is insignificant; Logan, 1983).
*Specific heat capacity of magma (Spera, 2000).

vided a sample air-flow rate of 1.2 L·min^{-1}. Power was supplied by a 12 V car battery. The dust monitor recorded volumetric particle concentrations >0.35 μm in diameter, as time-weighted averages every minute. The NO$_x$ analyzer cycled through measuring NO$_x$, NO$_2$, and zero approximately every minute. Maximum NO$_x$ and NO$_2$ values within each sampling period were recorded and corrected for the zero value. There was a slight time offset between particle and NO$_x$ measurements (particle concentrations were 1 min averages; NO$_x$ levels were determined over the first 15–20 s of each cycle). Gas-phase species were collected on filters housed in multiple-stage, 47-mm-diameter cartridges. Gas and aerosol were pumped at ~20–30 L·min^{-1} through particle filters and alkali-impregnated filters to collect acidic gases. Sampling times ranged from ~50–160 min at near-crater sites and 3–6 h at background sites. Exposed filters were triple sealed in plastic bags and stored in a freezer. Collected species were extracted from filters with 10 cm^3 of distilled deionized water. Gaseous SO$_2$ and HNO$_3$ were determined as SO$_4^{2-}$ and NO$_3^-$ by Dionex ion chromatography (e.g., Mather et al., 2004). Sulfur dioxide fluxes were determined by traversing under the plume using a miniature ultraviolet spectrometer (e.g., McGonigle et al., 2002).

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