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Volcanic emissions and the early Earth atmosphere

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Abstract

Despite uncertainties in our understanding of early Earth volcanism and atmospheric composition, thermodynamic modelling is able to offer estimates of the global production of reactive trace species (NO, OH, SO_3, Cl, Br and I) from early Earth volcanism, and thereby to shed light on processes which may have been different in Earth's early atmosphere. Model results show that thermal decomposition of magmatic H_2O, CO_2 and SO_2 in high-T mixtures of magmatic and atmospheric gases (at $T > 1400$ °C) generate high levels of reactive trace gas species. Production of these reactive trace species is insensitive to atmospheric CO_2 in mixtures where the atmospheric gas is the minor component and will hence continue during periods of low atmospheric CO_2. Fluxes of NO, OH, Cl, Br and I from early Earth volcanism are predicted to exceed those from modern Earth volcanism as the higher temperature of early Earth emissions compensates for lower levels of O_2 in the atmosphere, compared to the modern Earth. Under certain conditions, the volcanic NO flux from early Earth volcanism is found to be comparable to other sources of reactive N such as lightning NO and photochemical HCN. This is one possible source of fixed nitrogen which may alleviate any postulated Archean nitrogen crisis. Our thermodynamic model reveals that production of SO_3 (a potential precursor for near-source volcanic sulphate and hence 'primary' volcanic aerosol) is likely to be significantly lower from early Earth volcanism. Uncertainty in the pathway to near-source sulphate in modern volcanism (i.e., the reaction of SO_3 with water or direct emission) introduces a large uncertainty into the production rate of near-source volcanic sulphate on the early Earth.
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1. INTRODUCTION

Recent studies have highlighted the importance of atmospheric gases in the rapid oxidation of volcanic emissions through formation of high-temperature reaction mixtures (Gerlach, 2004; Martin et al., 2006; Bobrowski et al., 2007). Oxidation processes in these mixtures lead to chemical activation of inert reservoirs such as N_2 and HX (X = halogen) to give radical NO and X. These radical species play an important role in atmospheric chemistry, and recent studies have gone some way to assessing the likely global and local volcanic fluxes and impacts of these species (Mather et al., 2004b; Bobrowski et al., 2007).

In the absence of biological and anthropogenic emissions to the atmosphere (i.e., on the early Earth), volcanism had the potential to be a much more important influence on atmospheric chemistry and composition. The early Earth may have exhibited higher rates of volcanism (e.g., Richter, 1985) and hence the rate of atmospheric processing by volcanic activity is potentially much greater. Furthermore, higher magmatic temperatures (Nisbet et al., 1993; Herzberg et al., 2007) would suggest that mixtures of magmatic and atmospheric gases would equilibrate at higher temperatures (i.e., 1400–1600 °C) than on the modern Earth. It can also be speculated that 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 (de Wit and Hynes, 1995) or during the emplacement of early flood-basalt provinces (Ernst and Buchan, 2003; Blake et al., 2004).

Here, we use a gas-phase thermodynamic model to simulate the chemical changes that occur as high-T magmatic gases mix and react with atmospheric gases in order to

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estimate the potential fluxes of trace species into the early Earth atmosphere. We also apply this model to investigate lightning discharges in the early terrestrial atmosphere and compare results with published experimental data.

2. METHODS

Earlier studies have successfully employed a variety of thermodynamic models to calculate equilibrium speciation in high temperature volcanic gases. The principles behind these models will not be discussed here but further information can be found in Gerlach and Nordlie (1975), Symonds and Reed (1993), Gerlach (2004) and Martin et al. (2006).

2.1. The model

A thermodynamic model for volcanic emissions into the early Earth atmosphere was created using HSC Chemistry v5.11 (commercial software, Outokompu Enterprises). This model combines full inorganic chemistry for C–O–S–H–Cl–Br–F–I–N–Ar with organic chemistry for C–O–S–H–N–Cl limited to the derivatives of methane (i.e., C_1 compounds). We chose to exclude F-, Br-, I-bearing C_1 organics and all C_2 organics. This simplification is combinatorial, rather than chemical as the reactivity of organic compounds often follow smooth structure–activity relationships (SARs) (Hammett, 1937); inclusion of the C_1 chlorides is a sufficient test for the stability and formation of organic halides. We further exclude any species where the thermodynamic data may be unreliable as defined by a reliability class of 2 or greater in HSC Chemistry v5.11. The model contains 214 species of atmospheric, volcanic and organic importance (Appendix) and is a modified version of the optimised gas model used in Martin et al. (2006).

An important parameter of mixtures is the volume ratio of atmospheric (V_A) to magmatic (V_M) gas in the equilibrating mixture. If atmospheric gases are heated to temperatures close to the magmatic gas temperature prior to significant mixing (i.e., in lava domes or above hot degassed lava flows), there are no constraints on V_A/V_M. If the atmospheric gases are at ambient temperature at the point of mixing (i.e., mixing at an open vent) the equilibration temperature is a function of V_A/V_M. This presents a fundamental limitation of the model as calculations assume V_A/V_M is independent of temperature. However, for small V_A/V_M (i.e., <1) we can make the approximation that equilibration occurs at the temperature of the magmatic gas without introducing significant inaccuracy into the calculations. In all cases, we make the assumption that any mixing above V_A/V_M at which the mixture is equilibrated only results in dilution of the mixture, and the composition is frozen (i.e., quenched) at the equilibrium composition calculated at V_A/V_M. The corollary of this assumption is that quenching must occur at a single temperature which is close to that of the magmatic gas (i.e., the constant freeze-out model). These assumptions are consistent with earlier thermodynamic models of volcanic gases (Gerlach, 2004; Martin et al., 2006).

2.2. Atmospheric and magmatic gas input compositions

The nature and evolution of the early Earth atmosphere remains a subject of debate and is poorly constrained. It remains clear, however, that atmospheric and magmatic gas compositions are related. Previous studies hypothesised a predominantly CH_4–H_2–NH_3–H_2O early Earth atmosphere (e.g., Urey, 1952) due to outgassing of highly reduced gases from an undifferentiated mantle. The subsequent formation of the Earth's core (leaving a more oxidised mantle) would result in the emission of oxidised magmatic gases to produce a CO_2-rich atmosphere. However, it is now accepted that planetary accretion generated sufficient heating to allow the core to form simultaneously (Stevenson, 1983). Furthermore, no evidence exists in the geological record for a pronounced change in mantle oxidation state and thus the early Earth is likely to have had a CO_2-rich atmosphere, and not a "Milley–Urey" atmosphere, since at least 4 Ga (Canil, 1997; Delano, 2001; Kasting and Catling, 2003).

Paleosol measurements indicate that atmospheric CO_2 decreased to ~0.04 bar at 2.2 Ga due to weathering of silicates in the crust (Rye et al., 1995). It has been suggested that this transition from high (i.e., >0.2 bar) to low (i.e., <0.04 bar) atmospheric CO_2 resulted in an Archean nitrogen crisis which may have triggered the emergence of biological nitrogen fixation (Navarro-González et al., 2001). Recent models invoking organic haze aerosols (Sagan and Chyba, 1997; Pavlov et al., 2001) and reduced H_2 loss rates to space (Tian et al., 2005a) have suggested that atmosphere during this period had high levels of the reduced gases, CH_4 and H_2. These high levels of CH_4 are predicted by climate models (e.g., Pavlov et al., 2000) which deal with the faint young sun problem by invoking a significant CH_4 greenhouse effect to warm the early Earth.

The efficiency with which trace compounds form in mixtures of volcanic and atmospheric gas must therefore be investigated over a range of atmospheric compositions. The early Earth atmosphere is assumed to be a mixture of CO_2 and N_2 and calculations are made for the end-member compositions (EC and EN); these compositions are appropriate for periods of high atmospheric CO_2 (i.e., early Archean). Calculations are also made for modern (MN) and control (CN) atmospheres (Table 1). The control atmosphere contains only N_2 and Ar. Inclusion of minor atmospheric species (H_2O, H_2, CH_4 and NH_3) in the atmospheric gas compositions will be indicated in the text but generally these were omitted (see Section 4.4). All calculations are made at 1 bar.

The chemical composition of early Earth magmatic gases is not well constrained. For the purposes of modelling, we have used a magmatic gas composition from the

Table 1
The atmospheric gas compositions used in this study given as mole fractions (X_i)

	N_2	CO_2	O_2	Ar
N_2-rich early Earth (EN)	0.8	0.2	—	—
CO_2-rich early Earth (EC)	0.2	0.8	—	—
Control N_2–Ar (CN)	0.8	—	—	0.2
Modern Earth (MN)	0.8	—	0.2	—

Table 2
Magmatic gas compositions used in this study given as mole fractions (X_i), after Gerlach (2004)

	H_2O	CO_2	SO_2	H_2S	HCl	HF	HBr	H_2	CO	HI	S_2
KPO+	0.757	0.0326	0.194	0.0016	0.0017	0.0018	3.6×10^{-6}	0.00957	0.00091	3.6×10^{-8}	0.00077
KPO−	0.757	0.0326	0.194	—	0.0017	0.0018	3.6×10^{-6}	—	—	3.6×10^{-8}	—

high-T Pu'u 'O'o vent, Kilauea Volcano (KPO, Gerlach, 2004) as one of the closest examples to primitive mantle degassing on the modern Earth. This is consistent with assumptions made in laboratory simulations of volcanic lightning in the early Earth atmosphere (Navarro-González et al., 1998). Magmatic gases contain reduced gases (H_2S, H_2, CO and S_2) which can inhibit the formation of trace oxidised compounds. Removal of these gases allows further insight to be gained into the redox potential of high-T magmatic and atmospheric gases because the effects of oxidising components (H_2O, CO_2 and SO_2) can be studied in isolation from the reducing components (H_2, H_2S, CO and S_2). The two basic magmatic gas components used in this study are therefore denoted KPO+ and KPO− (Table 2). HI was determined using the estimate that HI = 0.01 * HBr (Martin et al., 2006); this is not intended to reflect the true amount of HI in magmatic gases (although the limited measurements available do support a Br/I ratio of this order of magnitude, Aiuppa et al., 2005), but simply to allow the thermodynamics of iodine compounds to be investigated. The KPO+ gas is at equilibrium at 1140 °C and so the molecular composition given above only applies at this temperature. However, the molecular composition uniquely defines the atomic composition (total C–O–S–H–F–Cl–Br–I) and by assuming thermodynamic control, the molecular composition at any temperature can be predicted. The temperature of volcanic emissions on the early Earth is uncertain (and disputed), however, Herzberg et al. (2007) provides evidence for the eruption of lavas at temperatures in excess of 1600 °C and so there is justification for making calculations for magmatic gases (and mixtures) at this temperature. In this study, we make calculations between $800 < T\,(°C) < 1600$ to simulate the full range of temperatures appropriate for mixtures of atmospheric and magmatic gases.

Results can be given in terms of a conversion efficiency (E_i) (as defined in (E1)) where $[x]$ is the mixing ratio of a trace species and $[X]$ is the mixing ratio of a specified major species e.g,. $E_{Cl} = [Cl]/[HCl]$

$$\text{(E1)} \quad E_i = \frac{[x]_i}{[X]_i}$$

3. RESULTS FOR "PURE" EARLY EARTH MAGMATIC AND ATMOSPHERIC GASES

3.1. High-T equilibrium in early Earth magmatic gases

Radical species play an important role in the chemistry of the atmosphere as they react rapidly even at low temperatures (Wayne, 2000). Previous studies have shown that thermal equilibration of magmatic gases at high temperatures (>1200 °C) gives rise to a series of high energy radical species. To determine the sensitivity of radical formation in magmatic gases to temperature, calculations were made for KPO+ gas at $800 < T\,(°C) < 1600$ (Fig. 1) in the absence of atmospheric gases. Fig. 1 shows that OH exceeds H over the entire temperature range, despite thermal dissociation of H_2O generating equal amounts of H and OH. Furthermore, dissociation of SO_2 and CO_2 should generate equal amounts of SO and O, and CO and O, yet free O is much less abundant. It appears that much of the free O generated by thermal decomposition recombines to form a more stable species such as OH (either from oxidative dissociation of H_2O or direct oxidation of H) or oxidises H_2S and S_2 to SO_2. It should be noted that the redox state of the system is invariant with temperature (as the atomic composition remains fixed) and the apparent oxidation of S at higher-T is offset by net reduction of hydrogen (i.e., decreasing H_2S and H_2O and increasing H_2) and carbon (i.e., decreasing CO_2 and increasing CO).

A simple comparison of the equilibrium constants for an analogous set of dissociation reactions at 1400 °C (Table 3, sourced from HSC Chemistry v5.11 database) suggests that CO_2 has the greatest potential of the major magmatic gas species to produce oxidants, however since $H_2O \gg CO_2$ in most magmatic gases it is likely that H_2O is the dominant source of oxidants in magmatic gases. The comparability of the equilibrium constants suggests that within the range of reasonable magmatic gas compositions the oxidising potential can be considered independent of the relative amounts of H_2O, CO_2 and SO_2.

3.2. High-T equilibrium in anoxic atmospheric gases

The formation of NO from atmospheric N_2 and O_2 has a large kinetic barrier, and in the modern Earth is surmountable only by catalytic enzymes or in high-T environments such as lightning strikes or volcanoes (Logan, 1983; Huebert et al., 1999) via the following equilibrium:

$$\text{(R1)} \quad N_2 + O_2 = 2NO$$

The formation of NO from lightning is expected to be reduced in the early Earth atmosphere due to the lower oxidation potential of CO_2 (R2) compared to O_2 (i.e., the equilibrium constant for (R2) is much less than that of (R1) at a given temperature).

$$\text{(R2)} \quad N_2 + 2CO_2 = 2NO + 2CO$$

Navarro-González et al. (2001) predict that decreasing CO_2 during the Archean (due to weathering of silicates in the crust) would lead to a nitrogen crisis as the rate of nitrogen fixation by lightning via (R2) would fall; they also suggest that this crisis may have prompted the emergence of biological nitrogen fixation.

Using the model, calculations were made between $800 < T\ (°C) < 3000$ to calculate NO_x/N_2 for various atmospheric gas compositions (MN, EC, EN) (Fig. 2). This

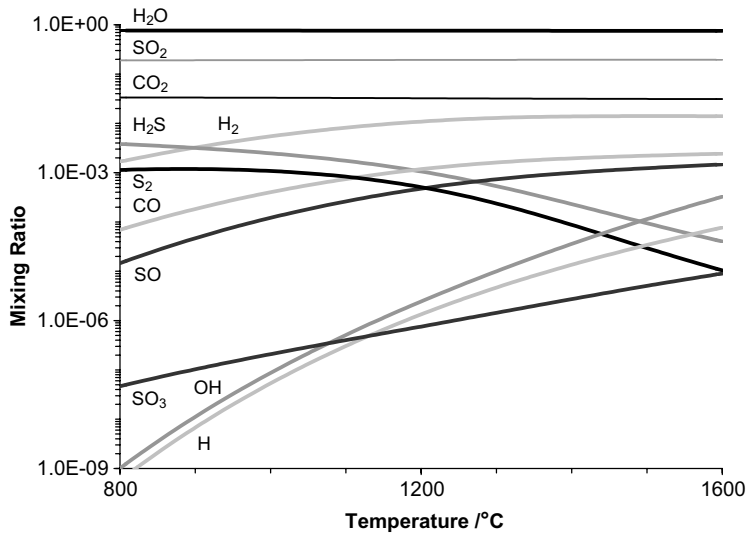

Fig. 1. Calculated mixing ratios for species in a volcanic gas (X_i) using KPO+ magmatic gas over the range $800 < T$ (°C) < 1600. At high-T, the net oxidation of S is balanced by net reduction of H and C. The mixing ratios of reactive radicals (i.e., OH) greatly increase at high temperatures.

Table 3
Equilibrium constants at 1400 °C (taken from HSC Chemistry v5.11 database)

Reaction	log (K)
$CO_2 \rightarrow CO + 1/2O_2$	−4.3
$H_2O \rightarrow H_2 + 1/2O_2$	−4.8
$SO_2 \rightarrow SO + 1/2O_2$	−5.4

temperature range includes quenching temperatures associated with lightning discharge gases ($2000 < T$ (°C) < 3000) and volcanism ($800 < T$ (°C) < 1600). Fig. 2 reveals that at 1400 °C, the conversion efficiency of NO in early Earth atmospheric gases is 10× less than modern Earth atmospheric gases. At temperatures above 3000 °C, formation of NO in the early atmosphere becomes comparable to that in the modern atmosphere. Model calculations show that CO_2 is ~80% dissociated into CO + O and O_2 is ~50% dissociated into O + O at 3000 °C; hence, free O is available for reaction with N_2 in mixtures formed from either early (EC, EN) or modern (MN) Earth atmospheres.

Experimental determinations using simulated lightning in early atmospheres (Navarro-González et al., 2001) show that the efficiency of NO formation by lightning in the early Earth atmosphere is 10× less than in the modern atmosphere. Our thermodynamic model shows that these experimental results are consistent with a quenching temperature of ~2000 °C, consistent with predicted quenching temperatures associated with lightning from earlier thermodynamic models (Yung and McElroy, 2003).

4. HIGH-*T* MIXTURES OF EARLY EARTH MAGMATIC AND ATMOSPHERIC GASES

4.1. Nitrogen and oxygen chemistry

Measurements of elevated levels of oxidised N species (NO, NO_2 and HNO_3) in near-source volcanic plumes suggest that hot volcanic vents promote fixation of atmospheric N_2 into biologically available NO_x (Mather et al., 2004a,b). Calculations were made for equilibrium NO/N_2 at 1400 °C for mixtures of early (EN, EC), control (CN) and modern (MN) atmospheres with KPO+ and KPO− magmatic gas over the range $0.01 < V_A/V_M < 1$ (Fig. 3). Fig. 3 shows that for $V_A/V_M < 0.1$, thermal equilibration of magmatic gases with early atmospheric gases (EN and EC) does not give a significant increase in NO/N_2 compared to the control (CN); the decrease in NO/N_2 implies that oxidation is limited by oxidants derived from the magmatic gas. This result has an important consequence; volcanic emission of NO is likely to continue throughout periods of low atmospheric CO_2 (i.e., ~0.04 bar; Rye et al., 1995) when other sources of NO (e.g., lightning) become less efficient. At $V_A/V_M > 0.1$, the increase in NO/N_2 indicates that atmospheric gases (i.e., CO_2) become the major source of oxidants in the mixture. The conversion efficiency for NO at $V_A/V_M = 0.1$ for KPO− and EN, EC or CN atmospheric gases is approximately 10× less than for modern atmospheric gas. For KPO+, the conversion efficiency with EN, EC or CN is 100× less than for modern atmospheric gas. This difference in the conversion efficiencies can be interpreted by considering the role of the reduced gases which scavenge oxidants:

(R3) $H_2S + 3O \rightarrow SO_2 + H_2O$

(R4) $H_2 + O \rightarrow H_2O$

At higher V_A/V_M, the conversion efficiency of NO in mixtures derived from KPO+ and KPO− tend to the pure atmospheric gas limit (Fig. 2). We can therefore infer that although the formation of NO is approximately independent of the relative amounts of H_2O, CO_2 and SO_2 in the mixture (from Section 3.1), the formation of NO decreases with the amount of reduced gases in the mixture. However, as discussed in Section 2.2, early Earth magmatic gases are expected to have a similar oxidation state to KPO

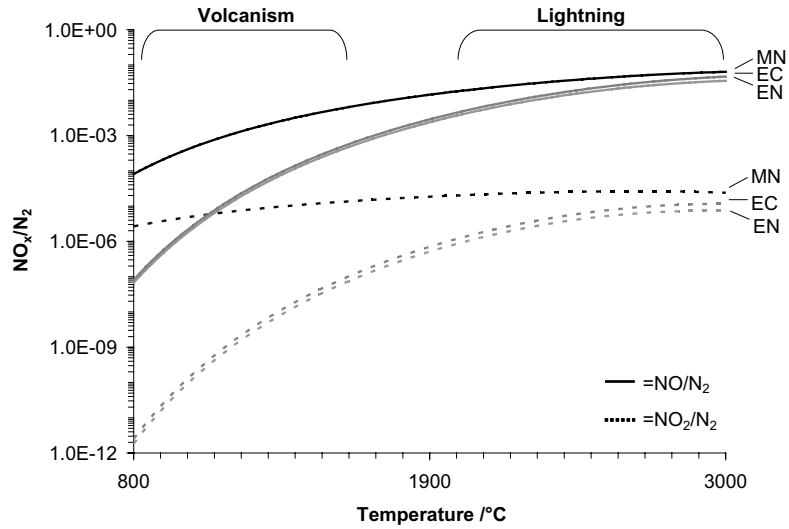

Fig. 2. Calculated equilibrium NO_x/N_2 ratios for modern earth (MN), CO_2-rich early Earth (EC) and N_2-rich early Earth (EN) atmospheres over the range $800 < T$ (°C) < 3000, corresponding to the typical peak temperatures experienced during volcanism (800–1400 °C) or lightning (>2000 °C). For a quenching temperature of $T = 1400$–2000 °C, NO/N_2 for an EC atmosphere is ~0.1 times that of the MN atmosphere.

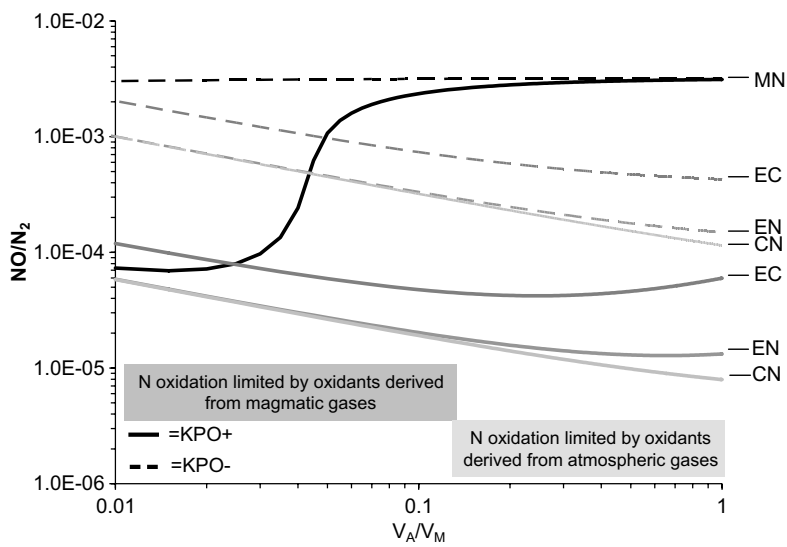

Fig. 3. Results for NO/N_2 in mixtures of magmatic (KPO+ and KPO− shown as solid and dashed lines, respectively) and atmospheric gases at 1400 °C over the range $0.01 < V_A/V_M < 1$. Only above $V_A/V_M = 0.1$ does mixing with EN and EC atmospheres enhance formation of NO. The compositional discontinuity can be clearly seen in the curve for MN with the volcanic gas KPO+.

magmatic gases; it then follows that the amount of reduced gases would also be similar. No dramatic change in the stability of oxidised compounds with increasing V_A/V_M (as present in the modern Earth mixture) is predicted in mixtures derived from early Earth atmospheric gases, this shows that these mixtures are well below the compositional discontinuity (Gerlach and Nordlie, 1975). Calculations were made for equilibrium OH/H_2O under similar conditions (Fig. 4). Fig. 4 shows that below $V_A/V_M = 0.1$ there is no change in OH/H_2O between early Earth and control mixtures, but a significant change for the modern Earth mixture.

Calculations were made for NO/N_2 over the range $800 < T$ (°C) < 1600 for a $V_A/V_M = 0.1$ mixture of early Earth (EN) and modern Earth atmospheric gas (MA) with magmatic gas (Fig. 5). This V_A/V_M was chosen because this value gives a <10% change in the equilibration temperature and so the model is more applicable than at higher V_A/V_M. Fig. 5 suggests that an early Earth volcano with gases at 1400 °C could emit comparable levels (within an order of magnitude) of NO as a modern volcano with gases at 1000 °C (despite the lack in atmospheric oxygen). It remains unclear whether further oxidation of NO to HNO_3 (Mather et al., 2004a) would occur. This treatment was repeated for OH (Fig. 6), and it was found that OH emitted from an early Earth volcano would to exceed that emitted from a modern volcano.

These results show that volcanic emission of NO and OH does not depend on the atmospheric composition until the onset of atmospheric oxygenation; this allows flux

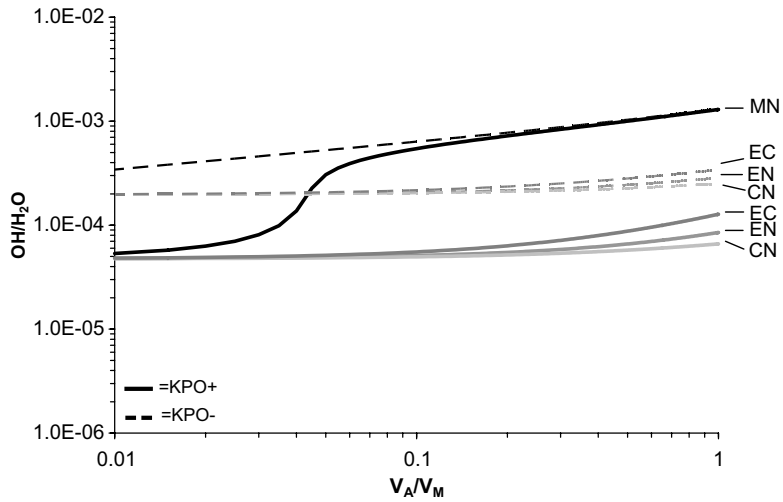

Fig. 4. Results for OH/H_2O in mixtures of magmatic and atmospheric gases at 1400 °C over the range $0.01 < V_A/V_M < 1$.

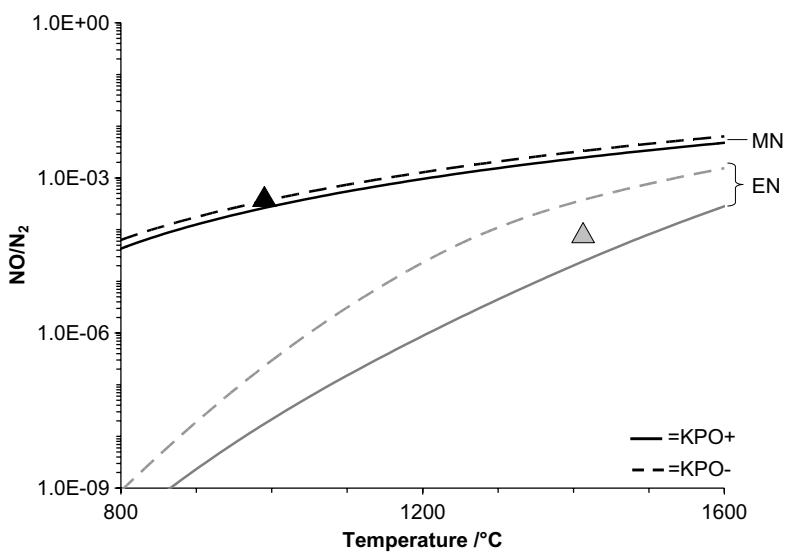

Fig. 5. Results for NO/N_2 in a high-T mixture of magmatic and atmospheric gases over the range $800 < T$ (°C) < 1600. Predictions for an early and modern Earth volcano are denoted by grey and black triangles, respectively.

estimates to be made despite uncertainties in the atmospheric composition. These flux estimates can be used to establish if volcanic emissions of NO and OH are significant relative to other sources e.g., photochemistry and lightning (Section 5).

4.2. Halogen chemistry

Volcanic halogen chemistry has been the focus of much research activity because of the involvement of halogen species with catalytic ozone depletion in the modern Earth's atmosphere (e.g., Bobrowski et al., 2007). The formation of high-T mixtures between magmatic and atmospheric gases was shown to be a plausible mechanism for the generation of oxidised halogen species such as Cl and Br; these species are thought to be oxidised downwind to form ClO and BrO (Gerlach, 2004).

Calculations were made to predict equilibrium X/HX (where X = halogen) at 1400 °C over the range $0.01 < V_A/V_M < 1$ for mixtures of atmospheric (EN, MN, CN, EC) and magmatic (KPO+) gas. Fig. 7 shows that X oxidation is insensitive to atmospheric CO_2 at 1400 °C below $V_A/V_M = 0.1$, as was found for N oxidation. The trend for X/HX of I > Br > Cl reflects the decreasing H–X bond strength. Calculations were also made for Cl/HCl and Br/HBr over the range $800 < T$ (°C) < 1600 for a $V_A/V_M = 0.1$ mixture of early (EN) and modern atmosphere (MN) with magmatic gas (Fig. 8). For the early atmosphere, the X/HX curves are a much stronger function of temperature due to increased importance of thermal

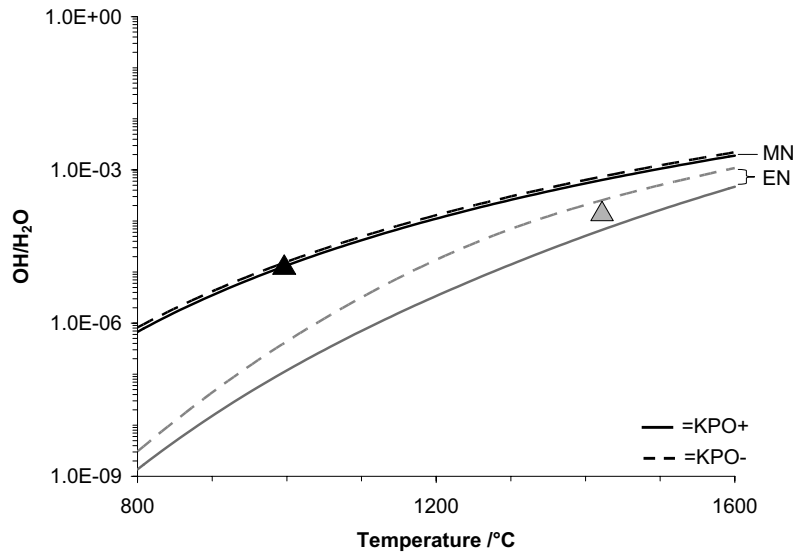

Fig. 6. Results for OH/H_2O in a high-T mixture of magmatic and atmospheric gases over the range $800 < T$ (°C) < 1600. Predictions for an early and modern Earth volcano are denoted by grey and black triangles, respectively.

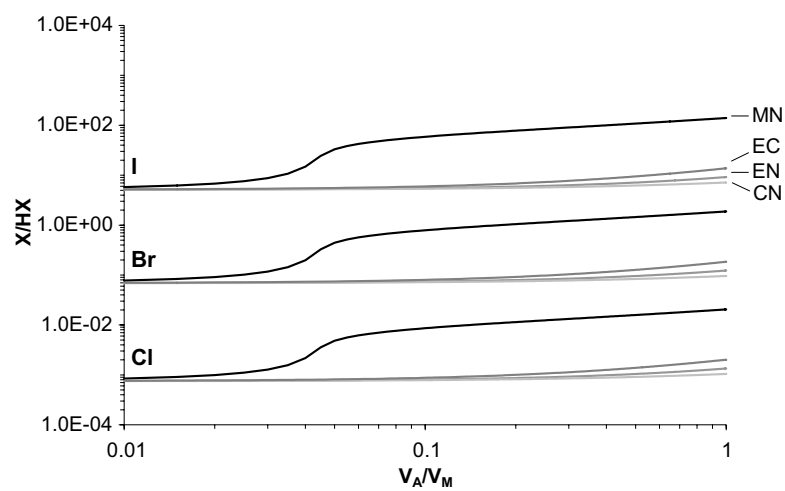

Fig. 7. Results for HX/X in mixtures of magmatic and atmospheric gases at 1400 °C over the range $0.01 < V_A/V_M < 1$.

dissociation ($HX \rightarrow H + X$) over oxidative dissociation ($HX + O \rightarrow HO + X$) under these conditions. Fig. 8 shows that an early Earth volcano emitting gas at 1400 °C may emit comparable amounts of reactive Br and Cl as a modern volcano which emits at 1000 °C.

4.3. Sulphur chemistry

An important component of the modern sulphur cycle is the inevitable oxidation of a high proportion of sulphur emissions to sulphate aerosols in the atmosphere. These emissions include industrial (SO_2), volcanic (H_2S and SO_2) and biogenic ($(CH_3)_2S$) sulphur (Wayne, 2000). In addition to these emissions, recent studies of near-source volcanic aerosols have measured particulate $SO_4^{2-}/SO_2 \sim 0.01$ (e.g., Mather et al., 2003). The mechanism for the formation of this near-source 'primary' volcanic sulphate is currently unknown, although thermodynamic modelling suggests that oxidation of SO_2 to SO_3 followed by reaction with water or direct emission from the melt are plausible routes to sulphate (Martin et al., 2006; Mather et al., 2006).

A much broader range of sulphur oxidation states are likely to have been stable in the pre-oxygenated atmosphere (Kasting, 2001) due to the absence of the levelling effect imposed by O_2. Farquhar et al. (2000) provide strong evidence for the timing of oxygenation of the early atmosphere from the existence of mass-independent S isotopic fractionation ($\Delta^{33}S \neq 0$) in early rocks (>2.45 Ga). A similar timing (2.32 Ga) was inferred by Bekker et al. (2004). The isotopic composition of S in oceanic sulphate before 2.45 Ga ($\Delta^{33}S < 0$) implies that the principal source of this sulphate was gas-phase photochemical oxidation of volcanic SO_2 in an oxygen poor atmosphere ($<10^{-5}$ present atmospheric levels) (Farquhar et al., 2000). The anomalous $\Delta^{33}S$ signature was then damped, with the rise of oxygen until ~2 Ga, after which mass-independent isotopic fractionation of S

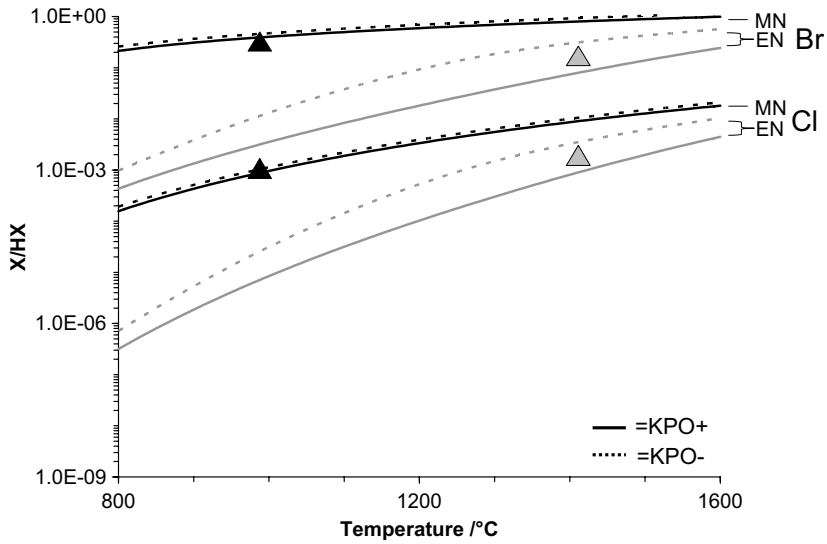

Fig. 8. Results for X/HX in a high-T mixture of magmatic and atmospheric gases over the range $800 < T\,(°C) < 1600$. Predictions for an early and modern Earth volcano are denoted by grey and black triangles, respectively.

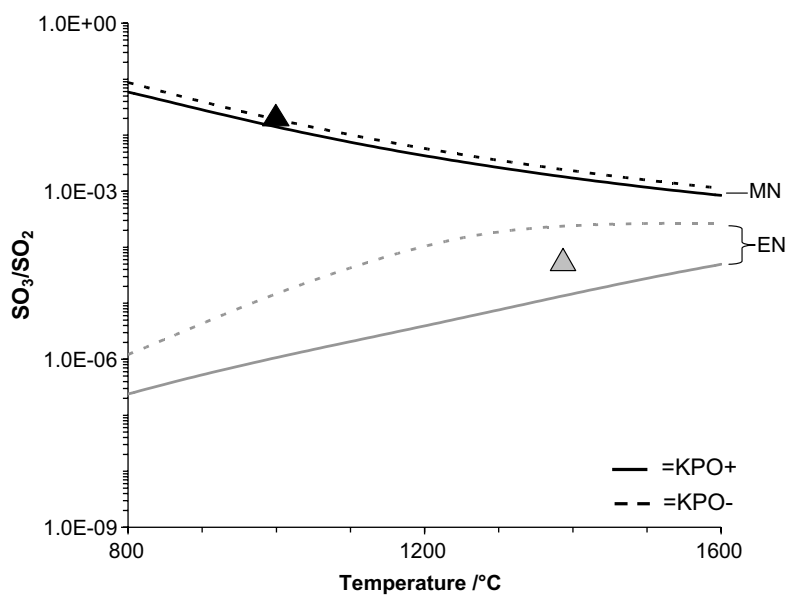

Fig. 9. Results for SO_3/SO_2 in a high-T mixture of magmatic and atmospheric gases over the range $800 < T\,(°C) < 1600$. Predictions for an early and modern Earth volcano are denoted by grey and black triangles, respectively.

was restricted to sulphur species processed in the stratosphere (Farquhar and Wing, 2003).

Studies of modern near-source volcanic sulphate have found no evidence for mass-independent fractionation of sulphur or oxygen isotopes (Mather et al., 2006). Therefore, a significant flux of near-source sulphate on the early Earth would have diluted the reservoir of mass-independent ($\Delta^{33}S \neq 0$) sulphate. Calculations were made to verify that SO_3/SO_2 is insensitive to atmospheric CO_2 and this was indeed found to be the case. The SO_3/SO_2 ratio was calculated over the range $800 < T\ (°C) < 1600$ to allow a comparison to be made between early and modern volcanism (Fig. 9). The increased temperature of early Earth magmatic gases was found to inhibit the formation of SO_3 and therefore the formation of SO_4^{2-} by reaction of SO_3 with water. Also, any direct emission of SO_4^{2-} may be expected to decrease with temperature (although by how much is uncertain) due to the increasing thermodynamic instability of metal sulphates with respect to metal oxides (Martin et al., 2006). Hence, we can predict that near-source volcanic sulphate ($\Delta^{33}S = 0$) would have made only a minor (<1%) contribution to total early Earth sulphate with the remainder derived from photochemical oxidation of SO_2.

4.4. Organic chemistry

The model presented here differs from the earlier model of Martin et al. (2006) in that the model includes organic species which are unstable in high-T O_2-rich mixtures. Calculations were made at 1400 °C for KPO+ magmatic gas and an atmospheric gas of 80% N_2, 15% CO_2 and 5% CH_4 over the range $0.01 < V_A/V_M < 1$. It was found that atmospheric CH_4 inhibits the formation of NO and other trace oxidised species but this effect is minor (i.e., <5% change in NO/N_2) over all reasonable mixture compositions ($0.01 < V_A/V_M < 1$). The corollary of this observation is that the inclusion of CH_4 only weakly reduces the mixture and so all organic species remain unstable over the range of V_A/V_M investigated. The extended thermodynamic model is found to gives similar results (i.e., agreement for all species which are predicted to form above ~1 ppb) as the optimised model of Martin et al. (2006) over the range of atmospheric compositions appropriate for early and modern Earth volcanism. The inclusion of organic compounds in the extended model is thus redundant, and the optimised model of Martin et al. (2006) can be used with confidence in future studies of volcanic emissions and the Earth's atmosphere.

5. ESTIMATES OF GLOBAL FLUXES FROM EARLY EARTH VOLCANISM

5.1. Methodology

Estimates of the global volcanic flux of OH, NO, Cl, Br, I and SO_3 are difficult to make as the total global volcanic gas flux is unknown. Therefore, we define the relative global flux, A, as the ratio between the amount of a specific gas released by early (F_E) and modern (F_M) Earth volcanism in units of mol year^{-1} (E2).

$$\text{(E2)} \quad A = \frac{F_E}{F_M}$$

Although the best constrained modern Earth volcanic flux is for SO_2, the concentration of SO_2 in volcanic gases is highly variable which complicates our analysis. Hence, we use the H_2O flux as the scaling basis and take F_M to equal 17 Tmol year^{-1} (Wallace, 2005). The temperature of emission was assumed to be uniformly distributed between $(T^* - 100)$ °C and $(T^* + 100)$ °C where T^* is taken as the mean temperature of emission. Calculations were then made by integrating X/H_2O over the required temperature interval to estimate global fluxes using (E3). These calculations assume a globally averaged distribution of magma temperatures; any geographical clustering of volcanoes with similar magma temperatures will lead to large variations in regional fluxes, and therefore of the volcanic influence on local atmospheric chemistry.

$$\text{(E3)} \quad f_X = \frac{F_E}{200}\int\left(\frac{X}{H_2O}\right)_T dT = \frac{AF_M}{200}\int\left(\frac{X}{H_2O}\right)_T dT$$

The estimated fluxes are sensitive to our choice of F_M, this is unavoidable but estimates of the H_2O flux range from 5 to 55 Tmol year^{-1} and so the chosen value is in the middle of this range. A is unit-less and can be calculated from any proxy of the total volcanic H_2O flux; this allows us to choose the best constrained measure for the extent of early Earth volcanism (relative to modern Earth volcanism) for use in flux calculations. It is thought that eruption rates in the early Earth probably exceeded that of the modern Earth by a factor of 10–100 (Courtillot and Renne, 2003; Heliker et al., 2003; Thordarson and Self, 2003); therefore $A \sim 10$ for typical early Earth volcanism and $A \sim 100$ during periods of enhanced volcanism (i.e., the emplacement of flood basalt provinces).

5.2. Results

Estimated fluxes of OH, NO, SO_3, Cl, Br and I were calculated using (R3) as a function of the relative global flux (A) and mean temperature (T^*) using model results for a $V_A/V_M = 0.1$ mixture of KPO+ magmatic gas and early Earth (EN) atmospheric gases; similar results would be obtained using EC or CN atmospheres and so our choice of atmosphere is not critical. Flux contours were calculated for each log unit of flux (mol X year^{-1}) and are shown in Fig. 10a–f. The authors suggest that the range $10 < A < 100$ and $1400 < T^*$ (°C) < 1600 is most appropriate for early Earth volcanism although calculations are made at lower T^* and A for completeness. The steepness of each flux contour indicates the temperature dependence of the emission flux, and hence, the temperature dependence of equilibrium. Calculations are also made the estimate the emission flux of these trace species from modern Earth volcanism using model results for a $V_A/V_M = 0.1$ mixture of KPO+ magmatic gas and modern Earth atmospheric gas (MN) at a mean temperature of 1000 °C; these flux estimates are plotted onto Fig. 10a–f as an additional contour.

Fig. 10 a shows that early Earth volcanism would generate between 10^9 mol NO year^{-1} (for $A \sim 10$, $T^* \sim 1400$ °C) to 10^{11} mol NO year^{-1} for more extensive, higher-T volcanism ($A \sim 100$, $T^* \sim 1600$ °C). This higher temperature corresponds to the eruption temperature of komatiite magmas (Nisbet et al., 1993; Herzberg et al., 2007). If similar limits are taken for other species, the predicted emissions fluxes are 10^{11}–10^{12} mol OH year^{-1}, 10^8–10^{10} mol Cl year^{-1}, 10^8–10^9 mol Br year^{-1} and 10^7–10^8 mol I year^{-1}. The limits on SO_3 are $\sim 10^9$–10^{10} mol SO_3 year^{-1}; reaction of SO_3 with H_2O in the plume may produce a similar flux of SO_4^{2-}. However, if SO_4^{2-} is emitted directly from the melt a significantly larger flux would be predicted, e.g., taking $H_2O/SO_2 \sim 4$ and $SO_4^{2-}/SO_2 \sim 0.01$ then the emission flux of SO_4^{2-} would be $\sim 10^{11}$–10^{12} mol year^{-1} (for $10 < A < 100$). This uncertainty in the formation of near-source volcanic sulphate in the early Earth may be resolved by further studies of modern volcanic emissions. All oxidised trace species investigated, with the exception of SO_3, are predicted to be emitted at greater rates by early Earth volcanism than modern Earth volcanism.

5.3. Comparison with other sources

5.3.1. Photochemical OH and HCN

Whilst the total luminosity of the ancient Sun was only ~0.8 of current luminosity (Zahnle and Walker, 1982), the extreme ultraviolet photon flux was considerably higher than at

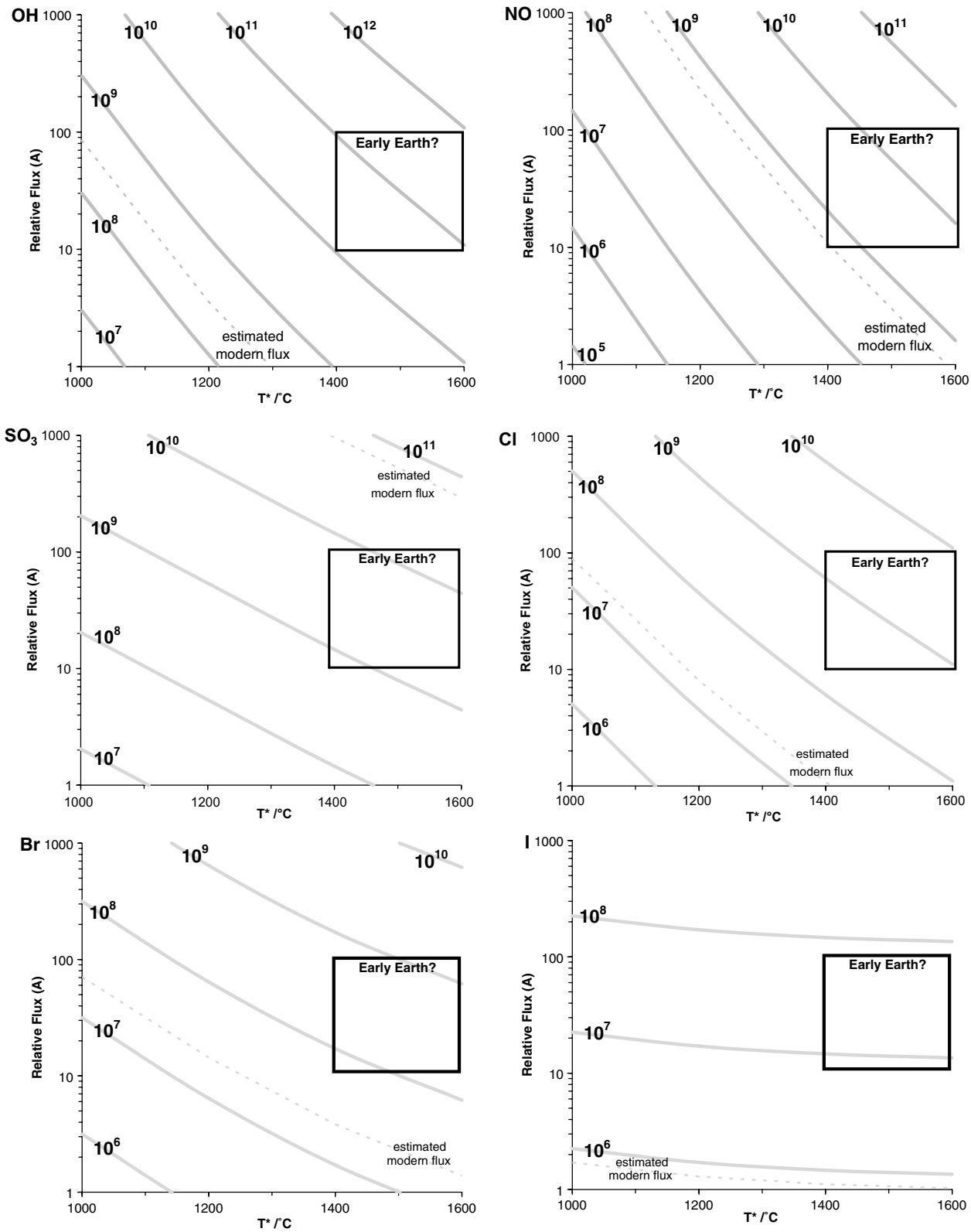

Fig. 10. Estimates of global volcanic fluxes (mol X year^{-1}) of different reactive species to the early Earth atmosphere, based the formation of a $V_A/V_M = 0.1$ mixture of atmospheric (EN) and magmatic (KPO+) gases, over a range of assumed mean temperatures (T^*). A is the ratio between the early Earth and modern Earth volcanic gas flux. The boxed region denotes the range the authors believe is appropriate for early Earth volcanism. An additional flux contour is given for the estimated modern flux to allow comparisons to be made.

present. Therefore, in the absence of atmospheric O_2 and O_3, high energy photochemistry would have had a considerable influence on the composition of the early Earth atmosphere.

Previous studies (Kasting et al., 1979) have shown that photolysis of H_2O was exceptionally efficient and capable of generating $\sim 3 \times 10^{12}$–3×10^{14} mol OH year^{-1}; this is greater than the maximum volcanic OH flux (e.g., at $A \sim 100$ and $T \sim 1600$, $\sim 1 \times 10^{12}$ mol OH year^{-1}). However, it must be remembered that volcanic emission of OH only occurs at low altitudes and is concentrated in the volcanic plume. Thus, whilst volcanic OH is quantitatively insignificant on a global scale, this source may be important for the low-T oxidation chemistry which occurs in the dilute plume (e.g., the oxidation of Br to BrO). We can also speculate that in the limit of poor vertical mixing, volcanic OH may be an important source of OH to the troposphere.

The importance of the photochemical production of reactive N is less clear (Kasting and Siefert, 2001; Navarro-González et al., 2001). It has been suggested that production of N atoms in the ionosphere (through photolysis of N_2) followed by reaction with CH_4 in the stratosphere leads to the production of photochemically stable HCN (Zahnle, 1986). HCN would then hydrolyze to release carboxylic acids and ammonium salts into the oceans. However, there are uncertainties in this hypothesis in that the estimated photochemical flux of HCN depends on the mixing ratio of atmospheric CH_4, the efficiency of vertical mixing in the early Earth atmosphere and the reactions (along with their rates) included in the photochemical model. Furthermore, Navarro-González et al. (2001) suggest that NH_3 may be a major photochemical intermediate; if true, rapid photolysis of NH_3 (Pavlov et al., 2001) followed by recombination of atomic N would lead to no net production of reactive N through photochemistry. Whilst the Zahnle (1986) mechanism in a CH_4-rich atmosphere has its proponents, the uncertainties are too large at present to conclusively assess the relative importance of volcanic NO and photochemical HCN in the early Earth.

5.3.2. Lightning NO

Navarro-González et al. (2001) predicts a lightning production rate of $\sim 3 \times 10^{10}$ mol NO year^{-1} decreasing to $\sim 3 \times 10^{8}$ mol NO year^{-1} as atmospheric CO_2 decreased over the Archean period. Our results show that for $A \sim 10$, the global in-vent NO flux for emissions with a mean temperature of 1400 °C ($\sim 5 \times 10^{8}$ mol NO year^{-1}) will exceed that produced from lightning for conditions of low atmospheric CO_2. For periods of more extensive ($A \sim 100$), higher temperature ($T^* \sim 1600$ °C) volcanism the global in-vent NO flux ($\sim 5 \times 10^{10}$ mol NO year^{-1}) will exceed the lightning NO flux even during periods of high atmospheric CO_2. Despite the uncertainties in volcanic activity during this period of Earth history, it may be suggested that the severity of any Archean nitrogen crisis would be limited by volcanic NO.

5.4. Comparison with previous estimates of early Earth volcanic NO flux

An alternative approach to estimating the volcanic NO flux was used by Mather et al. (2004b). In this earlier study, the total thermal energy released by a cooling lava was used to calculate the amount of NO produced based on an energy yield (in molecules NO J^{-1}) estimated with relation to experimental data presented in Navarro-González et al. (2001). This energy yield was taken as temperature independent between 927 and 1527 K to give NO flux estimates of $\sim 2 \times 10^{9}$ to $\sim 2 \times 10^{11}$ mol NO year^{-1} (for gases with CO_2 ~ 0.01 and CO_2 ~ 0.45) based on the eruption of komatiite lava at a rate of ~ 2 km^3 year^{-1}.

Our results show that the production of NO from volcanoes is less sensitive to the magmatic gas composition than implied in this previous study because other components of the magmatic gas (e.g., H_2O) also supply oxidants in the high-T mixture. Furthermore, as the thermal energy of a gas is approximately proportional to temperature (in Kelvin); an energy yield which is independent of temperature would require the production of NO to increase in a similar sense. Inspection of Fig. 5 shows that this is evidently not the case and the energy yield decreases significantly at lower temperatures where NO fixation becomes less efficient. Neglect of the temperature dependence of the energy yield would result in a slight over-estimation of early Earth volcanic NO fluxes by this earlier study.

5.5. Fluxes of H_2, H_2S, CO and S_2: implications for atmospheric redox state

(E3) allows the flux of the reduced gases (H_2, H_2S, CO and S_2) from early Earth volcanism to be estimated. Results are shown in Table 4 for $A \sim 10$ based on a $V_A/V_M = 0.1$ mixture of KPO+ magmatic gas and EN atmospheric gas. Our flux estimates for H_2 lie within the range predicted by Holland (2002); this earlier H_2 flux estimate was used by Tian et al. (2005b) to argue for a hydrogen-rich early Earth atmosphere. These reduced gases react with atmospheric O_2 and so the reduction potential (in units of mol O_2 year^{-1}) can be estimated by weighting each flux by the stoichiometric coefficients of the reaction with O_2. It can be seen that although higher-T volcanism leads to increased emission of H_2, this is very nearly balanced by a decrease in the emissions of H_2S and S_2 and so the change in reduction potential is minimal. In fact, as the atomic composition of the emissions remains fixed, summation of over all species

Table 4
Table of estimated fluxes from early Earth volcanism (at $A \sim 10$) of the major reduced gases (H_2, CO, H_2S) in units of mol year^{-1}

Species	v	1200 °C	1400 °C	1600 °C
H_2	0.5	2.4×10^{12}	2.9×10^{12}	2.9×10^{12}
CO	0.5	4.2×10^{11}	6.6×10^{11}	8.1×10^{11}
H_2S	1.5	2.2×10^{11}	4.6×10^{10}	7.6×10^{9}
S_2	2	1.0×10^{11}	1.7×10^{10}	2.0×10^{9}
Potential O_2 removal rate from atmosphere		2.0×10^{12}	1.9×10^{12}	1.9×10^{12}

The reduction potential is given in similar units. The stoichiometric coefficient, v, is calculated from the reactions of H_2, CO, H_2S and S_2 with O_2 to form the stable oxides H_2O, CO_2 and SO_2, respectively.

would reveal that the reduction potential of the emissions is wholly independent of temperature.

In this (thermodynamic) sense, the temperature and molecular composition of volcanic emissions have no bearing on the redox state of the atmosphere. However, the chemistry of the atmosphere is controlled by kinetic factors (e.g., Wayne, 2000) and under these conditions the redox state of the atmosphere may be sensitive to the molecular composition of volcanic emissions. For example, higher-T volcanism produces more H_2 and less H_2S than lower-T volcanism (Fig. 1); this may result in an increase in the oxidation state of the atmosphere if some fraction of H_2 can be lost to space before reaction with O_2 can occur. Also, if the chemical lifetime of H_2 were to exceed that of H_2S in the Archean atmosphere, higher-T volcanism may result in increased steady-state O_2 concentration compared to lower-T volcanism where the molar ratio H_2S/H_2 is predicted to be much greater. These conjectures may be tested with chemical kinetic models of the Archean atmosphere and our thermodynamic results may prove useful in this respect.

6. CONCLUSIONS

Although much uncertainty exists in our understanding of early Earth volcanism and atmospheric composition, thermodynamic modelling is able to offer estimates of the global production of trace species (NO, OH, SO_3, Cl, Br and I) from early Earth volcanism.

The model results show that thermal decomposition of magmatic H_2O, CO_2 and SO_2 in high-T mixtures of magmatic and atmospheric gases ($T > 1400$ °C) generate high levels of reactive radicals such as NO, OH, Cl and Br. The production of these species is insensitive to atmospheric CO_2 at $V_A/V_M < 0.1$ (i.e., in mixtures where the atmospheric gas is the minor component); production of these radicals will therefore continue during periods of low atmospheric CO_2.

Estimates of the fluxes of these species reveal that production of NO, OH, Cl, Br and I from early Earth volcanism exceeds production of these species from modern Earth volcanism. The increased temperature of early Earth volcanic emissions compensates for much lower levels of O_2 in the atmosphere, compared to the modern Earth. Our model also reveals that the uncertainty in the formation of near-source sulphate can lead to a large uncertainty in the amount of sulphate emitted into the early Earth atmosphere through passive degassing with consequent uncertainties with respect to the flux of primary particles from volcanoes to the early Earth atmosphere. Although a large flux of volcanic OH was estimated, this was found to be quantitatively smaller than the flux of OH produced through photolysis of H_2O in that atmosphere. However, volcanic OH may be important in the low-T chemistry occurring in the volcanic plume. Photochemistry may also generate large amounts of reactive N (in the form of HCN) which may prevent any Archean nitrogen crisis (due to decreasing lightning NO) from occurring; however, there are uncertainties in the rate at which HCN is formed which have yet to be resolved. In light of these uncertainties, this work makes the important finding that the Archean nitrogen crisis was less severe than previously suggested due to a significant flux of NO from volcanism and any reactive N produced by photochemistry would be additional to this.

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APPENDIX A

The list of gas-phase species used in the thermodynamic model:

Ar, Br, Br_2, BrBrO, BrCl, BrF, BrF_3, BrF_5, BrO, BrO_3, BrOBr, BrOO, C, C_2, C_2Cl, C_2Cl_2, C_2Cl_3, C_2Cl_4, C_2Cl_4O, C_2Cl_5, C_2Cl_6, C_2N, C_2N_2, C_2NO, C_2O, $C_2O_2Cl_2$, C_{60}, CCl, CCl_2, CCl_3, CCl_4, CH, CH_2, CH_2Cl, CH_2Cl_2, CH_2N_4, CH_2NO_2, CH_2O, CH_2OH, CH_3, CH_3Cl, CH_3NO_2, CH_3O, CH_3OH, CH_3ONO, CH_4, CH_4N_2O, CH_4N_2S, CH_4O_2, CH_4O_3S, CHCl,$CHCl_2$, $CHCl_3$, CHO, Cl, Cl_2, Cl_2O, Cl_3, Cl_4, ClClO, $ClClO_2$, ClF, ClF_3, ClF_5, ClO, ClO_2, ClO_3, ClO_3F, ClOCl. ClOClO, ClOO, CN, CN_2, CNCl, CNN, CO, CO_2, COCl, $COCl_2$, COOH, COS, CS, CS_2, F, F_2, FNO, FNO_2, FNO_3, FOO, H, H_2, H_2F_2, H_2O, H_2O_2, H_2S, H_2S_2, H_2SO_4, H_3F_3, H_4F_4, H_5F_5, H_6F_6, H_7F_7, HBr, HCCN, HCl, HClCO, HCN, HCO, HCOOH, HF, HI, HIO, HNCO, HNO, HNO_2, HNO_3, HO, HO_2, HOCl, HOCN, HOF, HS, HSO_3Cl, HSO_3F, I, I_2, IBr, ICl, IF, IF_5, IF7, IIO, IO, IO_3, N, N_2, N_2F_2, N_2F_4, N_2H_2, N_2H_4, N_2O, N_2O_3, N_2O_4, N_2O_5, N_3, N_3H, NBr, NCN, NCO, NF, NF_2, NF_3, NF_3O, NH, NH_2, NH_2F, NH_2NO_2, NH_2OH, NH_3, NHF, NHF_2, NO, NO_2, NO_2Cl, NO_2F, NO_3, NOBr, NOCl, NOF, NOF_3, NOI, NS, O, O_2, O_2F, O_3, OF_2, OSF_2, S, S_2, S_2Br_2, S_2Cl, S_2Cl_2, S_2F_{10}, S_2F_2, S_2O, S_3, S_4, S_5, S_6, S_7, S_8, SBr_2, $SBrF_5$, SCl, SCl_2, $SClF_5$, SF, SF_2, SF_3, SF_4, SF_5, SF_6, SN, SO, SO_2, SO_2Cl_2, SO_2ClF, SO_2F_2, SO_3, $SOCl_2$, SOF, SOF_2, SOF_4.

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