Oxidation State of Volcanic Gases and the Interior of Io

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We used thermochemical equilibrium calculations to constrain the oxygen fugacity (f_{O_2}) of volcanic gases on Io. Three types of calculations were done: (1) Upper limits for f_{O_2} from *Voyager* IRIS upper limits for the SO_3/SO_2 ratio and the O_3 abundance in the Loki volcanic plume; (2) lower limits for f_{O_2} from the observed SO/SO_2 ratio in Io's atmosphere; (3) oxygen fugacities as a function of temperature, total pressure, and O/S ratio for volcanic gases. We find that hot SO_2 (e.g., Loki volcanic gases) has oxygen fugacities between the Ni–NiO and hematite–magnetite oxygen fugacity buffers. Pele-type volcanic gases (i.e., SO_2–S_2 mixtures) have f_{O_2} values ranging from Ni–NiO to a few log f_{O_2} units lower. These f_{O_2} values are similar to those for most terrestrial volcanic gases and magmas. This coincidence indirectly indicates the predominantly silicate character of volcanism on Io. The oxidized nature of volcanic gases and their probable source magmas indicates that Io is differentiated and that metallic iron and free carbon are not present (or at least not abundant) in bulk silicate Io. This deduction agrees with the earlier inference from *Galileo* data of an iron core in Io. The inferred oxidation state of bulk silicate Io is plausibly due to loss of most of its initial water inventory via hydrogen escape and consequent oxidation of Fe and Fe^{2+}-bearing minerals to magnetite and other Fe^{3+}-bearing phases. Geochemical analyses of Io's surface and volcanic plumes, while difficult, are possible and can test our predictions. © 1999 Academic Press

Key Words: Io; volcanic gases; volcanism; oxidation state; oxygen fugacity; sulfur; lithosphere; mantle.

INTRODUCTION

The oxidation state and composition of outgassed volatiles on Earth is primarily governed by the iron oxidation state in the coexisting magmas (Gerlach 1993, Symonds *et al.* 1994). On Earth, the oxygen fugacity (f_{O_2}) of both acidic (i.e., SiO_2-rich) and basic (i.e., SiO_2-poor) magmas reflects the oxidation state of their respective source regions in the lithosphere and in the partially melted part of the upper mantle (asthenosphere) (Carmichael 1991).

This relationship could also be valid for Jupiter's moon Io which is the most volcanically active body of the Solar System. Io's volcanism is caused by tidal heating (Peale *et al.* 1979), and silicate magmas with temperatures of 1500–2000 K are observed (e.g., Blaney *et al.* 1995, Spencer *et al.* 1997b, McEwen *et al.* 1998). The composition of the magmas is presently unknown because Io's surface is generally covered by the S-bearing products of volcanic activity driven by SO_2 and sulfur gases (see Spencer and Schneider (1996) for a review). The intensive volcanic outgassing is ultimately responsible for the composition of Io's low-pressure patchy atmosphere and plasma torus (e.g., Lellouch 1996, Spencer and Schneider 1996). Here we use available data on the composition of a volcanic plume, the atmosphere, torus and surface, as well as observed temperatures of hot spots, to infer the oxygen fugacity of volcanic gases. These f_{O_2} values reflect the oxidation state of ionian magmas and Io's interior. We compare our calculations of Io's redox state with f_{O_2} values for terrestrial volcanic gases, and terrestrial and lunar igneous rocks. Finally, we discuss the oxidation state of Io's interior in terms of its composition and evolution.

COMPOSITION OF OUTGASSED VOLATILES ON IO

Sulfur dioxide is the only species definitively observed in volcanic gases on Io (Pearl *et al.* 1979). Spectroscopic upper limits for other gases, including sulfur vapor, are listed in Table I and indicate the predominance of SO_2 in the Loki plume. However, this one observation of the Loki plume is probably not representative of Io's volcanic gas chemistry. The variations of color and albedo features on Io's surface, the range of hot spot temperatures, and duration of eruptions indicate the existence of various types of volcanoes. *Galileo* observations in the visible range (Belton *et al.* 1996) show a "red" emission in the

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TABLE I

The Composition of the Loki Volcanic Plume and Io's Atmosphere

Gas	Pressure (bars)	Mole fraction
Loki plume[a]		
SO_2	$\sim 10^{-7}$	~ 1
SO_3	$<2 \times 10^{-11}$	$<2 \times 10^{-4}$
CO_2	$<5 \times 10^{-11}$	$<5 \times 10^{-4}$
H_2O	$<3 \times 10^{-9}$	$<3 \times 10^{-2}$
N_2O	$<2 \times 10^{-9}$	$<2 \times 10^{-2}$
O_3	$<5 \times 10^{-10}$	$<5 \times 10^{-3}$
COS	$<1 \times 10^{-10}$	$<1 \times 10^{-3}$
CS_2	$<2 \times 10^{-11}$	$<2 \times 10^{-4}$
S_n	$\sim 1 \times 10^{-9}$	$\sim 1 \times 10^{-2}$
H_2S	$<2 \times 10^{-8}$	<0.2
CH_4	$<3 \times 10^{-9}$	$<3 \times 10^{-2}$
NH_3	$<4 \times 10^{-10}$	$<4 \times 10^{-3}$
Io's atmosphere[b]		
SO_2	$\sim 10^{-9}$	0.9–0.97
SO	$3\text{--}10 \times 10^{-11}$	0.03–0.1
CO	$<3 \times 10^{-9}$	—
H_2S	$<10^{-10}$	—

[a] Calculated from Pearl *et al.* (1979) using $SO_2 = 0.2$ cm amagat and using averages of the upper limits they tabulate, except for S_2 from Pearl (1985).
[b] Lellouch *et al.* (1992) and Lellouch (1996).

eruptive plume of Ra Patera which might be caused by S-rich condensates or pyroclastics. This corresponds to possible sulfur lava flows suggested for this volcano (Pieri *et al.* 1984). McEwen and Soderblom (1983) suggested two major types of volcanic plumes on Io: Prometheus-type plumes with relatively low temperatures that are driven by SO_2, and Pele-type plumes characterized by high temperatures and short explosions that are driven by sulfur. Intermediate types of volcanoes probably exist also. In particular, observations of SO_2 around the Pele volcano (Sartoretti *et al.* 1994) indicate that it could be driven by a S_2–SO_2 mixture.

Io's low-pressure ($\sim 10^{-9}$ bars) patchy atmosphere is at least partially due to ongoing volcanic degassing (Lellouch 1996, Spencer and Schneider 1996). Sulfur dioxide and SO are the two gases detected definitively in the atmosphere (Lellouch *et al.* 1992, 1996; Ballester *et al.* 1994; Trafton *et al.* 1996). Atmospheric SO has an abundance of 3–10 vol.% (Lellouch *et al.* 1996) and could be produced photochemically (e.g., Kumar 1982, Summers and Strobel 1996, Wong and Johnson 1996) and volcanically (Zolotov and Fegley 1998a). If atmospheric SO is predominantly photochemical, volcanic gases might be more SO_2 rich than the atmosphere with an O/S atomic ratio ~ 2. Conversely, if atmospheric SO is predominantly volcanic, the O/S ratio in volcanic gases could be 1.90–1.97 (i.e., $SO_2 + 3 - 10\%$ SO).

The composition of Io's extended atmosphere and plasma torus also provides data on the composition of outgassed volatiles. The species in the torus are supplied from eruption of vol-

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canic plumes, escape of atmospheric gases, and sputtering from the surface (Spencer and Schneider 1996). Oxygen and sulfur are the most abundant elements in the torus. The O/S atomic ratio in the torus generally varies from 0.6 to 1.3 (e.g., Shemansky 1987, Moos *et al.* 1991). The maximum observed O/S ratio for the torus is ~ 2 (Hall *et al.* 1994). The variations in torus composition obtained by various instruments since the *Voyager* era could plausibly reflect temporal changes of outgassed volatiles.

Io's surface consists of volcanic condensates, pyroclastic deposits, and lava flows. Only sulfur dioxide frost has been detected definitively on the surface (e.g., Smythe *et al.* 1979, Fanale *et al.* 1979). The SO_2 frost was formed by condensation of volcanic gases. Other possible constituents of Io's surface include various types of elemental sulfur, sulfur oxides, and sulfates (Spencer and Schneider 1996). Some of these compounds could also be volcanic condensates. The surface O/S ratio varies from ~ 2, which corresponds to pure SO_2 frost covering 30–60% of the surface (McEwen *et al.* 1988, Sartoretti *et al.* 1996), to $<\sim 0.5$, which corresponds to the solid S_2O and sulfur deposits plausibly present around the Pele volcano and in some other places (Spencer *et al.* 1997a).

In general, all available data indicate that the composition of volcanic gases on Io probably varies from pure sulfur vapor to almost pure SO_2 (O/S of 0–2). Volcanic gases with O/S ratios >2 (i.e., SO_2–O_2 mixtures) appear implausible, but cannot be definitively ruled out.

THERMOCHEMICAL EQUILIBRIUM CALCULATIONS

We assume thermochemical equilibrium in the high-temperature volcanic gas in a volcanic conduit (Fig. 1). This is a reasonable assumption, because terrestrial volcanic gases approach closely a state of chemical equilibrium (Symonds *et al.*
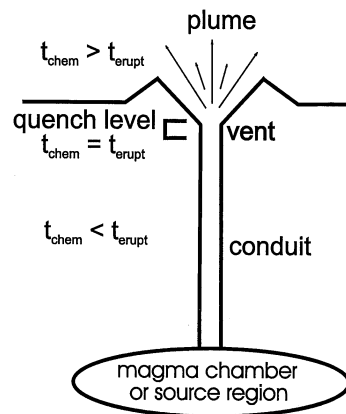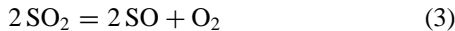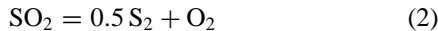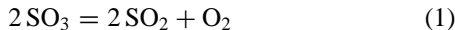

FIG. 1. A cartoon illustrating the model for volcanic gas chemistry on Io. Volcanic gases reach chemical equilibrium at higher temperatures and pressures where the characteristic chemical reaction time (t_{chem}) is less than the characteristic cooling time during the volcanic eruption (t_{erupt}). Volcanic gases do not reach chemical equilibrium at lower temperatures and pressures in the plume where $t_{chem} > t_{erupt}$. In between these two regions, in the vicinity of the vent, $t_{chem} = t_{erupt}$ and quenching of the high-temperature equilibria occurs. See Zolotov and Fegley (1998a) for details.

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1994). However, the supersonic volcanic gas eruptions on Io quench the gas chemistry in the vent vicinity. This is discussed by Zolotov and Fegley (1998a), who present thermochemical kinetic calculations, showing that Ionian volcanic gases are in equilibrium until quenched at the vent.

Thermochemical equilibrium calculations were done from 1000–2000 K, which covers the maximum observed temperatures of hot spots (~2000 K) and suggested temperature of the magma (e.g., McEwen *et al.* 1998). The pressure of Io's volcanic vents is unknown, and following our prior work (Zolotov and Fegley 1998a,b), we consider a wide range (10^{-8}–100 bars). Different types of volcanic vents could have pressures in this range. Interactions of subsurface volatiles with silicate magma could lead to low-pressure gas emanations, but only relatively high gas pressures would provide the observed explosive activity. Vent pressures of ~1–100 bars seem to be more likely on Io. The pressures in erupted plumes are much lower. However, we are modeling gas chemistry in the volcanic conduit, not in the erupted plume after cooling, expansion, and quenching have occurred. All thermodynamic data used in the calculations are taken from Gurvich *et al.* (1989–1994).

Three sets of calculations were done. In the first and second sets, we used measured abundances and upper limits for the Loki plume and Io's atmosphere to calculate f_{O_2} from the net thermochemical reactions

$$2\,SO_3 = 2\,SO_2 + O_2 \qquad (1)$$

$$SO_2 = 0.5\,S_2 + O_2 \qquad (2)$$

$$2\,SO_2 = 2\,SO + O_2 \qquad (3)$$

$$2\,O_3 = 3\,O_2. \qquad (4)$$

The equilibrium oxygen fugacities for reactions (1) to (4) are given by

$$f_{O_2} = K_1 \left(\frac{X_{SO_3}}{X_{SO_2}} \right)^2 \qquad (5)$$

$$f_{O_2} = K_2 \left(\frac{X_{SO_2} P_T^{1/2}}{X_{S_2}^{1/2}} \right) \qquad (6)$$

$$f_{O_2} = K_3 \left(\frac{X_{SO_2}}{X_{SO}} \right)^2 \qquad (7)$$

$$f_{O_2} = \left(K_4 X_{O_3}^2 P_T^2 \right)^{1/3}, \qquad (8)$$

where K_1–K_4 are the equilibrium constants for reactions (1)–(4), X_i is the mixing ratio of gas i (from Table I), and P_T is the total pressure. The gases behave ideally at the temperatures and pressures considered. The f_{O_2} is independent of total pressure for reactions (1) and (3), but dependent on total pressure for reactions (2) and (4). In principle, the upper limits for other gases in the Loki plume (see Table I) could also be used to calculate limits on f_{O_2}. However, these calculations require knowledge of one or more (unknown) gas abundances (e.g., H_2, H_2O, CO). Thus, we did not consider other reactions in this set of calculations.

In the third set of calculations, we used the free energy minimization method (Van Zeggeren and Storey 1970) to calculate the f_{O_2} for the S–O system as a function of elemental bulk composition, temperature, and total pressure. We varied the O/S atomic ratio from 10^{-7} to 3. This range covers the bulk composition of Io's atmosphere, torus, and surface.

We compare the calculated oxygen fugacity from these three sets of calculations with the f_{O_2} values for several important mineral oxygen buffers of petrologic interest. Table II lists these buffers along with the temperature-dependent f_{O_2} values. We also considered the sodium sulfide–sodium sulfate (NNS) buffer, proposed for Io by Burnett (1995).

RESULTS

Upper Limits on f_{O_2} from Loki Plume Observations

Reactions (1), (2), and (4) were used for these calculations. The thermal decomposition of ozone (reaction 4) gives large upper limits for the f_{O_2} of the Loki plume ($f_{O_2} \gg 1$ bar) for all temperatures (1000–2000 K) and pressures (10^{-4} to 100 bars) considered. These upper limits on f_{O_2} are too high to give petrologically useful constraints. The spectroscopic upper limit for O_3 from Pearl *et al.* (1979) is probably orders of magnitude higher

TABLE II
Mineral Buffers of Oxygen Fugacity[a]

	Buffer	Equation	$\log_{10} f_{O_2} = A - B/T$		T range (K)
			A	B	
MH	Magnetite–hematite	$6\,Fe_2O_3 = 4\,Fe_3O_4 + O_2$	13.810	25,290	1000–1800
NNO	Nickel metal–nickel oxide	$2\,NiO = 2\,Ni + O_2$	8.716	24,300	1000–1728
QFM	Quartz-fayalite–magnetite	$2\,Fe_3O_4 + 3\,SiO_2 = 3\,Fe_2SiO_4 + O_2$	8.912	25,160	1000–1490
NNS	Sodium sulfate–sodium sulfide	$0.5\,Na_2SO_4 = 0.5\,Na_2S + O_2$	8.404	26,183	1000–1155
WM	Wüstite–magnetite	$2.4036\,Fe_3O_4 = 7.6142\,Fe_{0.947}O + O_2$	12.080	32,040	1000–1652
IW	Iron metal–wüstite	$2\,Fe_{0.947}O = 1.894\,Fe + O_2$	6.840	27,670	1000–1652

[a] The f_{O_2} data are calculated from thermodynamic data from Chase (1998) for Na_2S, and Robie and Hemingway (1995) for other substances.

than the actual O_3 abundance in the plume. For all practical purposes, the Loki plume does not contain any ozone.

Reaction (1), the thermal decomposition of SO_3, gives more reasonable upper limits for the f_{O_2} of Loki volcanic gases. These are plotted in Fig. 2a, and range from $<10^{-5}$ (1340 K) to $<10^{-7.5}$ bars (1000 K). These f_{O_2} values are less oxidizing than the MH buffer at temperatures above 1340 K. However, the upper limit on f_{O_2} from reaction (1) is still several orders of magnitude more oxidizing than the Ni–NiO (NNO) and QFM buffers.

We also evaluated f_{O_2} for the Loki gases based on the S_2/SO_2 ratio of ~0.01 reported by Pearl (1985) for that plume. These calculations were made using Eq. (6) at total pressures ranging from 10^{-4} to 100 bars. Higher total pressure leads to higher oxygen fugacities. The results in Fig. 2a show that the calculated f_{O_2} values are roughly around the NNO, QFM, and WM oxygen buffers depending on the assumed total pressure and temperature in the vent. At pressures of 1–100 bars and temperatures below 1400 K, the calculated f_{O_2} values lie between the MH and NNO buffers. At temperatures above 1400 K and similar pressures, the redox conditions are around the NNO buffer. These calculations show that the f_{O_2} in Loki volcanic gases and parental magmas could be slightly more oxidized than NNO and probably not more reduced than QFM. These conditions are definitely more oxidized than the IW buffer (i.e., Fe metal is unstable), and also indicate that sodium sulfates are more stable than sodium sulfides in the Loki source region.

Upper Limits on f_{O_2} from the Atmospheric SO and SO_2 Abundances

The oxygen fugacity calculated from the atmospheric SO and SO_2 abundances by Eq. (7) is shown in Fig. 2b. If the SO/SO_2 ratio in the atmosphere is simply that of a quenched volcanic gas, the calculated f_{O_2} values match those in the volcanic gas. However, if part of the atmospheric SO is produced photochemically, the calculated f_{O_2} values are only lower limits, as shown in the graph. A SO/SO_2 ratio of 3% gives f_{O_2} values about one order of magnitude more oxidized than a SO/SO_2 ratio of 10%. Both these lower limits for f_{O_2} lie above the IW buffer and about 2–4 log units below the NNO buffer. Even if all atmospheric SO is of volcanic origin, the redox conditions of volcanic gases are more oxidized than the IW buffer.

Oxygen Fugacity in the O–S System

SO_2 thermal dissociation. Sulfur dioxide decomposes predominantly to SO, SO_3, and O_2 depending on the temperature (Fig. 3a) and total pressure. Figure 3b shows that the calculated f_{O_2} is generally between the MH and NNO buffers at temperatures of 1100–1600 K and pressures of 10^{-4} to 100 bar. Oxygen fugacity decreases with decreasing total pressure and with decreasing temperature. However, the f_{O_2} for SO_2 dissociation decreases less steeply with decreasing temperatures than the f_{O_2} for mineral buffers. Thus, low temperatures provide more ox-
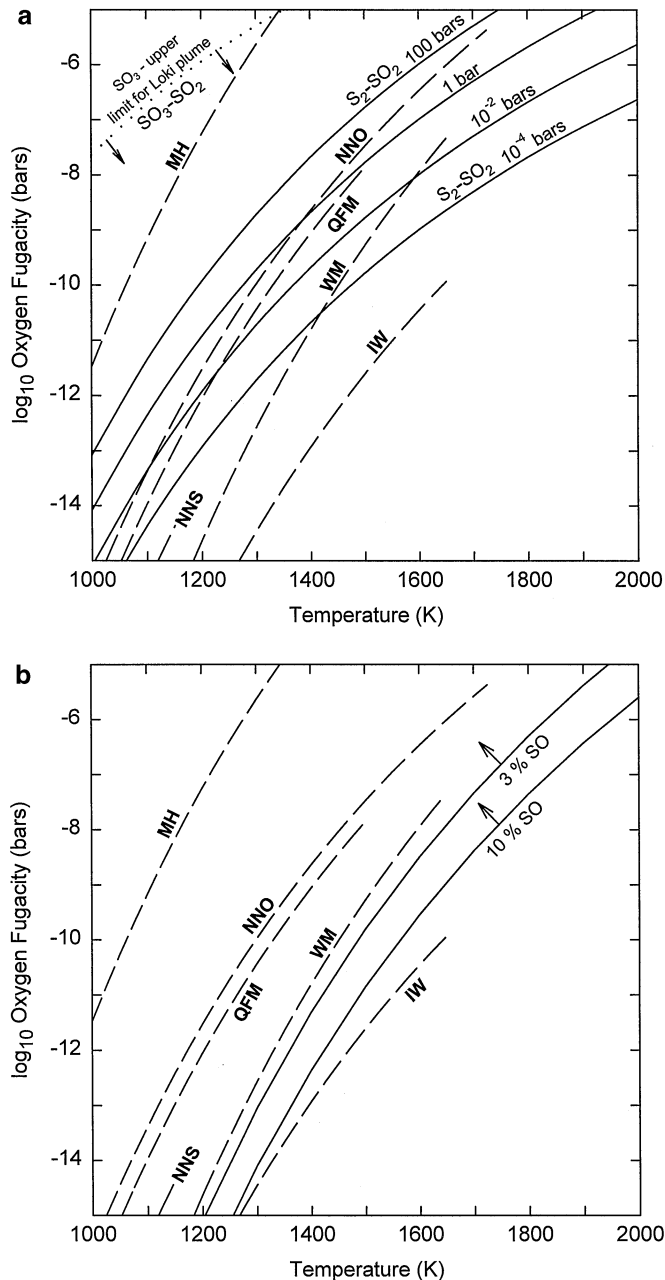

FIG. 2. Calculated oxygen fugacities (f_{O_2}) of volcanic gases are compared to the oxygen fugacities of important mineral buffers. The mineral buffers plotted in these and subsequent graphs are explained in Table II. (a) The f_{O_2} values (upper limits) calculated from reaction (1) (SO_3, dotted line) and reaction (2) (S_2, solid lines) are compared to the mineral buffer f_{O_2} curves. The f_{O_2} for reaction (2) is pressure dependent; values for 100, 1, 0.01, and 10^{-4} bars pressure are shown. (b) The f_{O_2} values (lower limits) calculated from reaction (3) and atmospheric SO/SO_2 ratios of 3% and 10% (Lellouch *et al.* 1996) are compared to the mineral buffer f_{O_2} curves.

idizing conditions relative to the oxygen buffers. The thermal dissociation of pure SO_2 generates oxidizing conditions, but the f_{O_2} does not exceed that for the MH buffer for high-temperature (>1150 K) gases.
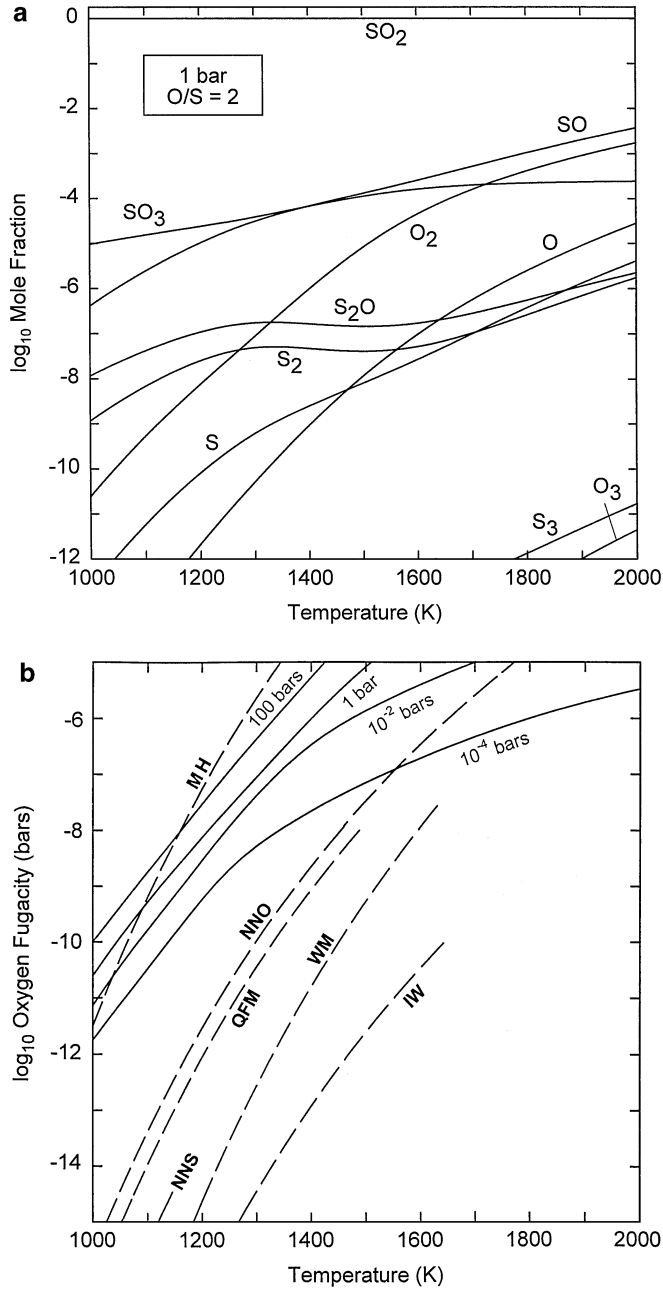
of bulk composition and total pressure at typical temperatures for basaltic magma (1400 K) and ultramafic (e.g., komatiitic) magma (1800 K). In Fig. 4a, the oxygen fugacity increases with increasing O/S ratio at constant total pressure, and changes gradually at O/S ratios of ~ 0.2–1.8. Sharp changes of f_{O_2} are observed near O/S ~ 2 (i.e., SO_2-rich compositions). Small deviations from SO_2 stoichiometry lead to large changes of f_{O_2},

FIG. 3. (a) Chemical equilibrium abundances in pure SO_2 volcanic gas as a function of temperature (1000–2000 K) at one bar total pressure. (b) The f_{O_2} in pure SO_2 volcanic gas at four different total pressures is compared to mineral buffer f_{O_2} curves.

Influence of bulk composition, temperature, and pressure. We calculated f_{O_2} for O/S ratios ranging from ~ 0 to 3. The end-members correspond to sulfur vapor (O/S $= 0$) and SO_3 (O/S $= 3$). Intermediate ratios can be thought of as mixtures of sulfur vapor and SO_2 (O/S from 0–2) and of SO_2 and O_2 (O/S of 2–3). We model various volcanic gas compositions in this range which might be emitted by the different types of Ionian volcanoes. Figure 4 shows the calculated f_{O_2} values as a function
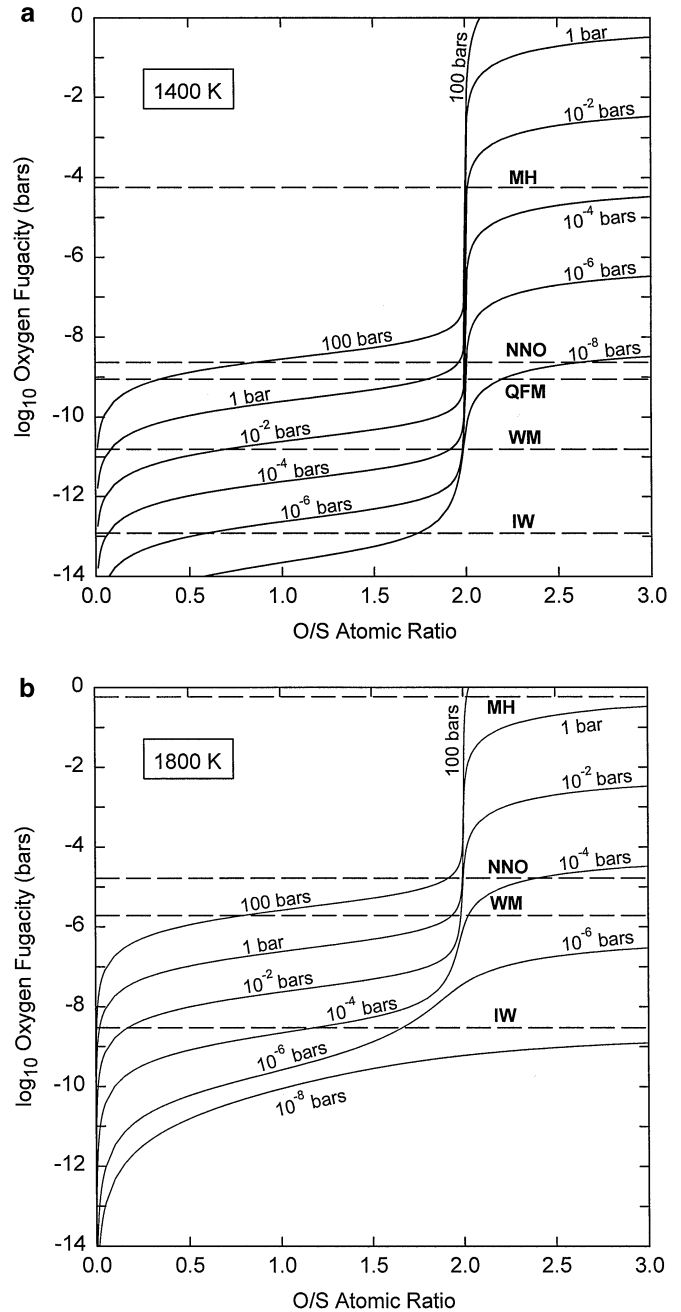
FIG. 4. The oxygen fugacity in ionian volcanic gases as a function of bulk composition (O/S ratio) at different total pressures at 1400 K (a) and 1800 K (b), typical temperatures for basaltic and ultramafic magmas, respectively. The dashed horizontal lines show the mineral f_{O_2} buffers.

but f_{O_2} again changes gradually at O/S ratios of ~2.1–3.0. At 1400 K, vent pressures of 1–100 bars, and O/S $\sim$ 0.3–1.7, the calculated oxygen fugacities correspond to $f_{O_2} = 10^{-9(\pm1)}$, which is in the range of the NNO and QFM buffers. An O/S ratio of 0.3–0.5 appropriate for solid S_2O and pyroclastic deposits around Pele (Spencer *et al.* 1997a, Zolotov and Fegley 1998b) provides an f_{O_2} value about one log unit lower than the QFM buffer at ~1 bar.

The f_{O_2} curves are smoother at higher temperatures and lower pressures (Fig. 4b). The higher temperature volcanic gases are also more reducing than those at lower temperatures. For example, Fig. 4b illustrates that f_{O_2} values are around the WM buffer for volcanic gases with O/S ratios of about 0.3 to 1.7 at vent pressures of 1–100 bars. Nevertheless, these f_{O_2} values are still more oxidizing than the IW buffer.

Figures 4a and 4b show that volcanic gases on Io become more reducing if they are erupted at very low pressures. For example, volcanic gases erupted at 1800 K may be as reducing as, or even more reducing than, the IW buffer if volcanic vent pressures are only 10^{-4} to 10^{-8} bars. The role of any such high-temperature and low-pressure vents on Io is unclear, but such low-pressures are unable to produce the observed explosive eruptions. Thus, our calculations show that two classes of volcanoes may potentially exist: more oxidized, higher pressure vents and more reduced, lower pressure vents. However, both basaltic and ultramafic volcanic gases are predicted to be fairly oxidized if they are erupted at pressures of about 10^{-2} bars and greater.

Figure 5 shows the calculated oxygen fugacity as a function of temperature and bulk composition at a total pressure of 1 bar. The oxygen fugacity increases with increasing temperature and
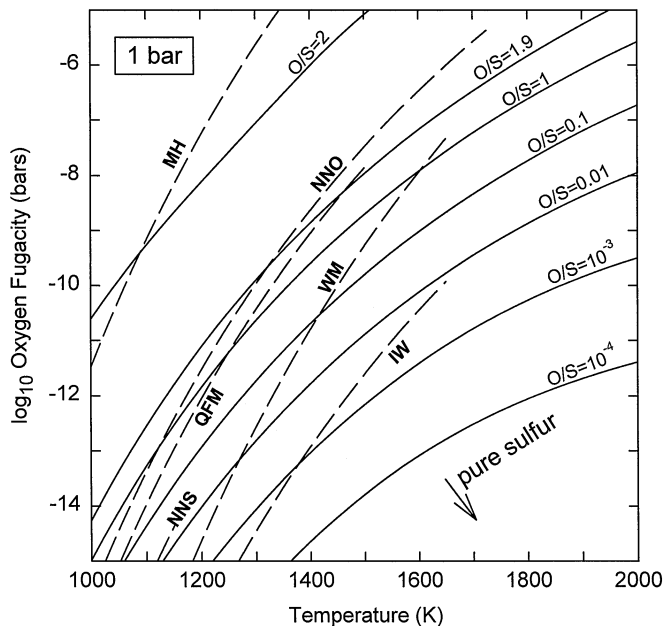

FIG. 5. The oxygen fugacity in ionian volcanic gases as a function of temperature and bulk composition (O/S ratio) at a total pressure of one bar. The dashed lines show the mineral buffer f_{O_2} curves.

O/S ratio. The compositions enriched in SO_2 (O/S from 1.9 to 2) have an oxidation state around the NNO and MH buffers. Sulfur-enriched compositions (O/S < 0.01–10^{-4}) give conditions more reducing than the WM and IW buffers, depending on temperature. The f_{O_2} values for S–O gases change more gradually with increasing temperature than f_{O_2} values for the oxygen buffers. This is the same behavior discussed above for pure SO_2. For example, at O/S = 1, the f_{O_2} values are more oxidized than NNO below 1120 K, lie between NNO and QFM at 1120–1240 K, and become more reduced than QFM at higher temperatures. Bulk compositions of O/S $\sim$ 1–1.9 and hot-spot temperatures (below 1500 K) match the f_{O_2} values for the NNO and QFM buffers.

Oxygen Fugacity in Fumarolic Gases

Volcanic gases that are emitted without eruption of magma are called fumarolic gases. Terrestrial data indicate that homogeneous gas phase reactions are important during cooling of fumarolic gases from ~1070 to 870 K (e.g., Taran *et al.* 1995). Some of these reactions continue to temperatures as low as ~600 K before quenching (Giggenbach 1987, Taran 1992). In other words, the chemical evolution of fumarole gases can be modeled by ignoring chemical interaction of the gas with the surrounding rocks. Here we apply this model to calculate equilibrium f_{O_2} for cooling ionian fumarole gases before their release onto the surface (where gas chemistry definitely quenches). As in previous calculations, f_{O_2} is calculated for thermochemical gaseous equilibrium in the S–O system. Figure 6 qualitatively demonstrates that f_{O_2} decreases with decreasing temperature and pressure of the gas. However, the evolution of f_{O_2} during cooling of fumarolic gases is not necessarily parallel to the f_{O_2} lines for the mineral buffers. Therefore, we should expect some redox reactions in fumarolic gases on Io as observed for fumarolic gases on Earth (Giggenbach 1987, Taran *et al.* 1995).

We used an adiabatic model for cooling of the gas after emission from a magma chamber. No heat exchange with the surroundings occurs during adiabatic cooling, so this model is relevant to hot, productive fumaroles. We calculated adiabatic gas expansion using Eq. (26a) from Kieffer (1982) with γ of 1.29. The gas has initial temperatures of 1400 or 2000 K at an initial pressure of 100 bars. We calculated f_{O_2} for the cooling gas and our results are shown in Figs. 6 and 7. The arrows in these figures show the direction of gas cooling and expansion. Comparison of these evolutionary lines with the positions of oxygen buffers indicates the potential for gas oxidation during the expansion. For example, the f_{O_2} evolution line for O/S = 1 intersects the NNO buffer at ~1280 K and ~13 bars and provides more oxidizing conditions than NNO at lower temperatures. These results show that internal oxidation of fumarolic gas might be partially responsible for the oxidation of Io's crust.

The Influence of Oxygen Fugacity on Abundances of Sulfur Gases

The mass fraction of volatiles in terrestrial silicate magmas typically do not exceed a few mass percent (Johnson *et al.* 1994)
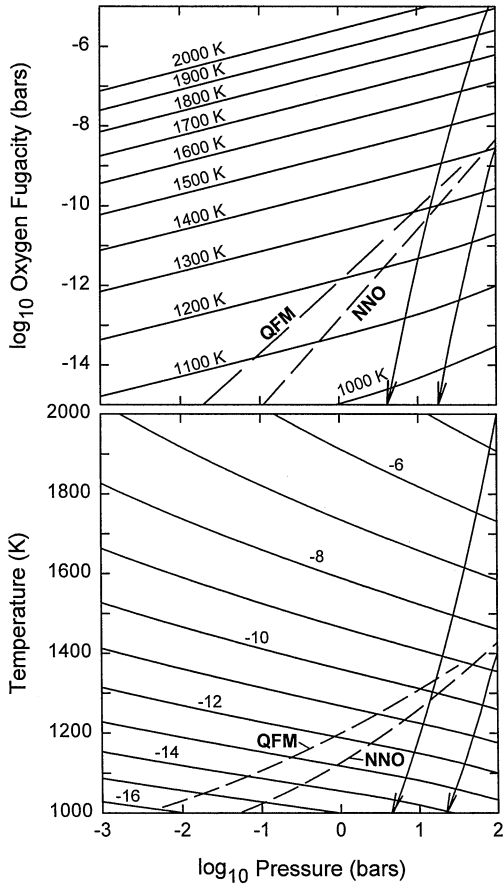
units lower than QFM. (Essentially pure SO_2 with trace S_2 or pure S_2 with trace SO_2 are generated at higher or lower f_{O_2} values, respectively.) It is interesting that this narrow f_{O_2} range also provides the maximum abundances for S_2O and SO, which are expected constituents of volcanic gases on Io (Spencer *et al.* 1997a, Zolotov and Fegley 1998a,b). In general, Fig. 8 demonstrates that changes in the SO_2/S_2 (or O/S) ratios in volcanic gases on Io could be due to variations of the redox states of their parental magmas. At 1400 K, a typical temperature of basaltic magma, plausible variations in gas chemistry could arise from f_{O_2} values ranging from NNO to about 2.5 log units lower.

The effect of temperature on abundances of gases at the f_{O_2} of the QFM buffer is displayed in Fig. 9. Sulfur dioxide is the most abundant gas at the temperature of basaltic magma ($\sim$1400 K) and at higher temperatures. The abundance of SO_2 decreases gradually as temperature decreases. Sulfur vapor (S–S_8) becomes more abundant with decreasing temperature. The S_2O abundance is relatively independent of the temperature, while SO formation is favored by high temperature, as we have discussed previously (Zolotov and Fegley 1998a,b).

DISCUSSION

Oxygen fugacity values inferred for ionian volcanic gases generally match the values for terrestrial volcanic gases, which
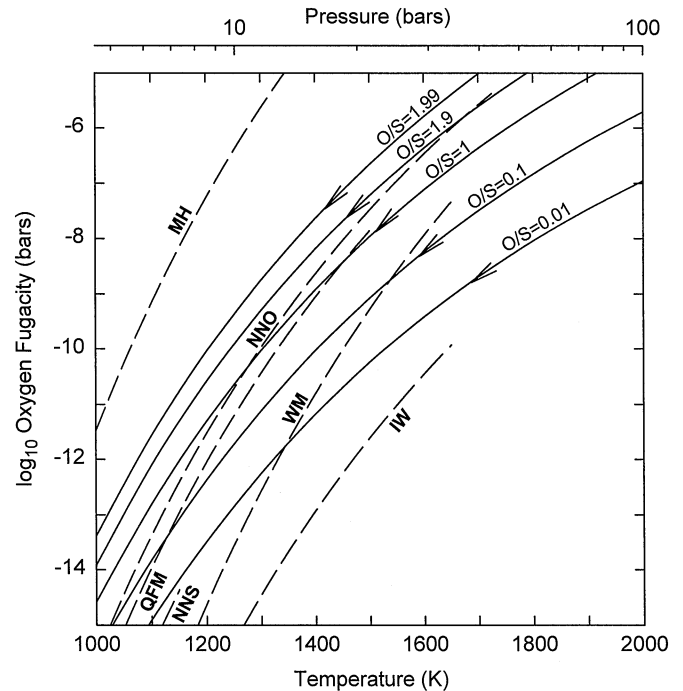
FIG. 6. Oxygen fugacity for a volcanic gas with O/S = 1 as a function of temperature and total pressure. The arrows show the adiabatic cooling paths for volcanic gases initially at 1400 or 2000 K and 100 bars and are described in the text.

and magma/gas mass ratios are generally high (>9) in the vent before the eruption (Wilson *et al.* 1987). Thus, the f_{O_2} of the volcanic gas bubbles in the magma is controlled by the redox state of the surrounding magma (Gerlach 1993, Symonds *et al.* 1994, Taran *et al.* 1995). The oxidation state of the host magma is an important factor in controlling the abundances of species in the volcanic gas. Conversely, the f_{O_2} and speciation of the volcanic gas reflects the redox state and mineralogy of the magma source region. Figure 8 shows the equilibrium abundances of volcanic gases in the S–O system as a function of oxygen fugacity at 1400 K and 1 bar total pressure. Sulfur-dioxide-rich gases are produced under conditions more oxidizing than the QFM and NNO buffers. The amount of SO_3 increases and the amount of SO decreases as the gas becomes more oxidizing. The sulfur gases (S_n) are unimportant constituents of volcanic gases more oxidized than NNO. The reduced conditions around the IW and WM buffers yield gases which are enriched in S_2, S_3, and S_2O. The SO_2–S_2 mixtures of intermediate composition, which plausibly represent an average volcanic gas on Io, could be formed only in a narrow f_{O_2} interval. At 1 bar and 1400 K, SO_2–S_2 gases are generated from QFM to an f_{O_2} about 1.5 log

FIG. 7. The evolution of f_{O_2} in ionian fumarolic gases during adiabatic cooling from 2000 K and 100 bars. Results are shown for O/S ratios ranging from 0.01 (i.e., S_2-rich gas) to 1.99 (i.e., SO_2-rich gas). The f_{O_2} of the cooling fumarolic gas decreases less steeply with decreasing temperature than the f_{O_2} of the mineral buffer curves. Hence during cooling, the gases become more oxidized relative to a mineral buffer such as QFM.
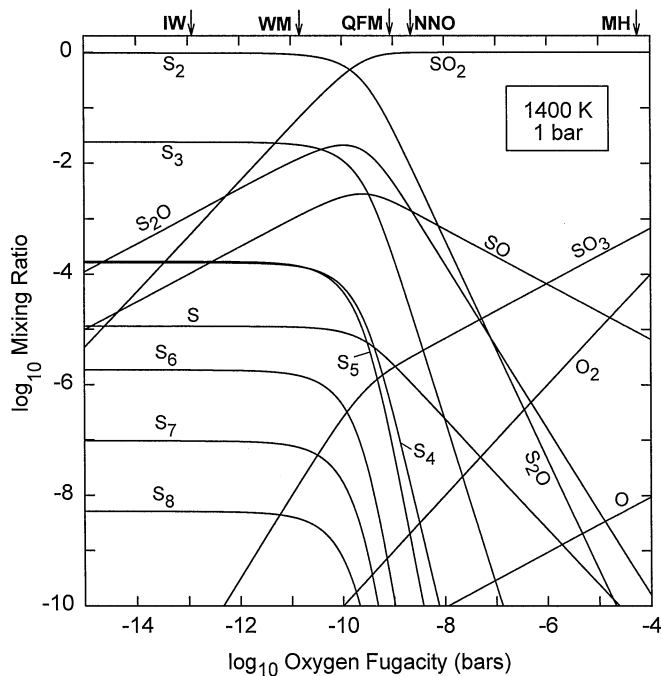
FIG. 8. Chemical equilibrium abundances in ionian volcanic gas as a function of oxygen fugacity at 1400 K and one bar total pressure. The O_3 mixing ratio is $<10^{-10}$ and is not shown. The gas has a variable bulk O/S ratio that varies from ~2 to ~0 as the oxygen fugacity decreases. The labeled arrows show the f_{O_2} values of different mineral buffers at this temperature.
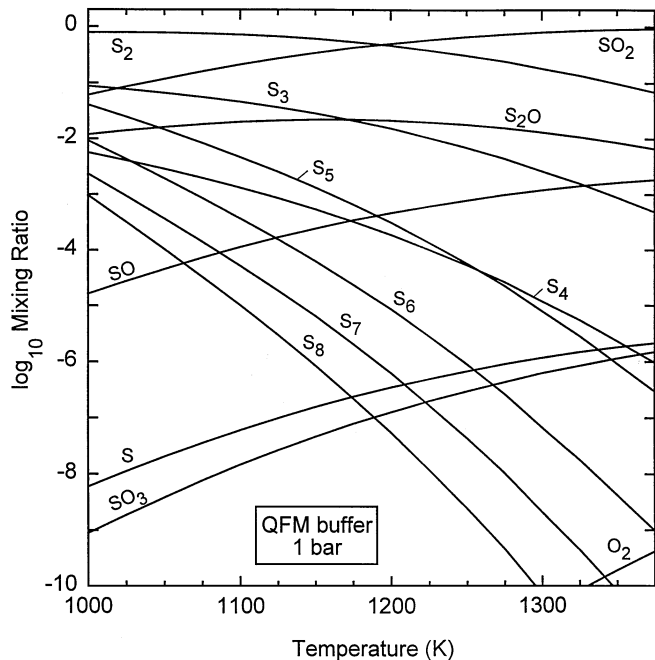
tend to lie within two log units above the NNO buffer and one log unit below the QFM buffer (see Fig. 10). The calculated f_{O_2} of the outgassed volatiles and implied oxidation state of the host magmas indicate that iron metal and elemental carbon are absent from the magma source regions on Io. The results clearly show that magmas and their volatiles did not originate from the core–mantle boundary of the satellite. Evidently, at the present time, Fe metal and FeS on Io are predominantly concentrated in the large core discovered by Galileo (Anderson *et al.* 1996). The lack or deficiency of C-bearing species in volcanic gases (see Table I) indirectly indicates the depletion of Io's current mantle in elemental carbon, which could have been completely depleted by past outgassing of CH_4, CO, and CO_2 (Consolmagno 1981).

Highly oxidized gases: Loki- and Prometheus-type volcanoes. Our calculations show that SO_2-rich volcanic gases have redox conditions between the NNO and MH buffers. Figures 10 and 11 show that these conditions overlap those for terrestrial igneous rocks (e.g., Carmichael 1991, Ballhaus 1993, Kasting *et al.* 1993) and volcanic gases (e.g., Symonds *et al.* 1994), but are more oxidizing than typical oxygen fugacities of lunar rocks (Sato *et al.* 1973, Papike *et al.* 1991).

The highly oxidizing conditions at which hematite is stable occur only for the thermal dissociation of pure SO_2 below 1100–1200 K (Fig. 3b). These SO_2-rich, low-temperature conditions were suggested for Prometheus-type plumes by McEwen and Soderblom (1983). Therefore, hematite could be stable in lava and pyroclastics from these volcanoes. In addition, Fe^{3+}-bearing
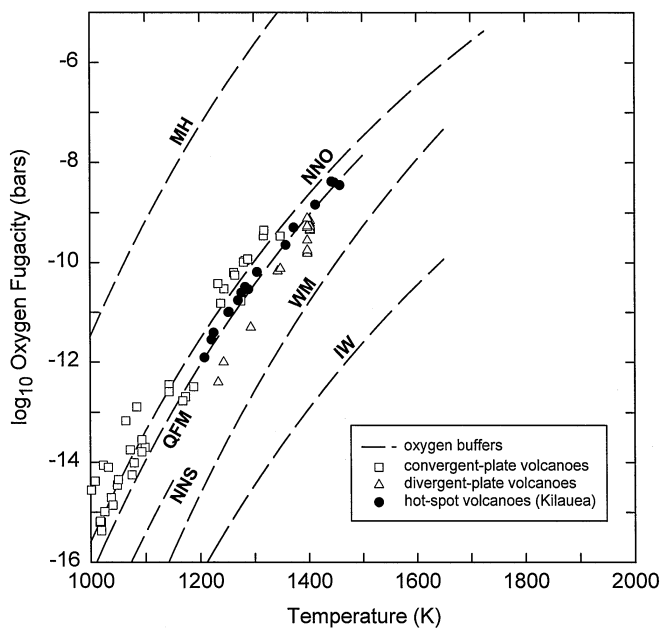

FIG. 9. Chemical equilibrium abundances in ionian volcanic gas as a function of temperature at one bar total pressure and the f_{O_2} of the QFM buffer. The gas has a variable bulk O/S ratio that is controlled by the temperature-dependent f_{O_2} of the buffer. Species with mixing ratios $<10^{-10}$ are not shown.

FIG. 10. The oxygen fugacities of terrestrial volcanic gases are plotted as a function of vent temperature. Mineral buffer f_{O_2} curves are shown for comparison. The calculated f_{O_2} values and vent temperatures for the volcanic gases are from Symonds *et al.* (1994).
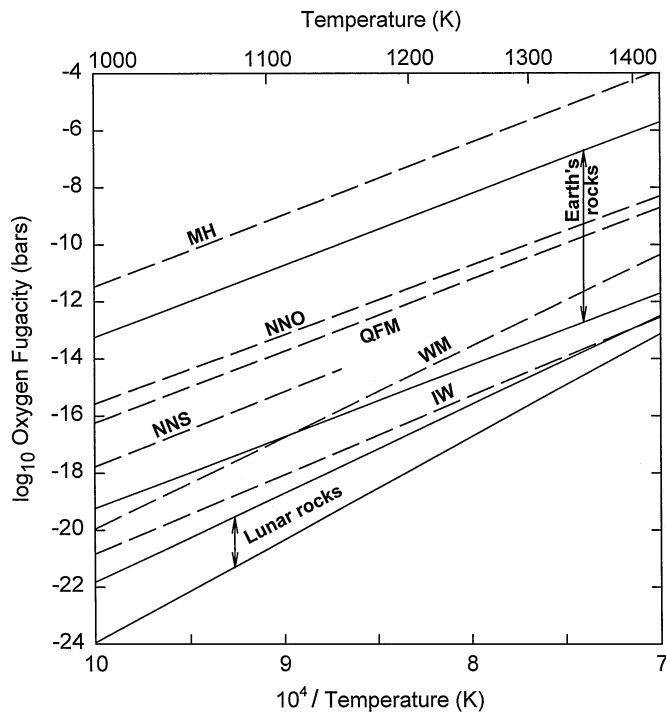
FIG. 11. Typical oxygen fugacity ranges for terrestrial (Carmichael 1991, Ballhaus 1993) and lunar igneous rocks (Papike *et al.* 1991).

compounds such as hematite and ferric sulfate might be partially responsible for the observed color of Io's surface (Nash and Fanale 1977). On the other hand, the Fe/Na ratio in the plasma torus is <0.04 (Na *et al.* 1998), which could indicate that Fe compounds are not major constituents of Io's surface. Alternatively, the low Fe/Na ratio in the torus could simply reflect the higher volatility and lower ionization potential of Na.

The relatively high f_{O_2} is plausibly due to alkali-rich magmas, because these magmas are generally enriched in Fe^{3+} and sulfate sulfur (e.g., Carmichael and Ghiorso 1986, Arculus and Delano 1987). Some Na-K-rich igneous rocks (granites, syenites, rhyolites, trachytes) contain hematite (Deer *et al.* 1963), while being depleted overall in Fe. Alkali melts might be responsible for the sulfur supply to the crust due to the high solubility of this element, mostly in the sulfate form (Nagasima and Katsura 1973, Papadopoulus 1973, Metrich and Clocchiatti 1996). On Earth, El Chichon lavas with anhydrite ($CaSO_4$) phenocrysts have f_{O_2} values 1.5–3.5 log units above NNO (Carmichael and Ghiorso 1986). In contrast with lunar magmas (Sato *et al.* 1973), a high f_{O_2} in ionian magmas should support sodium volatilization. High alkalinity for at least some of Io's magmas is indirectly supported by the presence of Na and K in Io's extended torus (Spencer and Schneider 1996). Keszthelyi and McEwen (1997) suggested the presence of alkaline rocks on Io as a result of deep magmatic differentiation. To conclude, we suggest that the oxidized SO_2-rich plumes are related to alkaline magmas and may be responsible for the supply of volatile alkali elements to Io's surface, atmosphere, and plasma torus. Some of these magmas

could be ultramafic mantle melts, in agreement with the high temperatures inferred for a number of hot spots.

Oxidizing conditions around the MH buffer are not reported for terrestrial volcanic gases (Symonds *et al.* 1994) and are rarely observed in terrestrial mantle magmas (Carmichael 1991). The natural occurrence of titanium in hematite (i.e., $Fe_2O_3 - FeTiO_3$ solid solutions) lowers the f_{O_2} for that buffer in comparison with pure hematite (e.g., Rumble 1976, Zolotov 1994). We suggest the MH buffer as an upper limit for the redox state of ionian volcanic gases and their respective magmas. Indeed, the (low) upper limit for SO_3 in the Loki plume (Pearl *et al.* 1979, Table I) and a tiny amount of SO_3 frost tentatively identified on the surface (Khanna *et al.* 1995) do not indicate conditions more oxidizing than those calculated for dominantly SO_2 gases. In addition, there is no reasonable buffer assemblage in silicate magmas which provides more oxidizing conditions than the MH buffer. The MH buffer leads to a predicted upper limit for the SO_3 mole fraction in ionian volcanic gases of 3×10^{-6} to 5×10^{-4} at 1–100 bars and 1000–1400 K. This is consistent with the *Voyager* upper limit for the SO_3 mole fraction. The assumed total pressure does not significantly affect the predicted SO_3 content. A titanohematite–magnetite buffer would give lower SO_3 abundances.

Pele-type plumes. These plumes are probably S-enriched in comparison with Prometheus-type plumes (McEwen and Soderblom 1983). At the same temperature and pressure, the more S-rich plumes correspond to more reduced gases and magmas. The proposed high temperature of Pele-type gases (McEwen and Soderblom 1983) also leads to more reduced conditions in comparison with mineral oxygen buffers. The f_{O_2} values calculated for volcanic gases with intermediate O/S ratios of ~0.3–1.7 match the f_{O_2} for terrestrial hot spot basalts (e.g., Kilauea, 0.5–1.5 log f_{O_2} units below NNO) and mid-ocean ridge basalts (1–4 log f_{O_2} units below NNO) (Christie *et al.* 1986, Wood *et al.* 1990, Carmichael 1991). By analogy with the Earth (Carmichael 1991), magmas of Pele-type volcanoes could be produced by the partial melting of peridotites in Io's mantle. Pele-type explosions are correlated with topographic highs and might be caused by the magma upwelling from a hot asthenosphere, which support the highlands (McEwen 1995).

Oxygen fugacity, sulfur solubility, and SO_2–magma interaction. The sulfur solubility in silicate magmas is dependent on oxygen fugacity. Figure 12 (modified from Kress 1997) shows that at the temperatures of mafic and intermediate magmas, sulfur has minimum solubility at about the NNO buffer (Katsura and Nagasima 1974, Lewis 1982, Carroll and Webster 1994). Under more oxidizing conditions than NNO, sulfur dissolves in sulfate form; it stays in sulfide form at more reduced conditions. An excess of sulfur under reduced conditions leads to iron sulfide formation. Under oxidizing conditions, sulfate sulfur in the magmas is mostly associated with Ca and Na (Carroll and Webster 1994), and sometimes anhydrite ($CaSO_4$) forms. Noseane ($Na_8Al_6O_{24}SO_4$) and hauyne (($Ca, Na)_{4-8}Al_6Si_6 \cdot O_{24}(S, SO_4)_{1-2}$) form in alkali-rich rocks, rather than sodium
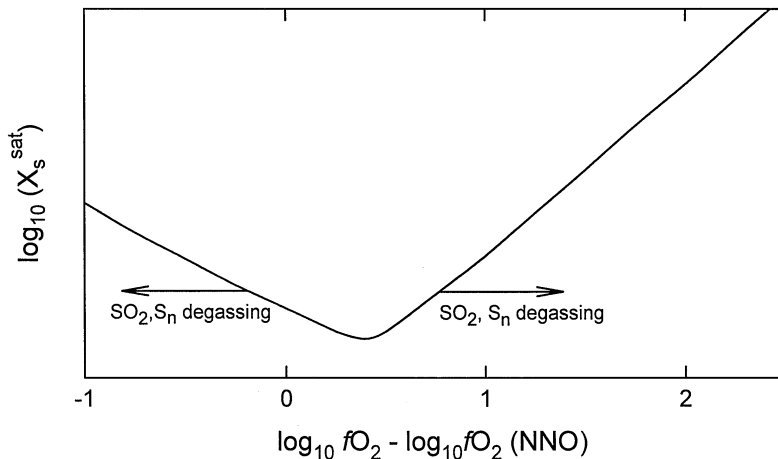
FIG. 12. Sulfur solubility as a function of oxygen fugacity in mafic magmas. The f_{O_2} is plotted as the difference (in log units) relative to the NNO buffer. Sulfur has minimum solubility around the NNO oxygen fugacity buffer. The arrows show changes in the magma redox state as a result of SO_2 or sulfur vapor degassing. Modified from Kress (1997).

sulfate (Deer *et al.* 1963, Carmichael and Ghiorso 1986). Alkaline magmas typically have high S^{6+}/S^{2-} ratios (e.g., Metrich and Clocchiatti 1996).

Sulfur degassing and volcanic eruption may be caused by changes in the oxygen fugacity of magma in the magmatic chamber. For instance, the addition of reduced magma to a magma chamber with oxidized magma leads to decreased sulfur solubility, outgassing of sulfur gases, and volcanic eruption (see Fig. 12). The mixing of reduced and oxidized magmas might have caused the Pinatubo explosion in the Philippines, which erupted a large amount of SO_2 (Kress 1997). Magma mixing might also be a driving force for some of the SO_2-rich eruptions on Io.
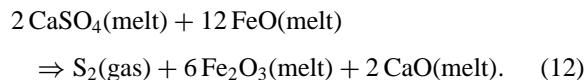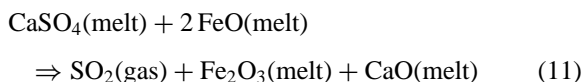
How does SO_2 degassing influence the oxidation state of the magma? According to terrestrial experience (Carmichael 1991), SO_2 degassing extracts oxygen from ferric iron in the basaltic magma, and the degassed magma becomes more reduced because the FeO/Fe_2O_3 ratio increases:

$$FeS(melt) + 3\,Fe_2O_3(melt) \Rightarrow SO_2(gas) + 7\,FeO(melt). \quad (9)$$
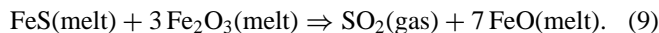
Degassing of S_2, which is sometimes the second most abundant species in ionian volcanic gases (see Fig. 8) may also lead to consumption of ferric iron in the melt:

$$2\,FeS(melt) + 2\,Fe_2O_3(melt) \Rightarrow S_2(gas) + 6\,FeO(melt). \quad (10)$$
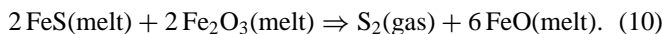
Therefore, f_{O_2} could decrease along with magma degassing from a magma chamber (see the lower left arrow in Fig. 12). For oxidized magmas, degassing of SO_2 and sulfur vapor could lead to magma oxidation via the net reactions:

$$CaSO_4(melt) + 2\,FeO(melt)$$
$$\Rightarrow SO_2(gas) + Fe_2O_3(melt) + CaO(melt) \quad (11)$$

$$2\,CaSO_4(melt) + 12\,FeO(melt)$$
$$\Rightarrow S_2(gas) + 6\,Fe_2O_3(melt) + 2\,CaO(melt). \quad (12)$$

Reactions (11) and (12) also lead to increased sulfur solubility (lower right arrow in Fig. 12), and to less outgassing of sulfur compounds. The magma oxidation state and the speciation of sulfur in volcanic gases may vary during an eruption because of reactions (9)–(12).

f_{O_2} and Io's differentiation. Galileo's discovery of a large iron-bearing core on Io (Anderson *et al.* 1996, Kivelson *et al.* 1996, Khurana *et al.* 1997) indicates a reduced bulk composition and a differentiated interior. This raises the question of why the outgassed volatiles, magma, and their source regions are apparently so oxidized.

By analogy with the Earth (e.g., Arculus and Delano 1987, Kasting *et al.* 1993), Venus (Lewis and Prinn 1984), and Mars (Dreibus and Wänke 1989), the silicate part of Io could have been oxidized by water, which is the most probable oxidizing agent for Io's mantle and lithosphere. Prinn and Fegley (1981) inferred that Io was formed in a region of the jovian subnebula where hydrous silicates condensed. During accretion and subsequent heating, the water released from hydrous silicates was consumed by reaction with carbon and iron to form H_2, CO, CH_4, and FeO (e.g., Consolmagno 1981). The reduced gases (mainly H_2) were eventually lost from Io. The oxygen released from water oxidized Fe to FeO (in silicates and magnetite), FeO-bearing silicates and magnetite to hematite, and FeS to sulfate. Over time, Io thus lost essentially all of its initial inventory of hydrogen. Any water in excess over carbon and Fe metal was plausibly lost by volcanic outgassing and photolysis (e.g., Lewis 1982, Lewis and Prinn 1984). As a result, the water originally accreted by Io was lost by hydrogen escape (H_2, CH_4) and oxidation of metal and sulfide. In contrast with the Earth, where the oxidation of the mantle

could have proceeded gradually due to subduction of hydrated oceanic crust followed by release of reduced volcanic gases (e.g., Arculus and Delano 1987, Kasting *et al.* 1993), oxidation of the silicate part of Io probably occurred during the early stages of Io's evolution. Io's low gravity should have led to easier H_2 escape resulting in earlier oxidation of Io's interior (relative to Earth). The presence of hydrous silicates in the matter forming Io is probably an important reason for the difference in oxidation state between the Moon and lunar-sized Io.

After most (or all) of Io's initial water inventory was consumed, we could also expect continued oxidation of Io's lithosphere by volcanic gases (e.g., CO, SO). Finally, the proposed deep magmatic differentiation of Io's lithosphere (Keszthelyi and McEwen 1997) leads to Na, K-rich, Fe-depleted magmas with high oxidation states. Alkaline magmas might be responsible for the continuing supply of oxidized sulfur to the lithosphere and surface.

CONCLUDING REMARKS

Volcanic gas chemistry on Io is probably every bit as rich and varied as volcanic gas chemistry on Earth. At the high temperatures (up to 2000 K) inferred for volcanic hot spots on Io, thermal dissociation of SO_2 will be significant, especially at lower pressures, and a number of S–O gases should be emitted in volcanic plumes. On Earth, volcanic gases erupted at temperatures ≥ 900 K are typically in thermochemical equilibrium (Symonds *et al.* 1994). Laboratory studies summarized by Gurvich *et al.* (1989–1994) show that SO_2–S_2 and SO_2–O_2 gas mixtures equilibrate rapidly at 1000 K and above. Kinetic calculations show that chemical reaction times are less than suggested eruption times for volcanic vents on Io (Zolotov and Fegley 1998a). Thus it appears inescapable that volcanic gases on Io reach chemical equilibrium before eruption onto its surface. Their molecular composition and oxygen fugacity reflect the redox state of source regions in Io's interior.

Sulfur-dioxide-rich volcanic gases (e.g., in the Loki plume and Prometheus-type plumes) have oxygen fugacities between the Ni–NiO and hematite–magnetite buffers. These redox conditions overlap those for terrestrial alkali basalts and convergent-plate volcanoes, but are much more oxidized than f_{O_2} values for lunar rocks, which are around (and below) the IW buffer. The SO_2-rich gases on Io may be produced by oxidized alkali magmas, which could also emit the Na and K observed in the plasma torus. Some of these magmas could be ultramafic high-temperature (>1400 K) melts. In addition, SO_2-rich gases may also be produced by evolved silica-rich, low-temperature magmas having dacitic and/or rhyolitic compositions. Reactions between the magmas and SO_2 could contribute to the high oxidation state of these gases.

Thermal dissociation of pure SO_2 gives a relatively high oxygen fugacity, which is inside the hematite stability field below about 1150 K. This leads us to expect that hematite and/or titanohematite is present in lava and pyroclastics associated with relatively low-temperature SO_2-rich plumes. However, it appears unreasonable to expect volcanic gases that are much more oxidized than the hematite–magnetite buffer. In any case, these gases would be highly reactive and SO_3-rich.

Outgassed volatiles with a bulk O/S ratio of unity (i.e., a 1 : 2 S_2–SO_2 mixture) will have f_{O_2} values ranging from NNO to three log units lower. This is about the same range as f_{O_2} values for terrestrial basaltic magmas and their associated volcanic gases. This coincidence is more evidence supporting of silicate volcanism on Io.

In general, our results show that volcanic gases on Io are fairly oxidized. This implies that the magma source regions are significantly more oxidized than the IW buffer, which plausibly prevails at Io's core–mantle boundary. However, we also find that volcanic gases erupted at high temperature (e.g., 1800 K) and very low pressures (10^{-4} bars and below) are as reducing as or more reducing than the IW buffer, but basaltic and ultramafic volcanic gases erupting at pressures $>10^{-2}$ bars, which are probably needed to drive explosive eruptions, are fairly oxidized.

Several observations, which can improve our knowledge of Io's volcanic gas chemistry and its redox state are:

1. Detection of gases other than SO_2 in volcanic plumes. Our results in this paper and our prior work predict that S_2–S_6, SO, and S_2O are reasonably abundant (>100 ppmv) in volcanic gases on Io. The gases in volcanic plumes can be analyzed using IR spectroscopy as done by *Voyager* (Pearl *et al.* 1979) and for terrestrial volcanic gases on Earth (Mori and Notsu 1997).

2. Measurements of the temperature, pressure, chemical composition, and oxygen fugacity for different types of volcanic vents on Io. This could be done using volcanic entry probes equipped with miniature mass spectrometers, and T, P sensors. The oxygen fugacity of volcanic gases can be calculated from ratios such as SO/SO_2, S_2/SO_2, SO_2/SO_3 as shown in the text, as well as from the CO/CO_2 and H_2/H_2O ratios.

3. Geochemical analyses of lava flows and volcanic condensates on Io's surface. A combination of IR spectroscopy (for relatively volatile condensates) and *in situ* elemental analyses (for more refractory rocky material) can be used to do this. Elemental analyses and photometry on Venus's surface (740 K, 96 bars) have been done in ~ 60 min and similar, if not better, performance should be possible on Io's surface with currently available technology.

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