

## NOTE

# Volcanic Production of Sulfur Monoxide (SO) on Io

Mikhail Yu. Zolotov

*Planetary Chemistry Laboratory, Department of Earth and Planetary Sciences, Campus Box 1169, Washington University,  
One Brookings Drive, St. Louis, Missouri 63130-4899, and Vernadsky Institute of Geochemistry and  
Analytical Chemistry, Russian Academy of Sciences, Kosygin Str. 19, Moscow 117975, Russia*

and

Bruce Fegley, Jr.

*Planetary Chemistry Laboratory, Department of Earth and Planetary Sciences, Campus Box 1169, Washington University,  
One Brookings Drive, St. Louis, Missouri 63130-4899  
E-mail: bfegley@levee.wustl.edu*

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**We use thermochemical equilibrium calculations to show that SO is expected in volcanic gases erupted on Io, and derive the range of temperatures, pressures, and elemental compositions that provide the observed SO/SO<sub>2</sub> ratio of 3–10% in Io's atmosphere. Our predictions could be tested during the Galileo Europa Mission (GEM), by Earth-based and Hubble Space Telescope observations in the millimeter and UV regions, or by a mass spectrometer and/or infrared spectrometer on an Io Volcanic Observer mission.** © 1998 Academic Press

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Sulfur monoxide is the second most abundant gas observed in the atmosphere of Jupiter's moon Io (Lellouch *et al.* 1996). Earth-based, hemisphere-average millimeter wave-observations give SO/SO<sub>2</sub> ratios of 3–10% by volume. The observed abundance is consistent with SO production by SO<sub>2</sub> photolysis (e.g., Kumar 1982, 1985; Summers and Strobel 1996; Wong and Johnson 1996). On the other hand, Io's low pressure ( $\sim 10^{-9}$  bar), patchy SO<sub>2</sub> atmosphere is at least partially due to volcanic outgassing (e.g., Lellouch 1996; Spencer and Schneider 1996). Gaseous SO<sub>2</sub> has been observed in volcanic plumes and over volcanically active regions (Pearl *et al.* 1979; Sartoretto *et al.* 1994). Here we show that high temperature volcanic gases exsolved from magmas can provide the observed SO abundance in Io's atmosphere.

Io's surface topography and temperatures of the hot spots, which range up to 1700 K (Veeder *et al.* 1994; Blaney *et al.* 1995; McEwen *et al.* 1997; Spencer *et al.* 1997b; Stansberry *et al.* 1997), are evidence for predominantly silicate volcanism. The observed hot spot temperatures are plausibly only lower limits to the actual temperatures because of the limited spatial resolution of the infrared observations and the rapid formation of cooler crust (Howell 1997) on the lava flows. Nevertheless, at least some of the hot spot temperatures suggest the eruption of high temperature silicate magmas such as basalts and even komatiites (Veeder *et al.* 1994; Blaney *et al.* 1995; Spencer *et al.* 1997b). On Earth, eruption temperatures  $\geq 900$  K are high enough for thermochemical equilibrium in volca-

nic gases exsolved from magmas (Symonds *et al.* 1994). Thus, Ionian volcanic gases exsolved from magmas during eruption may also chemically equilibrate (see below).

We modeled volcanic gas chemistry on Io in the 1000–2000 K range that covers the eruption temperatures of many terrestrial and lunar silicate magmas. We used 1400 K as a nominal temperature because it is a typical eruption temperature for basaltic magmas on Earth, such as at Kilauea (Symonds *et al.* 1994). The total pressure and bulk elemental composition of the volcanic gases are also inputs to our modeling. Although the pressures at which Ionian volcanic gases exsolve from magmas are unknown, pressures up to  $\sim 100$  bars in volcanic conduits on Io appear plausible depending on the depth of the volcanic source region. We note that *Voyager* observations indicate a pressure of  $\sim 10^{-7}$  bars in an observed plume (Pearl *et al.* 1979), but we are modeling volcanic gas chemistry inside volcanic conduits and not in the plumes. We used pressures of  $10^{-8}$  to 100 bars in our modeling; intermediate pressures in this range reproduce the observed SO/SO<sub>2</sub> ratio at observed hot spot temperatures. We considered the chemistry of sulfur and oxygen, because these are the two major elements observed in Io's atmosphere, are the major components of Io's torus, and are generally considered to be the most abundant elements in the nonsilicate portions of Io's surface (Lellouch 1996; Spencer and Schneider 1996). Observed O/S atomic ratios range from  $\sim 0.3$  (deposits around the Pele volcano (Spencer *et al.* 1997a)) to  $\sim 2$ , which is a typical value for the atmosphere (Lellouch *et al.* 1996) and a maximum value for the torus (Hall *et al.* 1994). We used O/S atomic ratios from  $10^{-7}$  to 3 (i.e., essentially from pure sulfur to SO<sub>3</sub> gas). A nominal O/S atomic ratio of unity, which is an average value for the torus, was chosen for some computations. Ideal gas thermochemical equilibrium calculations were done using our existing codes (Fegley and Lodders 1994; Fegley *et al.* 1997). Thermodynamic data for S<sub>1</sub>–S<sub>8</sub>, S<sub>2</sub>O, SO, SO<sub>2</sub>, SO<sub>3</sub>, O, O<sub>2</sub>, O<sub>3</sub>, and solid sulfur were taken from Gurvich *et al.* (1989–1994).

Eruption velocities of Ionian volcanic gases have been estimated as 0.2 km s<sup>-1</sup> in the underground conduit (Kieffer 1984). Typical eruption times ( $t_{\text{erupt}}$ ) from volcanic source regions at 30 to 50 km depth in the lithosphere and in a partially molten asthenosphere (Spencer and Schneider 1996) are thus 150–250 s.

TABLE I  
Chemical Lifetimes for SO Destruction (s)<sup>a</sup>

T (K)	10 <sup>-3</sup> bars	10 <sup>-4</sup> bars	10 <sup>-5</sup> bars
1,000	0.6	3	18
1,200	0.05	0.2	1
1,400	0.008	0.04	0.2

<sup>a</sup> For the reaction  $\text{SO} + \text{SO} \rightarrow \text{S} + \text{SO}_2$  and  $\text{O}/\text{S} = 1.0$ .

We verified that thermochemical equilibrium is attained in the erupting volcanic gas by comparing the eruption times ( $t_{\text{erupt}}$ ) to the chemical lifetimes ( $t_{\text{chem}}$ ) for volcanic gas chemistry (Prinn and Fegley 1987). At the higher temperatures and higher pressures in the source region and conduit,  $t_{\text{chem}} < t_{\text{erupt}}$  and thermochemical equilibrium is rapidly attained. Conversely, at the lower temperatures and lower pressures in the plumes,  $t_{\text{chem}} > t_{\text{erupt}}$  and thermochemical equilibrium is not reached. In between these two regions is an intermediate level, near the volcanic vent, where  $t_{\text{chem}} = t_{\text{erupt}}$  and thermochemical equilibrium in volcanic gases exsolved from the magma is quenched.

The SO abundance decreases as the volcanic gas cools because SO is converted to other sulfur gases via net thermochemical reactions exemplified by



The equilibrium constant ( $K_1$ ) for reaction (1) is given by

$$K_1 = \frac{P_{\text{SO}_2}^2 P_{\text{S}_2}}{P_{\text{SO}}^4} = \frac{X_{\text{SO}_2}^2 X_{\text{S}_2}}{X_{\text{SO}}^4} \frac{1}{P_T} \quad (2)$$

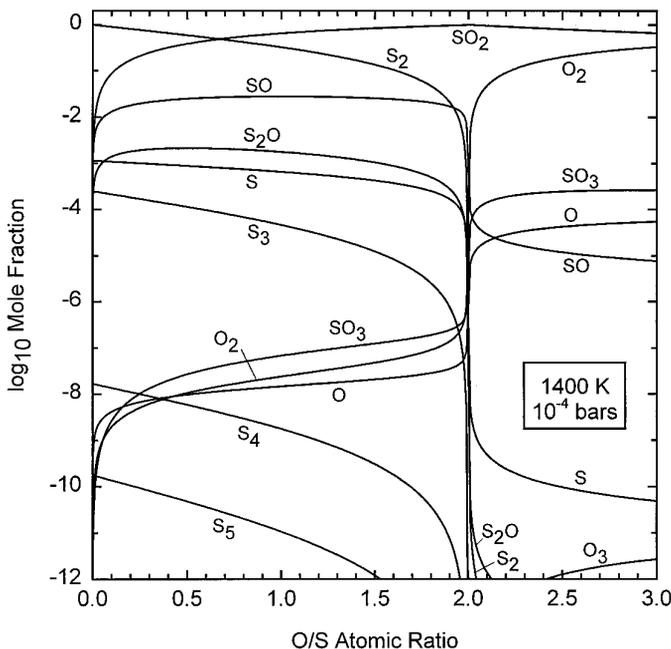


FIG. 1. Ideal gas thermochemical equilibrium abundances of the important species in Ionian volcanic gas as a function of the bulk O/S atomic ratio at 1400 K and 10<sup>-4</sup> bars total pressure. The mole fractions of gases not shown are lower than 10<sup>-12</sup>.

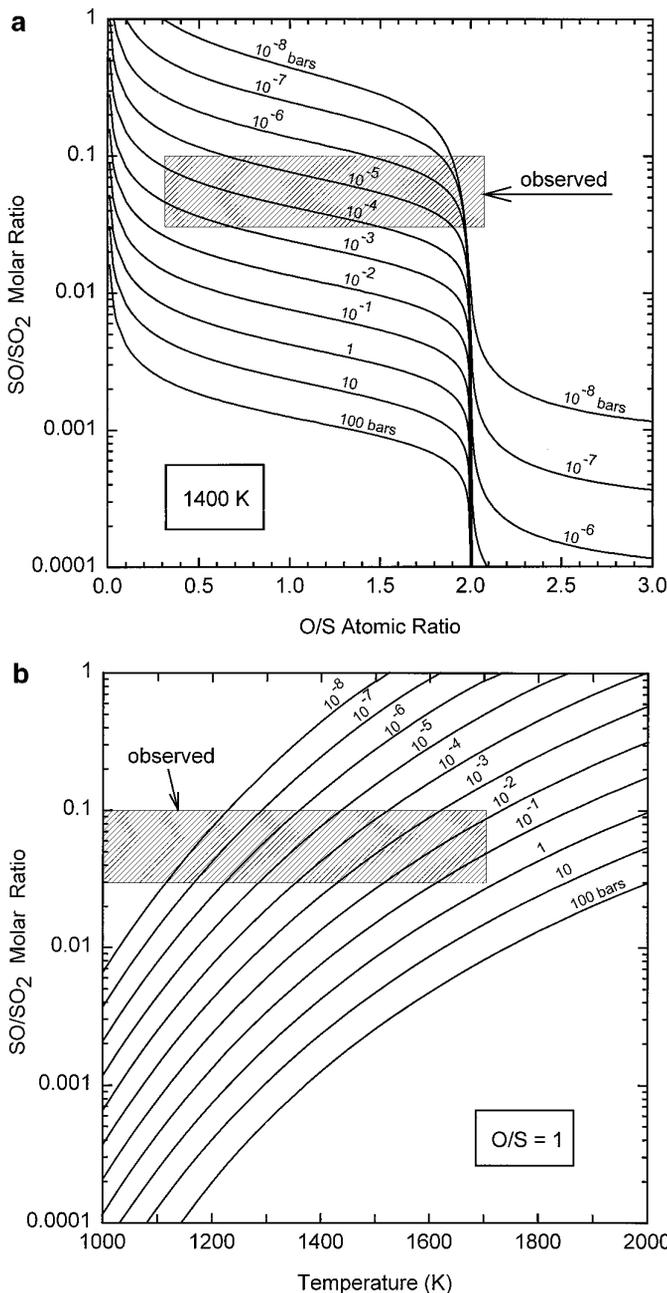


FIG. 2. (a) The SO/SO<sub>2</sub> molar ratio in Ionian volcanic gases as a function of total pressure and the bulk O/S ratio at 1400 K. (b) The SO/SO<sub>2</sub> molar ratio in Ionian volcanic gases as a function of temperature and total pressure for a fixed bulk composition (O/S = 1). The shaded boxes show the observed SO/SO<sub>2</sub> ratio (0.03–0.10) and hot spot temperatures (up to 1700 K).

where  $P_T$  is the total pressure,  $P_i$  is the partial pressure of gas  $i$ , and  $X_i = P_i/P_T$  is the mole fraction of gas  $i$ . Rearranging Eq. (2) to solve for the SO mole fraction,

$$X_{\text{SO}} = \left[ \frac{X_{\text{SO}_2}^2 X_{\text{S}_2}}{P_T K_1} \right]^{1/4}, \quad (3)$$

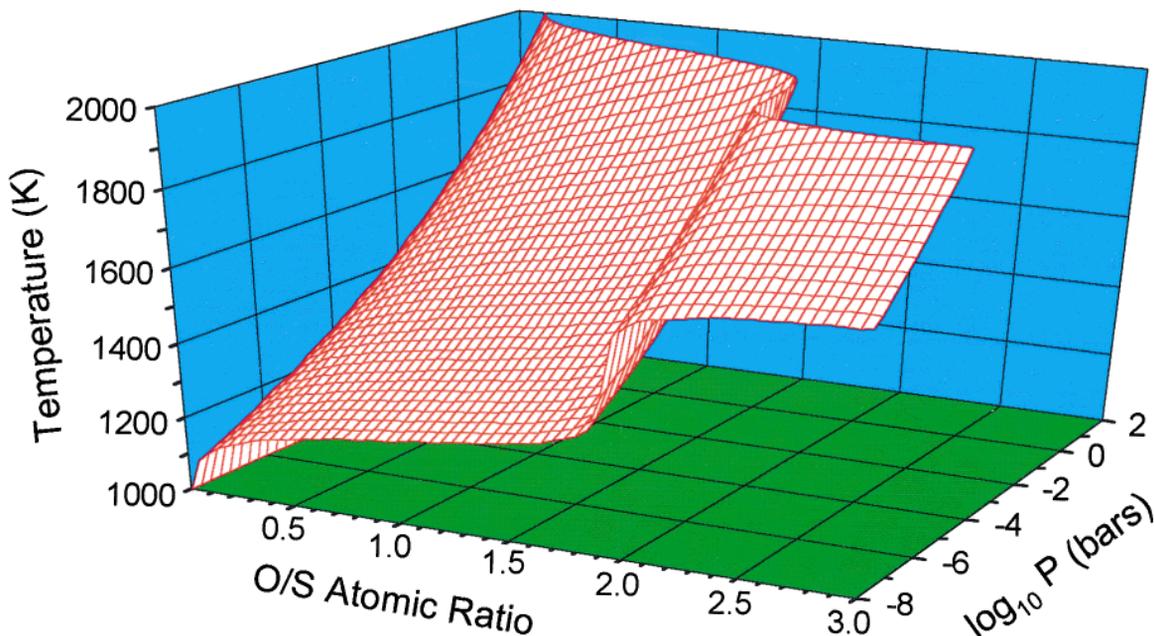


FIG. 3. The temperatures, pressures, and bulk compositions needed to produce an SO/SO<sub>2</sub> ratio of 10% in Io's atmosphere. The shape of the 3% contour is similar but located at temperatures 100–300 K lower.

illustrates that the SO mole fraction is inversely proportional to the fourth root of the total pressure. The elementary reaction



is important for SO destruction in the photochemical models (Summers and Strobel 1996) and also rapidly destroys SO in the cooling volcanic gas. The chemical lifetime ( $t_{\text{chem}}$ ) for SO loss via reaction (4) is given by

$$t_{\text{chem}}(\text{SO}) = 1/(k_4[\text{SO}]), \quad (5)$$

where the square brackets denote molecular number densities from the equilibrium calculations and the rate constant  $k_4 = 5.8 \times 10^{-12} \exp(-1760/T) \text{ cm}^3 \text{ s}^{-1}$  (Summers and Strobel 1996). Representative  $t_{\text{chem}}$  values listed in Table 1 are less than the estimated  $t_{\text{erupt}}$  values of 150–250 s. The SO chemical lifetime is even shorter at higher temperatures and pressures. Thus, it appears that volcanic gases on Io equilibrate in the vicinity of the volcanic vent, but that volcanic gas equilibrium chemistry is quenched in the cooler, lower density plumes. A similar situation is observed on Earth, because equilibrium calculations show that volcanic gases have equilibrated at the vent temperature but cease reacting once erupted (Symonds *et al.* 1994).

Figure 1 shows the effect of bulk elemental composition (i.e., the O/S atomic ratio) on chemistry of Ionian volcanic gases at constant temperature (1400 K) and pressure ( $10^{-4}$  bars). SO is generally the third most abundant gas, after SO<sub>2</sub> and S<sub>2</sub>, for O/S atomic ratios <2, which are observed in Io's atmosphere and torus. The relatively high abundance of S<sub>2</sub>O in Fig. 1 is also interesting and suggests that S<sub>2</sub>O may also be emitted from volcanic vents on Io. The abundance of SO is about 1000 times lower at O/S ratios of 2–3. Sulfur dioxide is still the dominant species at these high O/S ratios, while O<sub>2</sub> and SO<sub>3</sub> are now the two next most abundant gases. It is unclear whether or not such high O/S ratios are relevant to Io; observations of volcanic SO<sub>3</sub> would probably be the best way to search for such highly oxidized volcanic gases.

Figure 2a illustrates the effects of pressure and elemental composition on the SO/SO<sub>2</sub> ratio at constant temperature (1400 K). As shown by Eq. (3), the SO/SO<sub>2</sub> ratio is inversely proportional to fourth root of total pressure at constant temperature. The SO/SO<sub>2</sub> ratio is also inversely proportional to the bulk O/S ratio of the volcanic gas. The shaded box shows the observed range (0.03–0.10) for the SO/SO<sub>2</sub> ratio (Lellouch *et al.* 1996) and the observed range of O/S ratios (~0.3–2.1) in Io's surface, atmosphere, and torus. At 1400 K the observed SO/SO<sub>2</sub> ratio is matched at pressures of  $\sim 10^{-3.5}$  to  $10^{-5.5}$  bars over a wide compositional range in Ionian volcanic gases. Figure 2a also shows that at constant temperature and pressure, bulk O/S ratios within the observed range on Io have only a minor effect on the SO/SO<sub>2</sub> ratio in the equilibrated volcanic gas.

The effects of temperature and pressure on the SO/SO<sub>2</sub> ratio at a constant bulk composition (O/S = 1) are displayed in Fig. 2b. The SO/SO<sub>2</sub> ratio decreases with increasing pressure at constant temperature and composition. The SO/SO<sub>2</sub> ratio also decreases with decreasing temperature at constant pressure and composition. A fairly large  $P$ - $T$  range overlaps the shaded box, showing the range of observed hot spot temperatures and SO/SO<sub>2</sub> ratios in Io's atmosphere.

The three dimensional graph shown in Fig. 3 shows the contour where SO/SO<sub>2</sub> = 10% as a function of temperature, total pressure, and bulk O/S ratio of Ionian volcanic gases. This plot shows that a wide range of conditions either observed or expected in volcanic hot spots on Io lead to formation of the observed abundance of SO. The shape of the contour is due to the variations discussed above of the SO/SO<sub>2</sub> ratio with temperature, pressure, and composition. In particular, the sharp inflection in the contour corresponds to O/S = 2. The observed SO/SO<sub>2</sub> ratio can also be produced in fairly oxidizing volcanic gases with O/S of two and greater, however, the allowable pressure and temperature range is more restricted than at lower O/S ratios consistent with observations of Io's atmosphere and torus.

The observations of Io's volcanic activity show various types of plumes (e.g., Spencer and Schneider 1996). Some of them could have low pressure, which favors SO formation at observed hot spot temperatures of  $\sim 1400$

K. The low pressure and high temperature volcanic gases could be formed by exsolution from magmas in the volcanic conduits: expansion of gas bubbles exsolved from magma forms a low pressure vapor, while the surrounding magma maintains the high temperature of the gas. Interaction of magma with subsurface volatiles could also lead to low pressure emanations. In addition, volcanic formation of SO does not necessarily require low pressure vents. For example, Figs. 2b and 3 show that the observed SO/SO<sub>2</sub> ratio could also be produced in high pressure and high temperature (1700–2000 K) vents, which plausibly exist on Io. Thus, a range of pressures and temperatures lead to formation of the observed SO abundance on Io.

We do not exclude photochemical formation of SO, however both volcanism and atmospheric photochemistry may play a role in determining Io's atmospheric composition. Our prediction that SO is produced volcanically on Io can be tested by observations at sufficiently high spectral and spatial resolution of volcanic plumes and hot spots. International Ultraviolet Explorer observations have detected SO on Venus (Na *et al.* 1990), Hubble Space Telescope (HST) UV observations detected sulfur gases on Jupiter after the comet Shoemaker-Levy 9 impacts (Noll *et al.* 1995), and HST UV observations detected SO<sub>2</sub> on Io (Ballester *et al.* 1994). We suggest that HST observations in the UV be used to search for volcanic SO on Io, perhaps in connection with IR observations of hot spot activity. Finally, our work shows the desirability of including a volcanic entry probe equipped with temperature and pressure sensors, a mass spectrometer, and/or an infrared spectrometer on the Io Volcanic Observer mission currently under study by NASA and ESA.

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