NOTE

Volcanic Production of Sulfur Monoxide (SO) on Io

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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$_2$ 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.

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$_2$ ratios of 3–10% by volume. The observed abundance is consistent with SO production by SO$_2$ photolysis (e.g., Kumar 1982, 1985; Summers and Strobel 1996; Wong and Johnson 1996). On the other hand, Io’s low pressure (≈10$^{-7}$ bar), patchy SO$_2$ atmosphere is at least partially due to volcanic outgassing (e.g., Lellouch 1996; Spencer and Schneider 1996). Gaseous SO$_2$ has been observed in volcanic plumes and over volcanically active regions (Pearl et al. 1979; Sartoretti 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 ≥900 K are high enough for thermochemical equilibrium in volcanic 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 ~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 ~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$_2$ 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 ~0.3 (deposits around the Pele volcano (Pearl et al. 1997a)) to ~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$_3$ 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$_2$–S$_8$, S$_2$O, SO, SO$_2$, SO$_3$, O, O$_2$, O$_3$, and solid sulfur were taken from Gurvich (1989–1994).

Eruption velocities of Ionian volcanic gases have been estimated as 0.2 km s$^{-1}$ 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)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>10^{-3} bars</th>
<th>10^{-4} bars</th>
<th>10^{-5} bars</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,000</td>
<td>0.6</td>
<td>3</td>
<td>18</td>
</tr>
<tr>
<td>1,200</td>
<td>0.05</td>
<td>0.2</td>
<td>1</td>
</tr>
<tr>
<td>1,400</td>
<td>0.008</td>
<td>0.04</td>
<td>0.2</td>
</tr>
</tbody>
</table>

* For the reaction SO + SO → S + SO₂ and O/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

\[ 4 \text{SO} \rightarrow 2 \text{SO}_2 + \text{S}_2. \quad (1) \]

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

\[ K_1 = \frac{P_{\text{SO}_2}P_{\text{S}_2}}{P_{\text{SO}}^4} = \frac{X_{\text{SO}_2}X_{\text{S}_2}}{X_{\text{SO}}^4} \quad (2) \]

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,

\[ X_{\text{SO}} = \left( \frac{X_{\text{SO}_2}X_{\text{S}_2}}{P_TK_1} \right)^{1/4}. \quad (3) \]
The temperatures, pressures, and bulk compositions needed to produce an SO/SO$_2$ ratio of 10% in Io’s atmosphere. The shape of the 3% contour is similar but located at temperatures 100–300 K lower.

Figure 2a illustrates the effects of pressure and elemental composition on the SO/SO$_2$ ratio at constant temperature (1400 K). As shown by Eq. (3), the SO/SO$_2$ ratio is inversely proportional to the fourth root of total pressure at constant temperature. The SO/SO$_2$ 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$_2$ 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$_2$ ratio is matched at pressures of ~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$_2$ ratio in the equilibrated volcanic gas.

The effects of temperature and pressure on the SO/SO$_2$ ratio at a constant bulk composition (O/S = 1) are displayed in Fig. 2b. The SO/SO$_2$ ratio decreases with increasing pressure at constant temperature and composition. The SO/SO$_2$ 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$_2$ ratios in Io’s atmosphere.

The three dimensional graph shown in Fig. 3 shows the contour where the SO/SO$_2$ ratio decreases with increasing pressure at constant temperature (1400 K) and pressure (10$^4$ bars). SO is generally the third most abundant gas, after SO$_2$ and S$_2$, for O/S atomic ratios < 2, which are observed in Io’s atmosphere and torus. The relatively high abundance of S$_2$O in Fig. 1 is also interesting and suggests that S$_2$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$_2$ and SO$_3$ 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$_3$ would probably be the best way to search for such highly oxidized volcanic gases.

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$_2$ and S$_2$, for O/S atomic ratios < 2, which are observed in Io’s atmosphere and torus. The relatively high abundance of S$_2$O in Fig. 1 is also interesting and suggests that S$_2$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$_2$ and SO$_3$ 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$_3$ would probably be the best way to search for such highly oxidized volcanic gases.
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$_2$ 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$_2$ 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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REFERENCES


