

# Volcanic Origin of Disulfur Monoxide (S<sub>2</sub>O) on Io

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We use chemical equilibrium calculations to model S<sub>2</sub>O formation by high temperature thermochemical reactions in volcanic gases on Io. The calculations predict formation of 1–6% S<sub>2</sub>O gas at observed hot spot temperatures in SO<sub>2</sub>–S<sub>2</sub> gas mixtures at pressures of 1–100 bars in volcanoes on Io. The S<sub>2</sub>O abundance increases with increasing pressure (up to ~6% at 100 bars) and is relatively insensitive to temperature and the bulk O/S ratio over wide ranges. Condensation of volcanic S<sub>2</sub>O provides a plausible explanation for the solid S<sub>2</sub>O that has been suggested to be present on Io's surface (e.g., around the Pele volcano).

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**Key Words:** Io; volcanic gases; Pele volcano; disulfur monoxide; sulfur oxides; sulfur dioxide; sulfur; geochemistry; volcanism.

## INTRODUCTION

The surface of Jupiter's moon Io is covered by sulfur- and oxygen-bearing compounds of volcanic origin, but to date only SO<sub>2</sub> frost has been unambiguously identified (e.g., Spencer and Schneider 1996). Solid disulfur monoxide (S<sub>2</sub>O), which is orange-red to dark red (Schenk and Steudel 1965, 1968), has been suggested to explain spectral features at 0.55–0.7 μm which are prominent in dark-red areas of Io's surface, such as the pyroclastic deposits around the Pele volcano (Sill and Clark 1982, Hapke 1989, Spencer and Schneider 1996, Spencer *et al.* 1997a). Other phases such as sodium sulfide (Na<sub>2</sub>S), realgar (AsS), ferric iron compounds, and solid sulfur allotropes (S<sub>4</sub>, S<sub>3</sub>) have also been suggested to explain the 0.55- to 0.7-μm spectral features (see Spencer and Schneider 1996, Spencer *et al.* 1997a for a summary and review). Spencer *et al.* (1997a) argue that mixtures of solid S<sub>2</sub>O (40%) with vacuum-weathered sulfur (30%) and sulfur glass (30%) give a better fit to the spectral features than do other candidate materials.

Earlier, Hapke (1989) proposed a mixture of solid S<sub>2</sub>O with SO<sub>2</sub> frost, polysulfur oxides (S<sub>x</sub>O)<sub>y</sub>, and basalt to explain these spectral features. It is also possible that S<sub>3</sub> and/or S<sub>4</sub> formed by partial decomposition of (unstable) solid S<sub>2</sub>O (Schenk and Steudel 1965, 1968, Tang and Brown 1975) contribute to the red coloration of S<sub>2</sub>O frost (Hapke and Graham 1989).

Sulfur dioxide gas has been observed in a volcanic plume over Loki and over the Pele volcanic region on Io (e.g., Pearl *et al.* 1979, Sartoretti *et al.* 1994, Spencer and Schneider 1996, and references therein). High temperature reactions in SO<sub>2</sub>–sulfur vapor mixtures produce S<sub>2</sub>O in the laboratory (Schenk and Steudel 1968) and have been suggested to produce S<sub>2</sub>O gas on Io (Sill and Clark 1982). Detailed studies of terrestrial volcanic gases show that volcanic gases erupted at temperatures ≥900 K are often in thermochemical equilibrium (Symonds *et al.* 1994). Also, laboratory studies summarized in Volume 1 of Gurvich *et al.* (1989–1994) show that SO<sub>2</sub>–S<sub>2</sub> and SO<sub>2</sub>–O<sub>2</sub> gas mixtures equilibrate rapidly at temperatures of ~1000 K and above. Although a volcanic origin for S<sub>2</sub>O on Io has been discussed in the literature (e.g., Spencer *et al.* 1997a), no quantitative and systematic modeling of volcanic gas chemistry on Io is currently available to test the proposed volcanic origin of the condensed S<sub>2</sub>O apparently observed on Io's surface. Here we show that high temperature thermochemical reactions can produce several volume percent S<sub>2</sub>O in SO<sub>2</sub>–S<sub>2</sub> volcanic gases on Io at observed vent temperatures, plausible pressures, and plausible bulk compositions (i.e., bulk O/S ratios). Elsewhere we show that volcanic gas chemistry on Io can also produce other species such as SO (Zolotov and Fegley 1998).

## MODEL

We made ideal gas thermochemical equilibrium calculations for the O–S system for plausible ranges of temperature, total pressure, and bulk composition for volcanoes on Io. The calculations were done using our existing thermochemical equilibrium codes (Fegley and Lodders 1994, Zolotov 1996) and included solid S, sulfur vapor ( $S_1$ – $S_8$ ),  $S_2O$ ,  $SO$ ,  $SO_2$ ,  $SO_3$ ,  $O$ ,  $O_2$ , and  $O_3$ . Thermodynamic data were taken from the compilation of Gurvich *et al.* (1989–1994). As noted by Fegley *et al.* (1997), the sulfur gas data in Gurvich *et al.* (1989–1994) are preferable to those in the JANAF Tables (Chase *et al.* 1985). In particular, the table for  $S_2O$  gas in JANAF contains incorrect  $\Delta_f H^\circ$ ,  $\Delta_f G^\circ$ , and  $\log K_f$  values, apparently because of computational errors made by JANAF during production of the  $S_2O$  gas table.

We assume thermochemical equilibrium inside the volcano and quenching in the vicinity of the volcanic vent. This assumption is supported by the high reactivity of heated  $SO_2$ –sulfur vapor and  $SO_2$ – $O_2$  mixtures in the laboratory (Schenk and Steudel 1968, Gurvich *et al.* 1989–1994, and references therein), by kinetic calculations of high temperature gas chemistry in the O–S system (Fegley and Zolotov 1997, unpublished work), and by observations of sulfur gases in terrestrial volcanic gases (Symonds *et al.* 1994).

Calculations were done from 1000 to 2000 K, which spans maximum measured hot spot temperatures of 1200–1700 K on Io (Blaney *et al.* 1995, McEwen *et al.* 1997, Spencer *et al.* 1997b, Stansberry *et al.* 1997) and the eruption temperatures of terrestrial and lunar magmas. Furthermore, as noted by Keszthelyi and McEwen (1997), the actual eruption temperatures could be at least 200 K higher than the hot spot temperatures. There are no observations for vent pressures on Io. We used a total pressure range of 100 bars to  $10^{-8}$  bars that spans suggested pressures of a few to a few tens of bars inside ionian volcanoes (e.g., Kieffer 1982) and the observed pressure of about  $10^{-7}$  bars in a  $SO_2$ -bearing plume (Pearl *et al.* 1979). However, as discussed by Zolotov and Fegley (1998), we are modeling volcanic gas chemistry inside volcanic conduits and not in the erupted plumes.

Although  $SO_2$  is observed in volcanic plumes on Io and in Io's atmosphere, it is not known if the plumes are pure  $SO_2$  or mixtures of  $SO_2$  and sulfur vapor, or possibly mixtures of  $SO_2$  and  $O_2$ . In fact, ionian volcanic gases plausibly contain several species produced by high temperature chemistry. For our calculations we considered O/S atomic ratios of  $10^{-7}$  to 3 in the S–O system. Available observations of O/S ratios on Io are  $\sim 2$  (assuming that only  $SO_2$  is present in the Loki plume observed by the *Voyager* IRIS, slightly less than 2 in the atmosphere (for  $SO/SO_2 = 3$ –10% (Lellouch *et al.* 1996)),  $\sim 1$ –2 in the plasma torus (Spencer and Schneider 1996), and  $\sim 0.3$ –2 on Io's surface (O/S  $\sim 0.3$

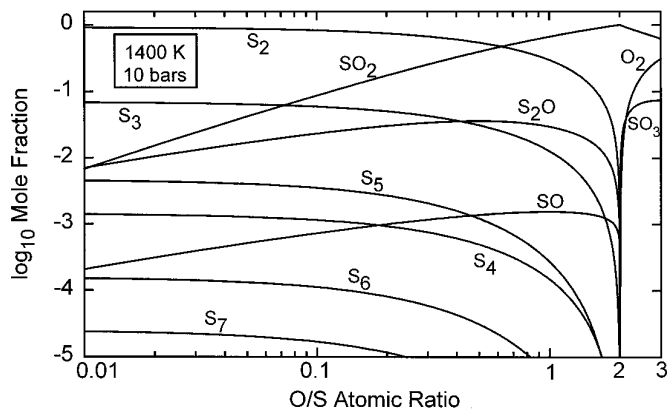


FIG. 1. Equilibrium abundances of major S and O gases at our nominal temperature and pressure of 1400 K and 10 bars as a function of the bulk O/S atomic ratio. The available observations and geochemical considerations suggest that volcanic gases on Io plausibly have bulk O/S ratios of 0 (pure sulfur vapor) to 2 (pure  $SO_2$ ). The effect of variable temperature and pressure on the abundance of  $S_2O$  is shown in Fig. 3.

for 40%  $S_2O$  + 60% S in pyroclastic deposits around Pele (Spencer *et al.* 1997a) and O/S  $\sim 2$  for 100%  $SO_2$  frost deposits (McEwen *et al.* 1988, Sartoretti *et al.* 1996).

In our modeling we use 1400 K (a typical temperature for basaltic magma), 10 bars (a suggested average vent pressure), and O/S = 1 as nominal values. However, our results are not dependent upon the eruption of basaltic versus other types of silicate (e.g., higher melting komatiitic or lower melting alkali-rich) magmas. Also our conclusions are not tied to the nominal values; a range of temperatures, pressures, and bulk compositions leads to the same conclusions.

## RESULTS

Figure 1 shows how the bulk O/S ratio affects the equilibrium speciation (at 1400 K and 10 bars) of volcanic gases on Io. We focus on O/S ratios of 2 and less because observed bulk O/S ratios on Io's surface, in its atmosphere, and in the plasma torus generally fall in this range. At O/S ratios greater than  $\sim 0.6$ ,  $SO_2$  is the dominant species, while  $S_2$  is the major gas at lower O/S ratios. Disulfur monoxide is the third most abundant gas (after  $SO_2$  and  $S_2$ ) at bulk O/S ratios of  $\sim 0.4$  to  $\sim 2$ , and the  $S_2O$  abundance is  $>1\%$  for bulk O/S ratios of  $\sim 0.02$  to  $\sim 1.8$ . The  $S_2O$  abundance is relatively insensitive to the bulk O/S ratio in this range because it varies from 1 to  $\sim 4\%$ , while the O/S ratio varies by almost a factor of 100 (from  $\sim 0.02$  to  $\sim 1.8$ ). The  $S_2O$  abundance decreases as the O/S ratio decreases below  $\sim 0.02$ , but as shown in Fig. 1  $S_2O$  becomes an increasingly important oxygen-bearing gas at low O/S ratios. The  $S_2O/SO_2$  ratio increases as the bulk O/S ratio decreases, until  $S_2O$  becomes more abundant than  $SO_2$  at O/S ratios  $< 0.01$ .

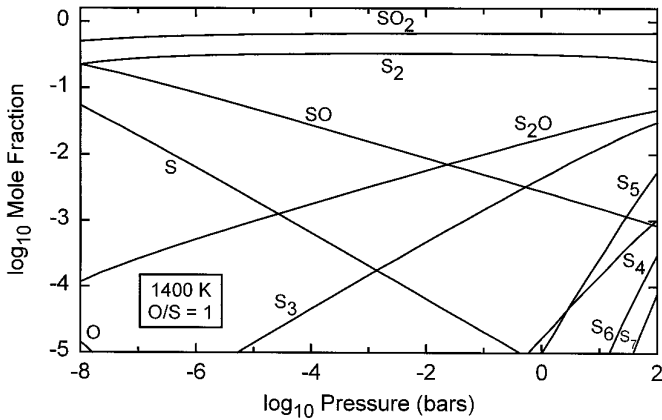


FIG. 2. Equilibrium abundances of major S and O gases as a function of total pressure at 1400 K and a bulk O/S atomic ratio of 1. This O/S ratio is equivalent to a volcanic gas composed of 67% SO<sub>2</sub> and 33% S<sub>2</sub> vapor.

The S<sub>2</sub>O abundance drops rapidly at O/S ratios >1.8 and is only 1.4 parts per million by volume (ppmv) at O/S = 2 (i.e., in heated SO<sub>2</sub>). Larger bulk O/S ratios lead to much lower S<sub>2</sub>O mole fractions, e.g., a S<sub>2</sub>O mole fraction of 10<sup>-12</sup> at O/S = 2.1, which is a SO<sub>2</sub>, O<sub>2</sub>, SO<sub>3</sub> gas mixture (see Fig. 1).

Figure 2 shows that the abundance of S<sub>2</sub>O is dependent on the total pressure. With the exception of SO<sub>2</sub> and S<sub>2</sub>, the abundances of other sulfur and oxygen gases also depend strongly on the total pressure. The abundances of S<sub>2</sub>O, S<sub>3</sub>–S<sub>8</sub>, and SO<sub>3</sub> increase and the abundances of SO, S, O<sub>2</sub>, and O decrease with increasing pressure. For our nominal vent temperature (1400 K) and composition (O/S = 1), the S<sub>2</sub>O abundance is >1% at total pressures ≥0.1 bars. Figure 2 also shows that SO and S<sub>2</sub>O are anticorrelated; lower pressure volcanic vents are potential sources of SO and higher pressure volcanic vents are potential sources of S<sub>2</sub>O. We consider volcanic formation of SO on Io in more detail elsewhere (Zolotov and Fegley 1998).

The three-dimensional plots in Figs. 3a–3c explore the effect of temperature, pressure, and composition variations on the S<sub>2</sub>O abundance and reinforce the conclusions reached above. For example, Fig. 3a shows the effects of composition (O/S atomic ratio) and total pressure on the S<sub>2</sub>O abundance at a constant temperature of 1400 K. The surface in Fig. 3a is fairly flat along the compositional axis, except near the sulfur vapor and SO<sub>2</sub> end members where O/S = 0 or 2, respectively. However, the surface is strongly sloped along the pressure axis with higher S<sub>2</sub>O abundances at higher pressures and lower S<sub>2</sub>O abundances at lower pressures. The surface disappears into the base of the plot where the S<sub>2</sub>O mole fraction decreases below 10<sup>-4</sup> (i.e., below 100 ppmv). Figure 3a thus shows that the S<sub>2</sub>O abundance is insensitive to the O/S ratio, except for the S-

enriched and SO<sub>2</sub>-enriched end member cases, but strongly depends on the total pressure.

Figure 3b shows the effects of composition and temperature on the S<sub>2</sub>O abundance at a constant total pressure of 10 bars. Again, the surface is fairly flat along the composi-

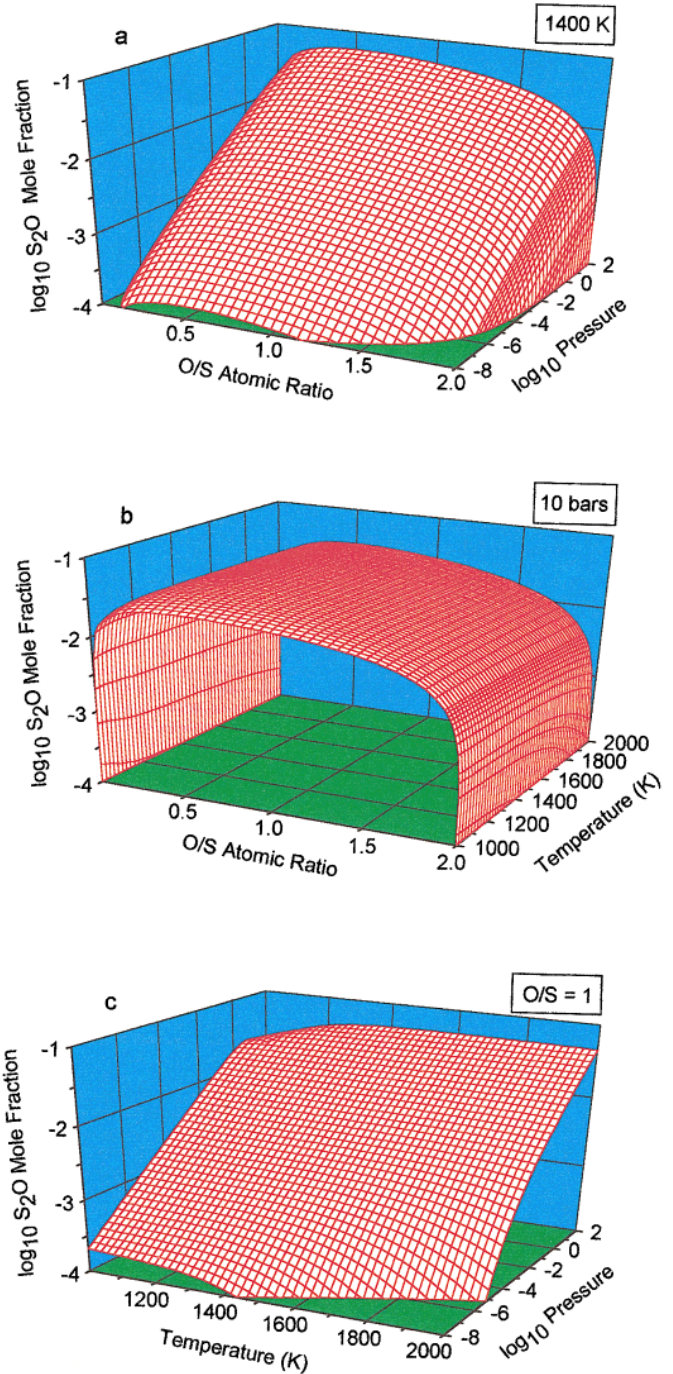


FIG. 3. Equilibrium abundance of S<sub>2</sub>O gas as a function of temperature, total pressure, and bulk O/S atomic ratio in the S–O system (a) at 1400 K, (b) at 10 bar total pressure, and (c) at O/S = 1.

tion axis, except very close to  $O/S = 0$  and  $2$  where the  $S_2O$  abundance drops off dramatically. The surface is also very flat along the temperature axis. The very weak dependence of the  $S_2O$  abundance on temperature and composition is also illustrated by the fact that the  $S_2O$  abundance only varies from 1 to 6% at  $O/S$  ratios of 0.05–1.5 (a factor of 30 variation) over temperatures of 1200–2000 K and total pressures of 1–100 bars. The maximum  $S_2O$  equilibrium abundance of 6% occurs at 100 bars, 2000 K, and an  $O/S$  ratio of 0.5.

Figure 3c shows the effects of temperature and pressure on the  $S_2O$  abundance at a constant bulk composition ( $O/S = 1$ ). The strong dependence of the  $S_2O$  abundance on total pressure is again evident from this plot. However, we now also get a better view of the effect of temperature on the  $S_2O$  abundance. At pressures of 0.01–100 bars, the  $S_2O$  abundance is almost independent of temperature in the 1200–2000 K range, but decreases with decreasing temperature below 1200 K. The  $S_2O$  abundance decreases with increasing temperature at lower pressures of 0.01– $10^{-8}$  bars.

## DISCUSSION

The results summarized above show that up to 6%  $S_2O$  can be produced in chemically equilibrated  $SO_2$ – $S_2$  gas mixtures at temperatures of 1000–2000 K and pressures of 1–100 bars. Thus, our calculations show that a volcanic source for  $S_2O$  on Io is plausible. Our results also support suggestions that condensed  $S_2O$ , which could be partially decomposed, causes the 0.55- to 0.7- $\mu\text{m}$  spectral features observed around the Pele volcano.

Spencer *et al.* (1997a) suggested that 40%  $S_2O$  mixed with 60% sulfur was needed to explain the color of the deposits around Pele, while our calculations predict only 1–6%  $S_2O$  in volcanic gases on Io. Laboratory studies show qualitatively that  $S_2O$  is less volatile than  $SO_2$  but more volatile than sulfur (Schenk and Stuedel 1965, 1968). Fractional condensation of  $S_2O$  may (at least partially) separate it from  $SO_2$  and sulfur, and produce  $S_2O$  concentrations of tens of percent. Preferential condensation of  $S_2O$  (relative to  $SO_2$ ) is indirectly supported by the deficiency of  $SO_2$  frost in areas around Pele (e.g., McEwen *et al.* 1988, Sartoretti *et al.* 1996), and by the presence of  $SO_2$  in the local atmosphere over this region (Sartoretti *et al.* 1994). However, the  $S_2O$  vapor pressure over solid  $S_2O$  is difficult to measure because  $S_2O$  undergoes (at least partial) reaction to polysulfur oxides and sulfur allotropes upon condensation and pure solid  $S_2O$  does not form (Schenk and Stuedel 1968, Tang and Brown 1975, Hapke and Graham 1989).

It is also possible that the 40%  $S_2O$  suggested by Spencer *et al.* (1997a) can be matched by a mixture of volcanic  $S_2O + S_3$  because some of the coloration of solid  $S_2O$  is

apparently due to  $S_3$  (Tang and Brown 1975, Hapke and Graham 1989). Our thermochemical models also predict  $S_3$  as an important volcanic gas at high pressure and  $O/S < 1$  (see Figs. 1 and 2). For example, at 1400 K and 10 bars,  $S_3$  becomes more abundant than  $S_2O$  at  $O/S$  ratios  $< 0.4$ . Condensation of volcanic  $S_3$  in addition to  $S_3$  formed by  $S_2O$  decomposition, may account for the 40% “ $S_2O$ ” suggested by Spencer *et al.* (1997a). Condensation of volcanic  $S_2$ , which is the most abundant gas at  $O/S$  ratios  $< 0.6$ , could be responsible for the 60% of various types of sulfur suggested by Spencer *et al.* (1997a) in the Pele deposits. However, this explanation requires that sulfur vapor allotropes in volcanic plumes do not react with one another before condensing on Io’s surface. Otherwise, the distinction between  $S_2$  and  $S_3$  vapor will not persist in the solid sulfur condensate.

Alternatively, the apparent discrepancy between 40% solid  $S_2O$  estimated by Spencer *et al.* (1997a) and the 1–6%  $S_2O$  formed at equilibrium in volcanic gases on Io may suggest another source, in addition to volcanic gas chemistry, for the condensed  $S_2O$ . Photochemical reactions may provide additional  $S_2O$  but this remains to be seen because  $S_2O$  was not included in the photochemical models of Summers and Strobel (1996) or Wong and Johnson (1996).

Our results support observations and suggestions that Pele is a high temperature volcano (e.g., McEwen and Soderblom 1983, Spencer and Schneider 1996). The rapid ( $\sim 1 \text{ km s}^{-1}$ ) and productive ( $\sim 10^8 \text{ g s}^{-1}$ ) explosions (Strom and Schneider 1982, Sartoretti *et al.* 1994) of Pele with huge eruptive plumes up to 460 km high are consistent with high vent pressures. If the spectral identification of  $S_2O$  in the deposits around Pele is correct, our results indirectly indicate that Pele’s vent pressure is  $\sim 1$ –100 bars and the bulk  $O/S$  ratio in eruptive gases is about 0.5 (i.e., a  $SO_2$ – $S_2$  mixture containing about 40%  $SO_2$ ). Observations of  $SO_2$  over Pele and the surrounding region (Sartoretti *et al.* 1994) support the concept that Pele’s volcanism is driven by  $SO_2$ -bearing gas.

The lack of spectral anomalies attributed to solid  $S_2O$  around the Surt and Aten volcanic centers (Spencer *et al.* 1997a) might be caused by lower pressures, compositional differences, or lower activity of those volcanoes. Surt and Aten were classified as Pele-type volcanoes by McEwen and Soderblom (1983). However, as noted by Spencer and Schneider (1996), Pele is apparently more active than either Surt or Aten and may not be closely related to them. Also, *Galileo* SSI observations are consistent with higher activity at Pele than at Surt or Aten in the time period since the *Voyager* flybys (Belton *et al.* 1996). On the other hand, the absence of “ $S_2O$ ” features around Prometheus-type volcanoes is consistent with the suggested predominance of  $SO_2$ , lower temperatures, and lower pressures in their plumes (McEwen and Soderblom 1983).

## SUMMARY AND FUTURE WORK

Our thermodynamic calculations of high temperature equilibrium chemistry predict formation of 1–6% S<sub>2</sub>O at observed hot spot temperatures in SO<sub>2</sub>–S<sub>2</sub> gas mixtures at pressures of 1–100 bars inside volcanoes on Io. Volcanic S<sub>2</sub>O may be responsible for the colored deposits around Pele (Spencer *et al.* 1997a) and S<sub>2</sub>O gas may also be a variable minor component of Io's atmosphere, especially in the vicinity of Pele. In addition to condensation, photochemical destruction (either via direct photolysis or reactions initiated by photochemistry) may be a significant loss process for volcanic S<sub>2</sub>O. We suggest that the chemistry, spectral properties, and vapor pressure of solid S<sub>2</sub>O be studied in more detail, and that S<sub>2</sub>O gas should be included in photochemical models of Io's atmosphere. Finally, this work and our prior modeling of volcanic SO production on Io (Zolotov and Fegley 1998) show the desirability of including a volcanic entry probe equipped with temperature and pressure sensors, and a mass spectrometer on the Io Volcanic Observer mission currently under study by NASA and ESA.

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