

**SOURCES OF Na FOR THE IO ATMOSPHERE.** D.S. Burnett, Susan B. Ellis, A. Rice, S. Epstein. Geological and Planetary Sciences Cal Tech Pasadena, Ca, 91125.

The physics and geology of Io have been extensively studied, but there has been little discussion of the chemistry. Relatively little is known about Io chemistry, but there are constraints. Further, it will be a long time before improvements will result from direct observation, given the severe difficulties with the Galileo mission. We are interested in exploring, via laboratory simulation experiments, plausible thermochemical and photochemical processes which determine the nature and amounts of surface constituents of Io.

The well-known density of Io shows that the planet overall is rocky. Because the orbit of Io is well within the magnetosphere of Jupiter and because Io only has a thin, transient SO<sub>2</sub> atmosphere, the surface is continually sputtered with magnetospheric ions. Complex processes ionize and accelerate the Io surface atoms to keV and MeV energies. Remarkably, only S, O, and Na ions were found by Voyager. Sputtering also produces an atomic cloud of Na and S (O not observable) with a trace of K. Both gaseous and solid SO<sub>2</sub> are known from spectroscopic studies. A trace of H<sub>2</sub>S and possibly CO<sub>2</sub> are present. Geologic features are interpreted in terms of elemental S, but there is no direct evidence for this constituent. We thus have a rocky planet which does not have rocks on the surface.

Our general goal is to understand the cycling of Na, S, and O through the crust and atmosphere on present-day Io and to understand how Io evolved to this state. A specific objective has been to determine the phases on the surface which are the source of the Na in the atmosphere of Io. There are 3 viable hypotheses for the nature and origin of the Io surface Na compounds: (I) Na<sub>2</sub>SO<sub>4</sub> from SO<sub>2</sub>-rock interactions [1]; (II) Na-sulfides from elemental S, rock interactions [2,3]; (III) directly-erupted volcanic Na [2,4], as atoms or, more reasonably, as NaO molecules. The viability of mechanism II was demonstrated by experiments which showed that liquid elemental S reacting with silicate glass at 1100-1200K produces Na-sulfides, most likely Na<sub>2</sub>S<sub>2</sub> [3]. The Na-sulfides could be entrained in S magmas (or dissolved at higher temperatures) and transported to the surface during S volcanism. The issue arises, however, whether elemental S is required to explain the Na-rich surface. Although widely accepted [see e.g. 5], elemental S is not a confirmed surface constituent [e.g. 6,7]. Consequently, it is important to test the alternative represented by mechanism I which does not require elemental S.

We have performed mechanism I simulations to test whether direct interaction of SO<sub>2</sub> with silicate materials (SO<sub>2</sub> alteration) can produce Na-S compounds. Experiments carried out under oxidizing conditions with a SO<sub>2</sub>-O<sub>2</sub> gas phase showed extensive interaction for a wide variety of silicate compositions at 1123K (mid-level crustal temperature for Io) [1]. Characterization by scanning electron microscopy (SEM) revealed extensive sulfate surface deposits for all experiments, but the nature of the sulfate changed systematically with the silicate Ca/Na ratio. Mixtures of CaSO<sub>4</sub> and Na-rich sulfate were formed from basaltic compositions having higher Ca/Na, but only alkali-rich sulfates formed from more granitic (low Ca/Na) compositions. For crystalline albite and an albite-orthoclase eutectic glass composition, K and Al-rich sulfates were formed. Many analyses show significant S excesses which are best interpreted as due to the presence of bisulfate (HSO<sub>4</sub>) components, and NaHSO<sub>4</sub> deserves consideration as an Io surface mineral.

Here we report studies of "direct" interaction mechanisms with pure SO<sub>2</sub> which do not involve external redox agents: (A). SO<sub>2</sub> disproportionation which can be represented

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schematically:  $\text{SO}_2 + \text{Na}_2\text{O} = \text{S} + \text{Na}_2\text{SO}_4$  or (B). sulfite formation:  $\text{SO}_2 + \text{Na}_2\text{O} = \text{Na}_2\text{SO}_3$ . For 4/7 compositions, no reaction products were seen with the SEM for the same temperatures and times as the oxidizing conditions experiments [1]. However, deposits on cm-sized silicate slices were always observed by photoelectron spectroscopy, which is much more sensitive than the SEM, and can distinguish oxidized and reduced S compounds. In all experiments where samples were not exposed to air for longer than about 10 minutes both oxidized and reduced S peaks were observed (Figure and Table). The reduced S peak disappears when samples are exposed to air for periods greater than a week, so both reduced and oxidized S compounds appear to form in all experiments, indicating mechanism A. A second set of experiments with powdered samples to provide greater surface area for reaction is undergoing infra-red characterization, but at high temperature, these sample capsules were filled with a yellow gas suggesting that elemental S is the reduced disproportionation product, as opposed to the alternative of Na-sulfide formation.

Assuming that burial of  $\text{SO}_2$  to temperatures approaching those of our experiments is plausible and that somewhat less oxidizing conditions do not qualitatively change the results,  $\text{SO}_2$ -rock alteration is a viable mechanism to account for the Io surface enrichment in Na. Overall, the model I simulations indicate that elemental S is not required to form Na compounds in crustal igneous interactions. The possibility of elemental S on Io can be regarded as a totally separate issue from the problem of the surface Na enrichment. Thus, the presence of Na compounds provides no constraint on elemental S, but, in turn, igneous formation of Na-S compounds is not tied to models of Io which contain elemental S. Measurements of minor constituents (e.g. K,Ca) in the Io atomic cloud and torus are the key to resolving these alternatives.

On a short time scale ( $< 10^3$  yr), except for minor effects of sputter erosion, relatively little chemistry occurs for Io surface materials. The dominant process is crustal recycling. Thermochemical reaction rates are probably negligible at Io surface temperatures, but due to heating during recycling (and to a lesser extent due to shallow intrusion of magmas), it is plausible that thermochemical equilibrium would be achieved. In this case it is likely that, regardless which of the above mechanisms extracts Na from silicate source regions, Na ends up as  $\text{Na}_2\text{SO}_4$  (or possibly  $\text{NaHSO}_4$ ). Sulfates are not observed in the Io reflectance spectrum [8], but the observational upper limit is sufficiently high that sufficient  $\text{Na}_2\text{SO}_4$  could be present to supply the Na atmosphere.

References: [1] M.L. Johnson and D.S. Burnett (1993) J.G.R. Planets, in press. [2] G.R. van Hecke and D.B. Nash (1984) unpublished manuscript. [3] M.L. Johnson and D.S. Burnett (1990) Geophys. Res. Lett. 17, 981-984. [4] F. Fanale, et al. (1982) In Satellites of Jupiter, D. Morrison, ed., 756-781, U.Arzt. Press Tuscon. [5] J.I. Moses and D.B. Nash (1991) Icarus 89, 277-304. [6] B. Hapke (1989) Icarus 75, 56-76. [7] A.S. McEwen and J.I. Lunine (1989) 75, 450-478. [8] R.R. Howell et al. (1989) Icarus 78, 27-37.

Sample	XPS Spectra	SEM
Albite	Nothing	Nothing
AbOr Eutectic Glass (a)	2 Peaks	Nothing
Obsidian (a)	2 Peaks	Nothing
Sodalime Glass (b)	(Oxidized Only)	Na-S
Ab <sub>9</sub> AnDi Glass (b)	(Oxidized Only)	Na-S + Ca-S
Chondrule Glass	2 Peaks	Na-S + Ca-S
Alkali Basalt (a)	2 Peaks	Nothing

(a) Less than 10 min. air exposure.

(b) Air exposed for > 1 week; reduced peak probably lost.

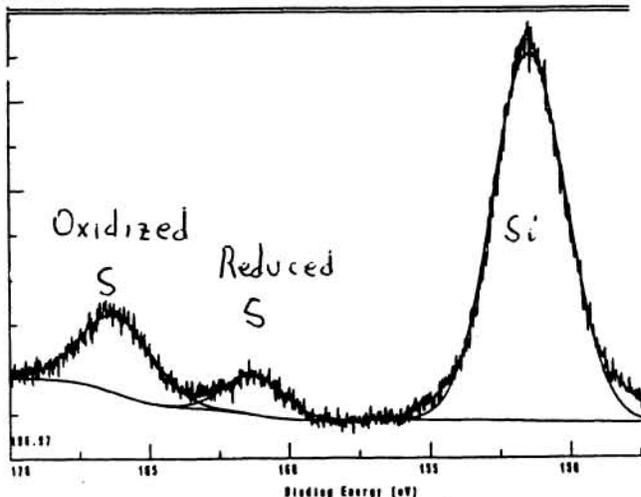


FIGURE Photoelectron spectrum of Mono obsidian +  $\text{SO}_2$  reaction products.