

IGNEOUS ORIGIN FOR THE Na IN THE CLOUD OF IO

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Abstract. We heated mixtures of sulfur and Na-bearing silicates in evacuated silica glass capsules to temperatures between 600°C and 950°C. At or above 850°C, Na-silicate glass reacts with elemental S to form a (Na,K) sulfide. Mobilization of this phase may account for the presence of Na and K on the surface of Io, and hence in the material sputtered into the Jovian magnetosphere.

Introduction

The atomic Na cloud around Io has been studied for approximately 15 years, but although much is known about the temporal and spatial variations of the cloud, its origin remains enigmatic (Cheng et al., 1986; Nash et al., 1986). Surface sputtering is the consensus mechanism for supplying Na atoms to the cloud. Estimated Na loss rates are very uncertain, ranging from $1-10 \times 10^{26}$ atoms/sec, not greatly less than equivalent estimates for S or O which are in the 10^{27} - 10^{29} atom/sec range (Cheng et al.). Despite the uncertainties, significant sources of Na on the surface of Io appear to be required.

We have performed simulation experiments to study the possibility that igneous interactions between elemental S and silicate materials have extracted Na from silicates and transported it to the surface along with elemental S.

Experimental

Sulfur and sodium-bearing silicates were loaded into vacuum-sealed silica glass capsules (6mm OD x 2mm ID), using reagent sulfur, 99.95% pure. Silicates were Amelia albite or soda-lime glass (approx. composition 17.7 wt % Na₂O, 3.3% MgO, 2.5% Al₂O₃, 69% SiO₂, 0.6% K₂O, 5.9% CaO, 0.9% TiO₂). Each capsule was loaded with 75±15 mg sulfur and 1 cm long pieces of 0.7mm diameter soda-lime glass rod, or 3-50 mg of albite as 0.1-1 mm pieces. Charges were held at temperatures between 600° and 945°C for periods of 3 to 22 days. Presumably because of the high vapor pressure of S at these temperatures (e.g. 35 atmospheres at 850°C), there was a significant capsule failure rate above 800°C. Charges were removed from the furnace and allowed to cool in air.

Results

X-ray analyses with a scanning electron microscope (SEM) yielded no significant concentrations of Na in yellow S. The best upper limit was set with a thin window Si(Li) detector, 0.2 weight % for a sample heated with soda-lime glass at 850°C for 14 days. This limit is consistent with limits on the solubility of elemental Na in S by Rosen and Tegman (1972) for an immiscible Na-rich sulfide melt coexisting with S at temperatures up to 650°C (maximum Na content in molten sulfur of 0.3%).

No reaction was noted between sulfur and silicates at 600, 632, or 750°C; however, the higher temperature (850° and 900°C) runs with soda-lime glass contained a brown run product as well as silicate and yellow sulfur. The brown phase altered in contact with the air, first turning green and translucent, then turning clear (gel?). It also decomposed under a focused nA electron beam in the SEM. At these higher temperatures losses of Na (up to 12%) and K (up to 50%) in the soda-lime glass, relative to unheated glass, were observed in heated glass samples, along with rim to center depletions of Na (but not always for K).

All high-temperature runs containing sulfur and soda-lime glass (850°C for 3, 7, 14, and 18 days; 900°C for 8 days) developed the brown phase. No brown material was seen in two sulfur charges run for 7 days at 850°C which did not contain sodium silicates or in runs in which the S was omitted. These experiments prove that the brown phase was formed by interaction of elemental S and soda-lime glass.

Brown or green material was observed: as flat crystals(?) occurring as films on both soda-lime and SiO₂ glass surfaces (Figure 1), as complex swirls within the quenched sulfur, suggesting an immiscible melt phase, and as angular chunks or dark spots in yellow sulfur.

We believe that this brown material is alkali sulfide (or sulfides) for the following reasons:

- 1) X-ray spectra of 7 regions on fragments from the 900°C run chosen for their green color show Na, K, and S X-ray spectra in 5 cases. The other two show only S, probably due to a thin coating of yellow sulfur over the green phase. Spectra from the 850°C runs also show Na, K, and S in isolated regions of the samples.
- 2) The dark color of the brown-green phase resembles descriptions of sodium sulfides, especially beta Na₂S₂ (see Oei, 1973; Rosen and Tegman, 1972; Pearson and Robinson, 1930); Na and K sulfites and sulfates are colorless. The dark color seen in our samples compared to colorless Na₂S may be due to the K present, as K sulfides are darker than Na sulfides (Feher and Berthold, 1953), or to trace amounts of Ti or Fe extracted from the soda-lime glass. The crystals shown

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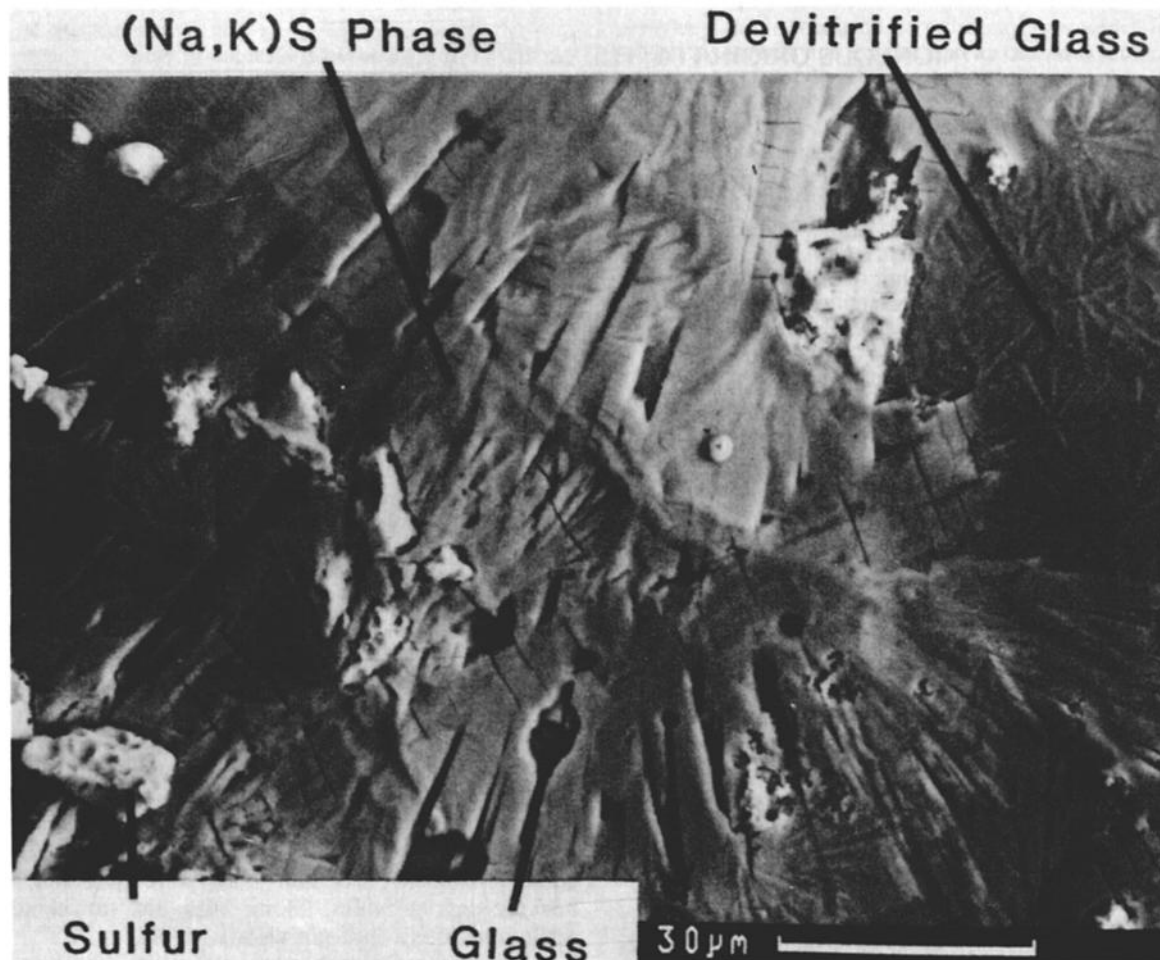


Fig. 1. SEM Back-scattered image of surface of soda-lime glass rod, 900°C run, showing sulfur (bright, porous), alkali sulfide phase (light gray flat prisms covering most of image; some crystals are cracked

transverse to their length), and devitrified glass (dark gray, right hand side). The radiating needles on the glass surface are $\text{CaMgSi}_2\text{O}_6$.

in Figure 1 resemble those of Na_2S_2 in Plate 1 of Pearson and Robinson (1930).

3) Semi-quantitative analyses of the X-ray spectra of six regions from the 900°C run give a 1:1 (Na+K):S ratio in four cases (Figure 2). These analyses are uncertain because they are not made on flat polished samples as is required for quantitative X-ray microanalysis; however, an attempt was made visually to orient the analyzed areas into flat-lying geometry. Some of the samples were rotated by +5 degrees with no noticeable changes in the X-ray spectra. The clustering of the alkali to sulfur ratio around 1 appears to be significant and rules out sulfates or sulfites for which the alkali to sulfur ratio would be 2.

There are complications in the data presented on Figure 2. It is likely that air exposure has partially oxidized/hydrated the green materials analyzed. This may lead to alkali sulfate formation which may explain the point with alkali/S about 2. Alternatively, both $(\text{Na,K})_2\text{S}$ and $(\text{Na,K})_2\text{S}_2$ may be present. We also cannot rule out the possibility that small amounts of sulfite or sulfate are present which, being colorless,

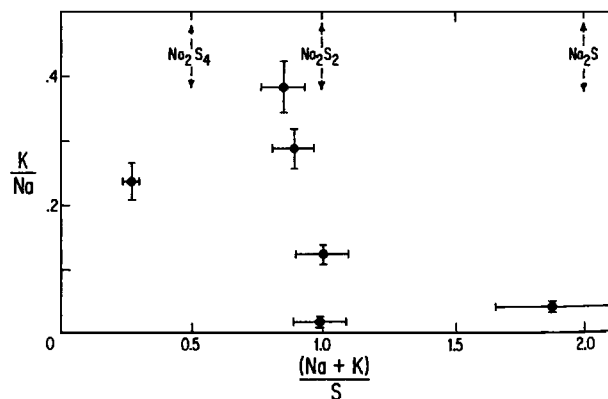


Fig. 2. Semi-quantitative analyses of alkali sulfide phase (ZAF correction; Amelia albite Na standard, Asbestos microcline K standard; anhydrite S standard). Four points show Na_2S_2 stoichiometry, and one is consistent with Na_2S . Note variable K to Na ratio.

would be easy to miss in the presence of a large amount of yellow-white S. The point on Figure 2 with low alkali/S can be explained by an admixture of S in the 5-10 micron beam spot as the sulfide and S are intimately mixed. The possibility that all analyses represent mixtures of (Na,K)₂S and S cannot be completely ruled out, but the clustering of such analyses near alkali/S=1 would not be expected. The variable K/Na probably reflects lack of equilibrium associated with only partial reaction of S and silicate.

Albite runs at 850 and 950°C did not contain brown-green material, and no Na-sulfur compounds have been found. The albite showed evidence of reaction, being essentially destroyed in the 950°C run; but this very likely reflects reaction with the SiO₂ glass container. These samples had extensive air exposure before the significance of dark-colored material was appreciated, thus there is a remote possibility that sulfides were present but have reacted. Alternately, sulfides may not be dark-colored if K, Ti, or other elements from the soda-lime glass are important coloring agents.

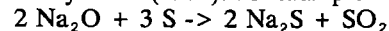
Discussion

We have shown that, while the solubility of Na in sulfur is probably not significant, elemental sulfur will react with silicate glass to produce alkali sulfides. It is quite plausible that analogous igneous processes could occur on Io and that alkali sulfides are a natural consequence of igneous activity on a S-rich planet. Alkali sulfides suspended in elemental S flows or erupted could be the source of the Na (and K) observed around Io. The phase we have formed, (Na,K)₂S₂, is presumably that favored by the kinetics of our experiments and need not be the actual compound formed on Io.

The absence of Si in the inner magnetosphere ion mass distributions (e.g. Krimigis and Rolef, 1983; Vogt et al., 1979) is a strong argument that direct sputtering of silicate materials cannot account for the atomic Na cloud; however there are indirect means, e.g. volcanic outgassing of alkalis followed by sputtering, that can preferentially derive the Na from silicates (compare Hapke, 1989).

The reflectance spectra for Io are compatible with large amounts of Na₂S (see e.g. Nash et al., 1986; Clark et al., 1986; Nash, 1988). Thus, several studies have proposed Na₂S as the Na compound on the surface of Io (see e.g. Fanale et al., 1982, Nash et al., 1986, Chrissey et al., 1988) but relatively little discussion has been given of how Na₂S might form. Na₂S is not found terrestrially or in meteorites, although (Na,Fe), (Na,Cr) and K-sulfides are known. VanHecke and Nash (1984) and Lunine and Stevenson (1985) propose that the interaction of elemental S and silicates would form Na-sulfides. VanHecke and Nash (1984) base their conclusion on thermodynamic calculations for Na₂S formation by reaction of S with Na ortho- or metasilicates. One could quibble about the relevance of these specific reactions, but our experiments demonstrate the plausibility of their basic suggestion. Because of the relatively low sputtering yield of Na₂S, Chrissey et al. speculate that polysulfides are dominant.

Based on terrestrial and meteoritic experience, it is not intuitive that sodium should form sulfides rather than silicates or oxides under igneous conditions. However, alkali sulfides are thermodynamically stable, as discussed by Lewis (1971). For example the reaction



is favorable thermodynamically at igneous temperatures (compare VanHecke and Nash), although the equivalent reaction with albite is not favorable, consistent with our observations. Lewis also noted that K sulfides are more stable than Na sulfides, and, indeed, K partitions more strongly than Na into the sulfide phase in our experiments.

Reaction of volcanic glass on Io with sulfur could provide a mechanism for forming SO₂ along with sulfides. The data on Io-derived material in the Jovian magnetosphere suggests that there is much more SO₂ than Na on the Io surface, but quantitative estimates are highly uncertain, and given the ease by which surficial deposits would be preferentially observed and sputtered, the importance of SO₂ relative to more reduced S compounds could be less than has been generally believed.

As noted, there is little terrestrial or meteoritic evidence for the theoretical stability of alkali sulfides. In the equilibrated enstatite (E6) chondrites, which are the best approximation to an equilibrium assemblage under very low oxygen fugacity (which favors sulfide formation), Na and K are found in feldspar, although other lithophile elements such as Ca, Ti, Mn, U, and Th are found in sulfides (Furst et al., 1981). Similarly, Murrell and Burnett (1986) found little partitioning of K from a silicate to an Fe/FeS liquid. Given these observations, our success in producing alkali sulfides may be due to the high S₂ fugacity in our experiments rather than low O₂ fugacity associated with enstatite chondrites.

Silicate melts continually invading the crust of Io (e.g. Kieffer, 1982, Lunine and Stevenson, 1985) provide high temperatures for reaction and a source of Na. Because a high sulfur fugacity appears necessary to form Na-sulfides, the existence of the Io Na cloud itself may be a strong argument for free sulfur on Io, as there is little direct evidence for elemental S (see e.g. Clark et al., 1986, Hapke, 1989). A complication to this interpretation is the possibility that direct reaction of SO₂ with silicates might form Na-sulfur compounds (VanHecke and Nash), independent of the presence of elemental S.

The origin of elemental S on Io is a major issue. CI chondrites contain a few percent free sulfur, lesser amounts bound up in hydrocarbons, and free sulfides. There are large amounts of S as free sulfates or sulfide in layer-lattice silicates (DuFresne and Anders, 1962; McSween, 1979). Thus, a CI source model for Io automatically delivers elemental and oxidized S (compare Lewis, 1982); however, the effect of planetary accretion on this disequilibrium assemblage is unclear.

Given elemental S and volcanic activity, neither evaporite deposits nor an aqueous/icy prehistory for Io, as suggested by Fanale et al. (1977), are required to explain the atomic Na cloud, although a literal CI-analog parent material would have to lose a lot of water. Perhaps the water could have been lost in the proto-Jovian nebula before Io accreted.

Although more experiments are required to explore the generality of our results and, especially, to define the role of oxygen fugacity and effects of the presence of other elements such as Ca or Fe, we propose that an igneous origin for the Na observed and in the Jovian magnetosphere should be seriously considered.

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