

SO₂ WEATHERING ON Io; M.L. Johnson, D.S. Burnett, S. Epstein, and A. Rice, Caltech, Pasadena, CA 91125

We are conducting laboratory experiments relevant to Io surface chemistry, which ion composition data for the Jovian magnetosphere show to be composed of S-O-Na compounds. The nature and origin of the Na compounds are enigmatic. Previous experiments (1) indicate that Na-sulfides are produced by direct interaction of elemental S with silicates, as would occur when silicate magmas invade the Io crust. This provides one mechanism for a Na-rich, Si-poor surface. However, although favored by many workers, elemental S is not a confirmed surface constituent. Consequently, we have studied whether direct interaction of silicates with SO₂, a confirmed surface constituent, can also produce Na-S compounds. SO₂-solid reactions producing CaSO₄ are likely to be important for Venus (2). The crustal cycling of SO₂ on Io, producing liquid SO₂ "aquifers" and geyser activity, has been discussed by Kieffer (3).

Experiments A likely Na-bearing SO₂-silicate reaction product is Na₂SO₄, but forming this requires an oxidizing agent or SO₂ disproportionation. The most likely reduced product should be elemental S or, possibly, Na-sulfides. SO₂ weathering experiments are therefore sensitive to redox conditions, and we are carrying out experiments under both oxidizing and reducing conditions. A wide range of interaction temperatures are possible. Crustal burial of SO₂ is likely, but above the critical temperature (~400K), the probability of crustal containment is unclear. Interaction at silicate magmatic temperatures (1400-1600K) may be unlikely, but it seems possible that mixtures of SO₂ and crustal silicates could periodically be capped by surface flows producing supercritical SO₂ at temperatures between the SO₂ critical point and magmatic temperatures. We have carried out experiments at 1000-1200K. In any case, these experiments can be used as a base for extrapolation to lower temperatures. Thus far, experiments in silica glass tubes have been made using soda-lime glass or albite crystals as silicates. It is clear that Io has undergone extensive igneous differentiation, and it is likely that most Fe is in a sulfide core; consequently soda-lime glass is a relatively plausible Io simulant. Run products are characterized using the SEM and by photoelectron spectroscopy (XPS).

Oxidizing conditions Conceptually, Na₂SO₄ formation is: Na₂O + SO₂ + 1/2 O₂. Convenient experiments are possible, decomposing K₂S₂O₈ to form SO₂. Free O₂ is formed and can be regarded as the oxidizing agent. (At experimental temperatures significant SO₃ is present, which could be the actual oxidizing agent, but the end result is the same.) A significant O₂/SO₂ for Io cannot be ruled out and has been suggested (4). For soda-lime glass, extensive Na₂SO₄ (low K/Na) formation occurs at both 923 and 1123K. In a single experiment with albite at 1123K the reaction product is an aluminous alkali sulfate with high K/Na. The albite and the K₂S₂O₈ were physically separated in this experiment; but we cannot rule out vapor phase K transport, although there is no evidence for this in the glass experiments. The albite result is surprising, but different reactions may occur under less extreme oxidizing conditions.

Reducing conditions A reducing agent that does not produce a stable sulfide will tend to react with SO₂ to produce elemental S [previously studied (1)], but a reducing (sulfurizing) agent which forms a stable sulfide promotes Na₂SO₄ formation. On Io this would be Fe or FeO; for initial experiments we used Cu metal plus silicates sealed in about 2 atm SO₂ (at high temperature). Extensive formation of Na₂SO₄ along with Cu

SO₂ WEATHERING ON Io: Johnson, M.L. et al.

oxides and sulfides (probably cuprous) occurred with both albite and soda-lime glass at 923K. Experiments are in progress with FeO-bearing silicates and SO₂ to test for Na₂SO₄ or Fe-Na-sulfide formation under less reducing conditions.

Pure SO₂ Weathering For Io models without FeO, S or O₂ there are no other obvious oxidizing and reducing agents; but SO₂ disproportionation is still possible. Somewhat surprisingly, albite sealed in SO₂ for 12 days at 873K showed relatively intense XPS sulfur peaks as shown in the Figure. The higher, more intense binding energy peak corresponds to an oxidized S species, probably Na₂SO₄, conceivably Na₂SO₃. The lower energy peak is due to a reduced species, elemental S or a Na-sulfide. Other XPS spectral regions demonstrate Na surface enrichment. This result was surprising in that the appropriate reactions should not go, thermodynamically. It is more likely that the oxidized S reflects a small amount of O₂ contamination in the SO₂, as there were vacuum problems in sealing off this sample. This interpretation was confirmed in a second experiment in which the SO₂ was trapped with liquid N₂ and the residual gas pumped until a pressure of less than 5 microns was obtained. The SO₂ was then released and sealed off with silicates. XPS analysis of albite heated to 1123K for a week showed no S peaks. Soda-lime glass heated in SO₂ at 1023K for 1 week showed a surface essentially totally coated with Na₂SO₄; however, no surface S could be detected on the SEM for a 2-week experiment at 923K. A quantitative measurement of the reaction rate at 1023K will be possible, but the apparent strong temperature dependence is surprising.

Summary Pure SO₂ appears not to weather albite. Reaction will occur at higher oxygen fugacities, but the minimum required fugacity is unknown. Na-rich glass is a plausible crustal constituent on Io; thus our soda-lime-glass experiments indicate that high temperature silicate-SO₂ interactions could produce Na-S compounds (probably Na₂SO₄) even if elemental S is not present. There is no observational evidence for Na₂SO₄ on Io based on 5 micron spectral bands; however, ≤25% Na₂SO₄ surface coverage is possible (5). Slow reaction rates could retard Na₂SO₄ formation.

References (1) M.L. Johnson and D.S. Burnett, *Geophys. Res. Lett.* 17, 981, 1990. (2) B. Fegley and R. Prinn, *Nature* 377, 55, 1989. (3) S. Kieffer, in *Satellites of Jupiter*, D. Morrison, ed. (4) S. Kumar and D.M. Hunten, *ibid.* (5) R.R. Howell, D.B. Nash, T.R. Geballe, D.P. Cruikshank, *Icarus*, 78, 27, 1989.

