The Reflection Spectrum of Liquid Sulfur: Implications for lo

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The spectral reflectance from 0 38 to 0.75 μ m of a column of liquid sulfur has been measured at several temperatures between the melting point (~118°C) and 173°C. Below 160°C the spectral reflectance was observed to vary reversibly as a function of temperature, independent of the previous thermal history of the column. Once the temperature exceeded 160°C, the spectrum would not change given a subsequent decrease in temperature The spectral reflectance of the liquid-sulfur column at all temperatures was very low (10–19%) Combining this information with Voyager spectrophotometry of Jupiter's satellite Io, it is concluded that liquid sulfur at any temperature on Io's surface would be classified as a "black area" according to the standards used by the Voyager imaging team in their spectrophotometric analysis (L Soderblom, T V. Johnson, D. Morrison, E. Danielson, B L. Smith, J. Veverka, A Cook, C Sagan, P Kupferman, D Pieri, J Mosher, C Avis, J. Gradie, and T. Clancy (1980). *Geophys. Res Lett.* 7, 963–966).

INTRODUCTION

For many years, investigators have suggested that solid sulfur might be a major surface component of Jupiter's satellite Io. This suggestion was based on the similarity between Io's spectral geometric albedo in the ultraviolet-visible range and laboratory reflectance spectra of solid sulfur (Wamsteker et al., 1974; Sill, 1973; Fanale et al., 1974). Sulfur-salt mixtures provided improved spectral agreement (Nash and Fanale, 1977). The detection of ionized species of the Io-associated circumiovian toroid (Kupo et al., 1976) and the development of the widely accepted sputtering mechanism for the Iogenic origin of this material (Matson et al., 1974) provided further support for the hypothesis that a condensed phase of sulfur is present on Io's surface.

Nelson and Hapke (1978) suggested that orange-red allotropes of sulfur might provide a still better fit to Io's spectral geometric albedo, noting from chemistry literature

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that these allotropes can be made by heating sulfur above its melting point and then rapidly quenching the melt to low temperature. They suggested that the presence of such allotropes would imply a volcanic origin. The proposed tidal heating mechanism of Peale *et al.* (1979) and the discovery of active volcanoes by the Voyager spacecraft (Morabito *et al.*, 1979) are consistent with this hypothesis.

Sagan (1979) suggested that the unusual temperature–viscosity property of liquid sulfur (it changes in viscosity above 160°C by a factor of $\sim 10^3$) would lead to a characteristic morphology–color association for sulfur lava extrusions, and proposed that the observed color relationships in fluvial patterns associated with Ionian calderas are consistent with liquid-sulfur flows. These color–viscosity relationships have been mathematically modeled and have been used as an independent argument for sulfur flows on Io (Pieri *et al.*, 1983; Baloga *et al.*, 1983).

THE PROBLEM

The unusual properties of quenched sulfur have been discussed extensively, partic-

ularly by the analytical chemistry group at the University of Washington (see, e.g., Meyer, 1964). They interpret the behavior of quenched sulfur as due to the presence of short-chain sulfur polymers in the liquid at temperatures between the melting point (~118°C) and 160°C. At 160°C long-chain polymers are formed which increase the viscosity of the melt by several orders magnitude. They report that the color of the melt is preserved upon rapid quenching to liquid-nitrogen temperatures (77°K), indicating that the polymeric structure is retained in the quenched melt. These colors are shown in published transmission spectra of sulfur allotrope films (Meyer et al., 1971). They note that the presence of impurities, particularly carbon, will cause the quenched melt to appear brown rather than red.

For the interpretation of Voyager images of Io, it would be desirable to produce reflection spectra of sulfur allotropes made from quenched sulfur melts. Although this problem appears straightforward, attempts by our group to produce quenched melts



FIG. 1. Schematic representation of the glass container used to produce the column of liquid sulfur measured in this study.

while retaining characteristic allotrope colors have been unsuccessful. This may be due to contamination and/or to quenching rate problems. Therefore, we leave this question open and in the present paper address only the question of the spectral reflectance of molten sulfur as a function of temperature.

Because Io is the most volcanically active body in the solar system, with very high estimated resurfacing rates (Johnson *et al.*, 1979; Pieri *et al.*, 1983), there is a possibility that a small fraction of Io's surface might at times be molten sulfur, as suggested by Sagan (1979). Therefore, it might be possible to combine these data with Voyager spectrophotometric information (Soderblom *et al.*, 1980) to identify those areas on Io which may have been covered by molten sulfur at the time of the Voyager encounters.

EXPERIMENTAL PROCEDURE

A special glass column was constructed so that it could be filled with powdered sulfur, and the reflection spectrum of a 3.8-cm thickness of molten sulfur could be measured. The column was filled under argon with USP grade sublimed sulfur manufactured by Mallinckrodt Inc. It was evacuated, $(P = 50 \ \mu g \ Hg)$ sealed and wrapped with heater tape over its entire length, except for the topmost position and the window. Figure 1 shows a schematic of the glassware. The temperature was monitored by an iron-constantan thermocouple in contact with the glass on the side of the column near the window. The temperature was regulated by a thermister activated temperature controller which was also in contact with the glass near the window.

The hemispheric spectral reflectance of the top surface of the column of liquid sulfur was measured through the window using a Beckman DK-2 recording spectrophotometer in the spectral range $0.375 \ \mu m < \lambda$ $< 0.75 \ \mu m$. The incident beam was normal to the window. Further details of this system and a variety of spectra from flat surface particulate mixtures are found in Nash and Fanale (1978).

We note that the reflection spectra obtained by this procedure differ from bidirectional reflectances. We have measured the bidirectional reflectance and the hemispherical reflectance of the same particulate sulfur used in this study, and there are some noteworthy differences. We have found that longward of 0.6 µm the bidirectional reflectance decreases as wavelength increases (Nash et al., 1980). However, the hemispherical reflectance of the same powdered-sulfur sample in the same wavelength range increases as wavelength increases (Nash and Fanale, 1978). This serves to highlight once again the need for spectrogoniometric study of laboratory materials before highly quantitative comparisons can be made using laboratory spectra and planetary spectral geometric albedos. The enhanced redness of reflectance curves obtained by bidirectional methods over those obtained by integrating spheres has been noted by others (Gradie and Veverka, 1982).

To correct for any contributions that the window might make to the spectral reflectance of the contents of the column, the spectral reflectance of the powdered sulfur was measured prior to heating and ratioed to the spectral reflectance of sulfur powder measured by conventional procedures (i.e., Nash and Fanale, 1978). This result, which represents the spectral properties of the window in the relevant viewing geometry, was used to correct the liquid-sulfur spectra that were gathered later. Because the spectral reflectance of the liquid was very low at all wavelengths, we measured it relative to a MgO standard that had been darkened with graphite. (This was done in order to compensate for the fact that our spectrophotometer has only two gain states both of which were too high.) This intermediate standard has been previously calibrated against freshly smoked MgO. The reflectances presented here are corrected for the intermediate standard and the window effects, and are therefore, relative to freshly smoked MgO, a conventional reflectance standard in the near uv-vis-ir.

The temperature in the column was slowly increased until melting began, and held constant until all the sulfur powder in the column had melted. Great care was taken to remove bubbles from the inside of the window.

A series of spectral reflectance measurements was made at temperatures beginning at the melting point (~118°C), and advancing in approximate 10°C intervals up to but not including 160°C. The temperature was then slowly reduced in constant decrements to 118°C, during which time a second series of spectral reflectance measurements was made. A third series of spectral reflectance measurement was performed as the temperature was increased again up to but not including 160°C. At each stepwise increase or decrease in temperature, a 30-min interval elapsed between the last adjustment of the temperature controller and the time of measurement of the spectral reflectance in order to allow the entire column to equilibrate at constant temperature at the time of the measurement. The color of the liquid sulfur was observed to change with temperature from yellow at or near 118°C to light red at ~156°C. Below 160°C this process was reversible and the same spectral reflectance was observed independent of the previous thermal history of the column.

The temperature was then left at 156° C for ~20 hr and the same procedure of stepwise temperature reduction down to 118° C and up again was repeated. The spectral reflectances measured did not differ from those of the previous run. The results of both runs are presented in the upper six spectra of Fig. 2.

The temperature was then raised above 160°C and the spectral reflectance measured at 162 and 173°C. An abrupt drop in spectral reflectance was noted at all wavelengths for temperature above 160°C, the effect being especially noticeable in the red. When the temperature had exceeded 160°C



FIG 2. Reflection spectra of the top of the molten liquid column at selected temperatures. Below 160°C the color changed as a function of temperature. Once the column was heated about 160°C the color would not change if the temperature was lowered again to just above the melting point.

the color change was irreversible. When the temperature was lowered to 120°C and held constant for 20 days, the spectral reflectance did not change. These spectra are shown as the lower two curves in Fig. 2.

Between 118 and 156°C the shift in wavelength at 10% relative reflectance as a function of temperature of the absorption edge of liquid sulfur is 4.54 Å/°C. This compares well with the value of 5.0 Å/°C reported by Meyer *et al.* (1972) for transmission spectra of thin films of sulfur over the same temperature range.

DISCUSSION

Our results show that at all temperatures at which sulfur is liquid, its spectral reflectance $(0.35 \,\mu\text{m} < \lambda < 0.75 \,\mu\text{m})$ measured is quite low, the maximum being 19% at 118°C ($\lambda = 0.75 \,\mu\text{m}$). When this result is compared to the spectrophotometry of selected areas on Io reported by the Voyager team (Soderblom *et al.*, 1980; Clancy and Danielson, 1981) we conclude that all those Io areas are too reflective to be liquid sulfur, except for the regions classified as "black caldera floor material" which have reflectivities less than 25% at all Voyager camera wavelengths. Molten sulfur at any temperature would be classified as "black" by the Voyager imaging results.

These black areas constitute approximately 5% of Io's total surface area (Carr et al., 1979. However, groundbased thermal infrared studies put a fractional limit of $\sim 10^{-4}$ for temperatures higher than 77°C (Morrison and Telesco, 1980). Since liquid sulfur must be hotter than 77°C, at most $\sim 0.2\%$ of the black spots observed on Io by Vovager could be molten sulfur. This implies that the remaining black spots are solid, and subject to resurfacing from other volcanic deposits. If so, given plume particulate resurfacing rates reported by Johnson et al. (1979), then the lifetime of a typical black spot (once solidified) is $\sim 10^4$ years, assuming 1 cm of covering material is required to obliterate a black spot. With the floor resurfacing rates of Pieri et al. (1983), this lifetime would be much less.

The finding that liquid sulfur at any temperature appears black to Voyager cameras has several additional implications for Io volcanism. First, the uniformly low albedo of molten sulfur implies that active sulfur calderas need not have been heated to the temperature range of black sulfur, but could have any range of temperatures above 118°C. This is consistent with the range of temperature-dependent flow morphologies observed (Pieri et al., 1983). Furthermore, some isolated flows on Io appear quite dark in the Voyager imaging data. These are consistent with either quenched black sulfur flows or active liquid flows with little or no overcrusting (Pieri et al., 1983), although the thermal data (Morrison and Telesco, 1980) severely limit the fractional area which may be liquid sulfur.

Finally, (a) if liquid-sulfur flows existed on Io during the Voyager encounters, (b) if quenching does effectively preserve the original allotropic colors (Nelson and Hapke, 1978), and (c) if the variegated and systematic color-morphology associations in flows are indeed the result of cooling sulfur lavas (Sagan, 1979), then nearly all flows on Io were either inactive at the time of the Voyager encounters, or most of the active flows were roofed over by quenched sulfur crusts.

CONCLUSION. FUTURE WORK

The spectral reflectance of liquid sulfur decreases and reddens as temperature increases. The overall spectral reflectance of liquid sulfur at all temperatures at which sulfur is molten is so low that any molten sulfur on Io's surface would have appeared black in the Voyager spacecraft images. In future missions (particularly Galileo), the imaging experiment might be suitably configured to make color distinctions between the very dark regions on Io.

Several outstanding questions remain. It has yet to be shown that large masses of sulfur will retain their color upon quenching. Ultrapure sulfur may be required in order to observe this effect. If so, we must understand how such purity is maintained in the presence of other likely materials such as the sulfides of sodium and potassium and sulfur dioxide.

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