CAN METASTABLE SULFUR ALLOTROPES EXIST ON IO? J.I. Moses, Caltech 170–25, Pasadena, CA 91125, AND D.B. Nash, San Juan Institute, 31878 Camino Capistrano, Suite 278, San Juan Capistrano, CA 92675

Considerable controversy exists regarding the presence or absence of elemental sulfur on Jupiter's satellite Io. The evidence for sulfur and sulfur compounds on and about Io has been reviewed recently (1). Although S_8 has been directly identified in emission in the thermal infrared spectra of Io (2), the suggestion that elemental sulfur (S_8) covers an extensive fraction of the surface of Io has been seriously questioned (3). Brightness changes associated with temperature–dependent behavior of the S_8 molecule are not observed on Io (4), and thick deposits of elemental sulfur are inconsistent with the observed topography on Io (5). We suggest that metastable sulfur allotropes formed during the "normal" cooling of a sulfur melt (as opposed to cooling by rapid quenching) can persist under certain geologic conditions on Io and may help alleviate objections concerning the presence of large amounts of stable orthorhombic α–S_8 on Io.

We find that sulfur samples that were heated to 393 K and 453 K for various lengths of time (up to 50 hours), then cooled quickly and kept at various temperatures after solidification (260 K to 318 K) show significant brightening at visible wavelengths as phase transformations from metastable to stable allotropes are initiated. The rate of spectral variation associated with the phase transformation depends on the original temperature of the melt, the length of time the samples remained molten, and the temperature at which the samples were kept after solidification. Figure 1 shows the reflectance variation of a monoclinic β–sulfur sample as it converts to stable orthorhombic α–sulfur, and Figure 2 shows the reflectance variation of a sample that contains about 25% polymeric molecules as well as the S_8 that originally began in a monoclinic (β) crystal lattice. The pure β–sulfur takes hours to convert to α–sulfur at 295 K, but polymers inhibit complete conversion to α–sulfur so that the metastable polymeric molecules within the solid can remain for years at 295 K.

The parameter that has the most potential for affecting the transformation rate is the "aging temperature" or the temperature at which the sulfur remains after solidification. The $\beta - \alpha$ transformation rate varies with aging temperature as illustrated in Figure 3, where the time constant on the ordinate represents the time required for the bulk of the transformation to have occurred. Both phase transformation theory and our data indicate that the transformation rate is exponential with temperature at low temperatures so that we can use Figure 3 to estimate the transformation rate at typical dayside temperatures on Io. We find that the $\beta - \alpha$ transformation at 120 K on Io would take $\sim 10^5$ years, quite a long time compared with Io's rapid resurfacing rate (1). The conversion of polymeric sulfur into α–sulfur would take even longer. Of course, these timescales presuppose that the sulfur cools infinitely quickly. In reality, any sulfur on Io would lose heat at a finite rate, and we need to determine how long the metastable allotropes are exposed to the temperature region at which the transformation rate is a maximum ($\sim$ 340 K) in order to determine whether significant progress in the β to α transformation could have occurred during the cooling process.

Cooling calculations that include both evaporative and radiative cooling indicate that small droplets (less than 1 cm radius) of liquid sulfur ejected during plume eruptions on Io can cool rapidly enough to preserve both monoclinic β–sulfur and polymeric μ–sulfur (e.g. Table 1). However, large pools or flows of molten sulfur will cool too slowly to preserve β–sulfur, although some polymeric sulfur may be retained. We conclude that metastable allotropes such as β– or μ–sulfur may be present on Io in areas of volcanic plume deposits and that some μ–sulfur may be found in areas where high–temperature ($>$ 432 K) liquid sulfur has collected before solidification (such as in calderas or in the source regions of volcanic sulfur flows). Since the metastable sulfur allotropes are generally darker and do not brighten as much as α–sulfur with a decrease in temperature, the "post–eclipse brightening" problem is not as serious if one considers metastable sulfur allotropes as well as orthorhombic α-sulfur.

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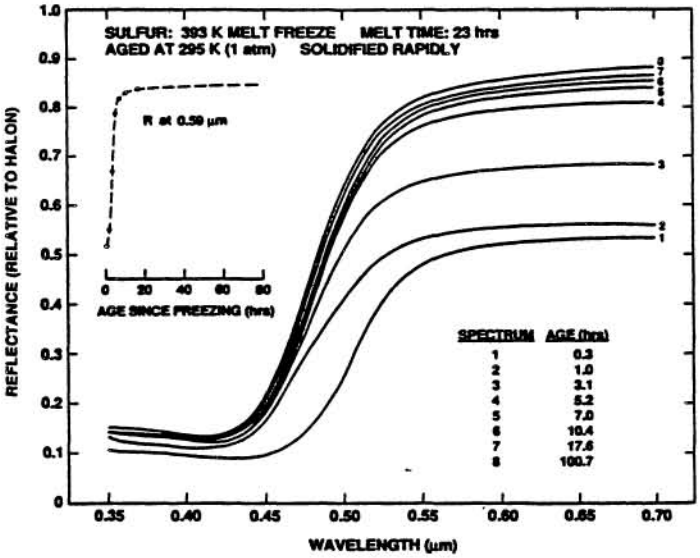

Figure 1. Temporal variation in the spectral reflectance of monoclinic sulfur at 295 K. The monoclinic (β) sample was created by heating and melting powdered sulfur α–sulfur at 393 K for 23 hours in a dry, N_2–filled oven, then by allowing rapid crystallisation at 295 K.

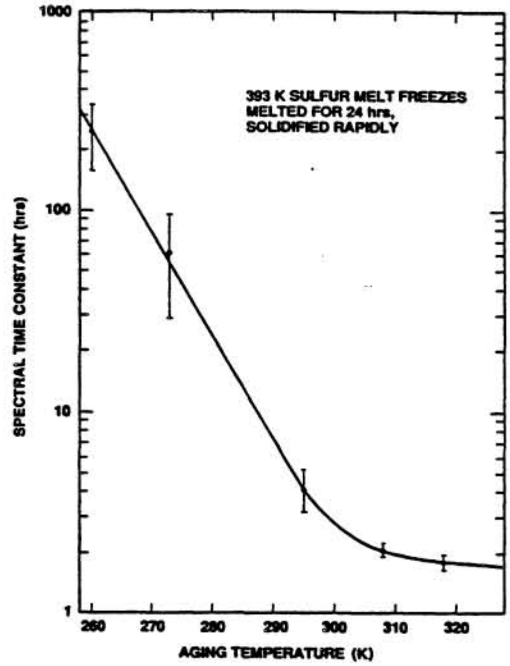

Figure 3. The effect of aging temperature on the transformation rate of β–sulfur into α–sulfur. The spectral time constant (ordinate) is inversely proportional to the transformation rate.

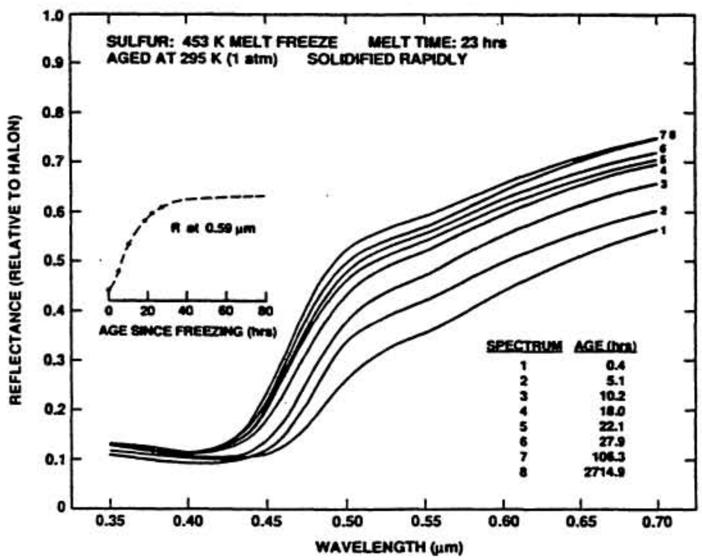

Figure 2. Temporal variation in the spectral reflectance of a 453 K sulfur melt freeze (β–sulfur plus μ–sulfur) sample that was heated to 453 K for 23 hours in a N_2–filled oven. The sample solidified and aged at 295 K.

Table 1: Time sequence for a molten sulfur droplet 0.1 μm in radius, imaginary refractive index $k = 10^{-3}$, cooling from 453 K to 120 K.

t (sec)	Radius (μm)	T (K)
0	1.00×10^{-1}	453
1.08×10^{-2}	9.62×10^{-2}	433.9
4.31×10^{-2}	9.29×10^{-2}	410.0
1.16×10^{-1}	9.09×10^{-2}	391.4
1.00	9.05×10^{-2}	382.7
10.0	8.99×10^{-2}	349.4
100	8.99×10^{-2}	246.6
1000	8.99×10^{-2}	133.0
4210	8.99×10^{-2}	120.0