SULFUR AND IRON SPECIATION IN GAS-RICH IMPACT-MELT GLASSES FROM BASALTIC SHERGOTTITES DETERMINED BY MICROXANES.

S. R. Sutton[1], M. N. Rao[2], and L. E. Nyquist[3], [1]Dept. of Geophysical Sciences and CARS, University of Chicago, Chicago, IL, 60637; [2]ESCG – Jacobs, Johnson Space Center, Houston, TX, 77058; [3]ARES, NASA Johnson Space Center, Houston, TX, 77058.

Introduction: Sulfur is abundantly present as sulfate near Martian surface based on chemical and mineralogical investigations on soils and rocks in Viking, Pathfinder and MER missions. Jarosite is identified by Mössbauer studies on rocks at Meridian and Gusev, whereas $MgSO_4$ is deduced from $MgO - SO_3$ correlations in Pathfinder MER and Viking soils. Other sulfate minerals such as gypsum and alunogen/ S-rich aluminosilicates and halides are detected only in martian meteorites such as shergottites and nakhlites using SEM/FE-SEM and EMPA techniques [1-4]. Because sulfur has the capacity to occur in multiple valence states, determination of sulfur speciation (sulfide/sulfate) in secondary mineral assemblages in soils and rocks near Mars surface may help us understand whether the fluid–rock interactions occurred under oxidizing or reducing conditions.

On Earth, volcanic rocks contain measurable quantities of sulfur present as both sulfide and sulfate. Carroll and Rutherford [5] showed that oxidized forms of sulfur may comprise a significant fraction of total dissolved sulfur, if the oxidation state is higher than ~ 2 log fO_2 units relative to the QFM buffer. Terrestrial samples containing sulfates up to ~25% in fresh basalts from the Galapagos Rift on one hand and high sulfide contents present in oceanic basalts on the other indicate that the relative abundance of sulfide and sulfate varies depending on the oxygen fugacity of the system [5,6].

Basaltic shergottites (bulk) such as Shergotty, EET79001 and Zagami usually contain small amounts of sulfur (~0.5%) as pyrrhotite. But, in isolated glass pockets containing secondary salts (known as GRIM glasses) in these meteorites, sulfur is present in high abundance (~1-12%) [3,7,8]. To determine sulfur speciation (sulfide, sulfate or elemental sulfur) in these glasses, Gooding et al. [8] and Burgess et al. [9] carried out vacuum pyrolysis experiments on these GRIM glasses (also called Lith C) using quadrupole mass-spectrometric methods. They found that the evolved S-bearing gases from these samples consisted of both SO_2 (from sulfate) and H_2S (from sulfide) in varying proportions. However, as mass-spectrometric studies do not provide details about spatial association of these S-species in these samples, we have studied the spatial distribution of sulfides and sulfates in GRIM glasses using sulfur K micro-XANES techniques in the present study. The microscale speciation of S may have important implications for the Rb-Sr isotope systematics of EET79001 Lith C glasses [10].

In reference to oxidative weathering of surface basalts on Mars yielding secondary iron sulfates, Solberg and Burns [11] examined a GRIM glass in EET79001 by Mössbauer spectroscopic techniques and showed that the percentage of Fe^{3+} in Lith C is <2%. They suggested that the Lith C contains very little Fe^{3+} despite the occurrence of oxidized sulfate in them, indicating that the conditions leading to the formation of these glasses were insufficiently oxidizing to produce Fe^{3+} from Fe^{2+} in these glasses. To understand the implications of these observations for the formation of the GRIM glasses, we determined the oxidation state of Fe in the GRIM glasses using Fe K micro-XANES techniques.

The S and Fe K micro-XANES measurements were performed on thin sections from EET79001: 506 from Lith A and 507 from Lith B.

Results: (a) *Oxidation state of Fe in GRIM glasses 506 and 507 from EET79001.* In 506, two XANES line scans were measured. The Fe oxidation was uniform along both traverses with mean values of 2.06 ± 0.02 (1σ) and 2.11 ± 0.03, respectively. In 507, the Fe oxidation state was also uniform along a traverse with a mean value of 2.07 ± 0.03. These results are consistent with the Fe in all these glasses being dominated by the ferrous state, consistent with the Mössbauer results [11].

(b) *Oxidation state of S in Lith B (507) GRIM glass*: S K XANES spectra were obtained for twenty, sulfur-bearing spots in a globule-rich area in this glass. All but one of these spectra were qualitatively similar showing a first peak at ~2470 eV and a broader second peak at ~2478 eV (Fig. 1). The first peak is diagnostic for iron sulfide species (e.g., [12]). The second peak is partially a multiple scattering feature from the iron sulfide but the low intensity ratio of the first to second peak indicates the presence of another species (Fig. 1). There are two possible interpretations for this additional component: other monosulfides or a more oxidized species. Monosulfide spectra can have first peak energies up to 2478 eV [12] and a mixed monosulfide interpretation has been suggested for sulfur speciation in reduced basaltic glasses [13]. Based on the major element composition of the GRIM glasses, MgS and CaS are the most likely candidates. However, previous electron microprobe analyses on these GRIM

glasses showed a strong correlation between Fe and S [7] but no correlation between S and Mg or Ca. These results argue against this second species being one or more monosulfides. The presence of a more oxidized component, most likely coordinated with Fe, is required.

One of the twenty spot spectra is clearly sulfate (S^{6+}) showing the diagnostic first peak at 2482 eV (Fig. 2). However, in all other spectra, the 2482 eV sulfate peak is absent so that this oxidized component is most likely sulfite (S^{4+}). Sulfite has a sharp first peak at 2478 eV [12], a peak that is apparent in the glass spectra to varying degrees but is never dominant. The intensity of the sulfide first peak (2470 eV) relative to the above-edge normalization level indicates that the sulfide/sulfite ratio is variable ranging from about 1 to 3, i.e., sulfide dominant in most spots.

(c) Oxidation state of sulfur in Lith A (506) GRIM glass: The spectra for 506 glass are quite distinct from those for 507 showing a broad band (peak) between 2470 eV and 2480 eV suggesting mixed speciation (Fig. 3). In contrast to the 507 glass, electron microprobe measurements on the 506 glass indicated no correlation between Fe and S but strong correlations between S, Ca and Al [7]. These results indicate that the dominant S coordination is likely to be with Ca and the XANES spectrum for CaS [12] is qualitatively similar to these glass spectra. The main difference is that the glass spectra typically have significant intensity at ~2470 eV, presumably associated with minor FeS, and variable intensity at ~2480 eV, likely to be associated with $CaSO_4$. Thus, we interpret the 506 glass spectra to derive from coordination mixtures of Ca sulfide, Ca sulfate/sulfite and minor Fe sulfide with most spectra dominated by Ca sulfide coordination. A line scan across a 506 glass veinlet showed an oxidation state gradient with significant sulfate on the exterior (silicate contact) of the glass vein even though the Fe oxidation state remained uniform.

The occurrence of both reduced (sulfide) and oxidized (sulfate/sulfite) sulfur species in the GRIM glasses is in general consistent with the quadrupole mass-spectrometric/vacuum pyrolysis results on sulfur speciation [8,9].

Conclusions: (a) Iron in the 506 and 507 glasses is divalent consistent with the Solberg and Burns [11] Mössbauer measurements. (b) Sulfur in the 507 glass is a mixture of Fe sulfide and sulfite/sulfate with sulfide being more abundant. Only one sulfate-dominated spot was observed in the 507 glass indicating that highly oxidized sulfur is rare. (c) Sulfur in the 506 glass is dominated by Ca sulfide coordination with possible minor additions of Fe sulfide and Ca coordinated with oxidized sulfur. A sulfur oxidation state gradient was observed in a 506 glass veinlet with more reduced glass on the interior and oxidized sulfur on the exterior of the veinlet.

Thus, the sulfur speciation in both glasses is dominated by sulfide speciation. In Lith B (507), the coordination is between Fe and S whereas in Lith A (506), the dominant coordination for S is not with Fe but with another cation, most likely Ca. If the differences between GRIM glasses in A and B are substantiated by further analyses, it will have fundamental implications for our understanding of the genesis of EET79001, and possibly provide evidence for recent weathering processes in the Martian regolith.

References: [1] Gooding J. L. and Muenow D. W. (1986) *GCA, 50,* 1049-1059. [2] Wentworth S. J. et al. [2005] *Icarus, 174,* 383-395. [3] Rao M. N. et al. (1999) *GRL, 26,* 3265-3268. [4] Treiman A. H. et al. (1993) *Meteoritics, 28,* 86-97. [5] Carmichael I. S. E. and Ghiorso M. S. (1986) *EPSL, 78,* 200-210. [6] Carroll M. R. and Rutherford M. J. (1988) *Am. Min., 73,* 845-849. [7] Rao M. N. et al. (2004) *LPS XXXV,* #1501. [8] Gooding J. L. et al. (1990) *Meteoritics, 25,* 281-289. [9] Burgess R. et al. (1989) *EPSL, 93,* 314-320. [10] Nyquist L.E. et al. (1986) *LPS XVII,* 624-625. [11] Solberg T. C. and Burns R. G. (1988) *Proc. Lun. Planet. Sci. Conf. 19th,* 313-322. [12] Fleet M. E. (2005) *Can. Min., 43,* 1811-1838. [13] Fleet M. E. et al. (2005) *Can. Min., 43,* 1605-1618.
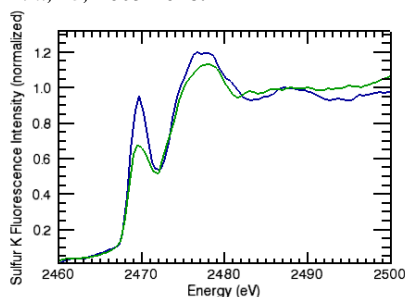

Fig. 1: Two spots on 507 glass showing high sulfide (blue) and lower sulfide (green) content based on the relative intensity of the 2470 eV peak.
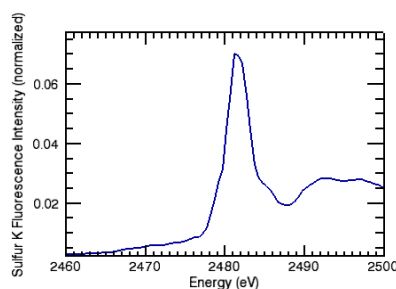

Fig. 2: The single 507 spot showing a sulfate spectrum identified by the sharp 2482 eV peak.
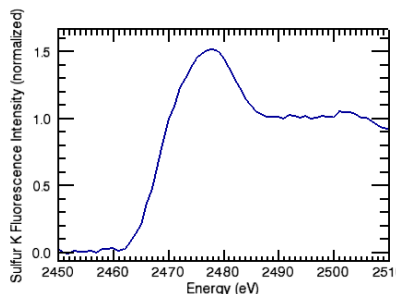

Fig. 3: Typical 506 glass spectrum showing a broad intermediate energy peak interpreted as due principally to Ca-S coordination.