

**IDENTIFICATION OF MARTIAN REGOLITH SULFUR COMPONENTS IN SHERGOTTITES USING SULFUR K XANES AND Fe/S RATIOS.** S.R. Sutton<sup>1,2</sup>, D.K. Ross<sup>3</sup>, M.N. Rao<sup>4</sup> and L.E. Nyquist<sup>5</sup>, <sup>1</sup>Dept. Geophys. Sci. and <sup>2</sup>CARS, Univ. of Chicago, Chicago, IL 60439 (sutton@cars.uchicago.edu), <sup>3</sup>Jacobs Tech, NASA Johnson Space Center, Houston, TX 77058, <sup>4</sup>SCI, NASA Johnson Space Center, Houston, TX 77058, <sup>5</sup>ARES, NASA Johnson Space Center, Houston, TX 77058.

**Introduction:** Based on isotopic anomalies in Kr and Sm [1], Sr-isotopes [2], S-isotopes [3], XANES results on S-speciation [4], Fe/S ratios in sulfide immiscible melts [5], and major element correlations with S [6] determined in impact glasses in EET79001 Lith A & Lith B and Tissint, we have provided very strong evidence for the occurrence of a Martian regolith component in some impact melt glasses in shergottites. Using REE measurements by LA-ICP-MS in shergottite impact glasses, Barrat and co-workers [7,8] have recently reported conflicting conclusions about the occurrence of Martian regolith components: (a) Positive evidence was reported for a Tissint impact melt [7], but (b) Negative evidence for impact melt in EET79001 and another impact melt in Tissint [8]. Here, we address some specific issues related to sulfur speciation and their relevance to identifying Martian regolith components in impact glasses in EET79001 and Tissint using sulfur K XANES and Fe/S ratios in sulfide immiscible melts. XANES and FE-SEM measurements in ~5  $\mu\text{m}$  size individual sulfur blebs in EET79001 and Tissint glasses are carried out by us using sub-micron size beams, whereas Barrat and co-workers used ~90  $\mu\text{m}$  size laser spots for LA-ICP-MS to determine REE abundances in bulk samples of the impact melt glasses. We contend that Martian regolith components in some shergottite impact glasses are present locally, and that studying impact melts in various shergottites can give evidence both for and against regolith components because of sample heterogeneity.

**Sulfur K XANES spectra of PTS #507:** Sulfur K XANES spectra for the impact glasses in polished thin section (PTS) #507 (EET79001, Lith B) and in PTS #506 (EET79001, Lith A) obtained by [4] are shown in Figs. 1 and 2, respectively. The pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ) spectrum (standard) in Fig. 1 shows two characteristic peaks: (a) one sharp primary peak at 2470 eV and (b) a secondary broad peak at ~2477 eV [9]. We have superimposed the pyrrhotite standard S K XANES spectrum over the XANES spectrum taken for typical sulfide blebs (~5  $\mu\text{m}$ ) in EET79001 #507 glass such that the amplitude of the 2470 eV peak is matched in the two spectra. This comparison shows that the relative intensity of the second peak (b) at ~2477 eV is much higher for #507 than for the pyrrhotite standard (*cf.* [9]); the intensity ratio b/a is ~1.1 in pyrrhotite but ~1.5-1.8 in the #507 sulfide blebs. The intensity enhancement at

~2477 eV is due to the occurrence of an *additional* sulfur component in sulfide blebs in #507 glass that is absent in the pyrrhotite standard. This additional component could be a sulfite  $\text{S}^{4+}$  species and/or mono-sulfides, such as CaS, MgS, or MnS, since these display characteristic peaks at 2477 eV [9]. However, the presence of mono-sulfides is unlikely because major element abundance studies [6] show that Ca and Mg are uncorrelated with S, whereas Fe shows a positive correlation with S ( $r^2 \sim 0.85$ ) [6]. These results suggest the presence of “Fe-sulfites” in the #507 blebs rather than monosulfides. Since crystalline sulfites have relatively sharp peaks near 2477 eV [9] and the bleb peak at that energy is broad, peak broadening is indicated resulting from the sulfite component being present in an amorphous state.

Sulfur cannot exist as “sulfite” near the Martian surface, which is highly oxidized, and no “sulfite” has been observed on Mars. To explain the #507 result, we propose the following scenario. Initially, Fe-sulfate minerals (ubiquitously occurring on Mars) were entrained into basaltic precursors prior to a glass-forming impact. On impact, shock-reduction occurred in shock-molten material where some of the sulfate was reduced *in-situ* to sulfide in some areas, but only partially reduced to “sulfite” in some other areas. In this way, both Fe-sulfide and Fe-sulfite can occur together in the shock-glass. (Although photo-reduction of sulfate to sulfite during XANES measurements is a possibility, we consider it unlikely in our case because of low sulfate abundance in #507).

**Fe/S (atomic) ratios in PTS#506: Extraneous Fe, S:** By FE-SEM studies of several sulfide blebs in EET79001,507 and in Tissint glasses, we found that the Fe/S (atomic) ratios are >1 (range: 1.03 – 1.19, some cases ~1.3), whereas igneous pyrrhotite globules yield Fe/S (atomic) ratios of ~0.89 – 0.93 [5]. These results indicate that the sulfide blebs in EET79001 and Tissint melt pockets are different from the immiscible sulfide globules produced by shock-melting of igneous pyrrhotite in the host rock. Because the Fe/S (atomic) ratios in impact-melt blebs are higher than those in the sulfide globules produced from igneous pyrrhotite, the presence of an additional mineral phase contributing only Fe but no S to the impact-melt sulfide blebs is indicated. One possibility is that some FeO phase (such as goethite which occurs ubiquitously on Mars) was entrained into the glass precursor along with Fe-

sulfate prior to impact. On impact, this mineral assemblage could have melted and formed an immiscible sulfide fluid *in-situ* as result of shock-reduction of Fe-sulfate (plus FeO) to Fe-sulfide. This fluid, on quenching, would have produced sulfide blebs with Fe/S >1.

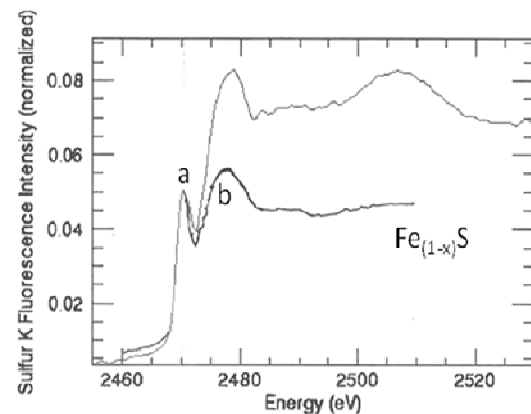
**Ca-sulfate in PTS#506:** Compared to the ubiquitous sulfide bleb clusters found in the #507 glass, there are few igneous Fe-sulfide globules in #506. Sulfur excesses are found in veins and fracture flows which yield negative Fe-to-S correlations in contrast to the positive Fe-to-S correlations seen in #507 [6]. However, the #506 glass shows positive CaO-to-S and Al<sub>2</sub>O<sub>3</sub>-to-S correlations which are absent in #507 [6].

Also in contrast to #507, the S K XANES spectra in #506 glass veins (Fig. 2) do not show a 2470 eV peak indicating the near-absence of Fe-sulfide in this glass [4]. However, the spectra for #506 display the broad peak at ~2477 eV that is characteristic of mono-sulfides, such as CaS and MgS as noted above. Among the three spectra shown in Fig. 2 for different glass vein positions in #506, two of them are similar to a CaS spectrum (broad peak at ~2477 eV) with a small shoulder at 2470 eV. However, the third spectrum yielded a peak at ~2482 eV clearly indicating the presence of the Ca-sulfate species. The minor shoulder near 2470 eV in all three cases is due to a small contribution from dissolved FeS in this glass. These results indicate the presence of Ca-sulfate (peak at 2482 eV) in one vein spot and Ca-sulfide (~2477 eV peak) in the other two spots. As noted above, elemental abundance studies in #506 show a positive correlation between Ca and S. Note that CaS (oldhamite) never has been reported in Martian meteorites. Thus, the Ca-to-S association found in these glasses must be due to CaSO<sub>4</sub>, which occurs ubiquitously on Mars, and which was entrained into glass precursors prior to impact. On impact, it was shock-reduced to a Ca-sulfide *in-situ*.

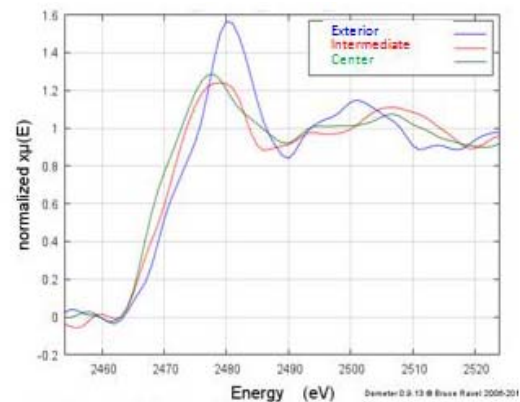
**Tissint black glass:** Here, we consider the relevance of these results to studies of black glass in Tissint [5]. In one melt-pocket (A) in Tissint, we found blebs with Fe/S (atomic) ratios >1 (range: 1.0-1.2), whereas in another melt-pocket (B) we found Fe/S ratios <1 (range: 0.49 – 0.81). To explain the results for (B), we suggest that there are other sources of sulfur, such as Ca-sulfate, present in the glass-precursor material for melt-pocket (B), which on shock-reduction was reduced *in-situ* to CaS during impact. This Ca-sulfide phase is responsible for bringing the Fe/S ratios down to ~0.5. On the other hand, the results for pocket (A), where the Fe/S ratios are >1, indicate the presence of Fe-sulfate plus an FeO-phase in the glass-precursors as noted above. Presently, we are planning to study additional Tissint glasses using S K XANES techniques.

**Conclusions:** Small amounts of sulfate-rich Martian regolith material were entrained heterogeneously into the impact glass precursors in some shergottites. Bulk Ce (REE) measurements of black glasses using ~90 μm LA-ICP-MS beams [7,8] may not have the requisite sensitivity to resolve redox changes like those recorded at the microscale in some glass veins within shergottites.

**References:** [1] M.N. Rao et al. (2011) JGR, 116, E08006. [2] L.E. Nyquist et al. (2012) 75<sup>th</sup> Met. Soc. Abs. #5262. [3] M.N. Rao et al. (2010) LPS XXXXI abs. #1161. [4] S.R. Sutton et al. (2008) LPS XXXIX, abs. #1961. [5] D.K. Ross et al. (2012) LPS XXXIV, abs. #1715. [6] M.N. Rao et al. (2004) LPS XXXV abs. #1501. [7] C.H. Aoudjehane et al. (2012) Science, 338, 785-788. [8] J.A. Barrat et al. (2013) GCA, 125, 23-33. [9] M.E. Fleet et al., (2005) Can. Min. 43, 1605.



**Fig. 1.** Typical sulfide spectrum obtained in #507 blebs (upper curve) and the pyrrhotite standard spectrum (lower curve). The standard curve is similar to that given by [8]. The edge feature (a) at 2470 eV is due to iron sulfide.



**Fig. 2.** Sulfur K XANES spectra for exterior (blue), center (green) and intermediate (red) positions within a ~50 μm wide glass vein in PTS#506 showing a trend toward higher oxidation state from center to exterior.