

## OXIDATION STATES OF GRIM GLASSES IN EET79001 BASED ON VANADIUM VALENCE.

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**Introduction:** Gas-rich impact-melt (GRIM) glasses in SNC meteorites are very rich in Martian atmospheric noble gases and sulfur suggesting a possible occurrence of regolith-derived secondary mineral assemblages in these samples. Previously, we have studied two GRIM glasses, 506 and 507, from EET79001 Lith A and Lith B, respectively, for elemental abundances and spatial distribution of sulfur using EMPA (WDS) and FE-SEM (EDS) techniques [1] and for sulfur-speciation using K-edge XANES techniques [2]. These elemental and FE-SEM micrograph data at several locations in the GRIM glasses from Shergotty (DBS), Zagami 994 and EET79001, Lith B showed that FeO and “SO<sub>3</sub>” are positively correlated (“SO<sub>3</sub>” represents a mixture of sulfide and sulfate). FE-SEM (EDS) study revealed that the sulfur-rich pockets in these glasses contain numerous micron-sized iron-sulfide (Fe-S) globules sequestered throughout the volume. However, in some areas (though less frequently), we detected significant Fe-S-O signals suggesting the occurrence of iron sulfate.

These GRIM glasses were studied by K-edge microXANES techniques for sulfur speciation in association with iron in sulfur-rich areas [2]. In both samples, we found the sulfur speciation dominated by sulfide with minor oxidized sulfur mixed in with various proportions. The abundance of oxidized sulfur was greater in 506 than in 507.

Based on these results, we hypothesize that sulfur initially existed as sulfate in the glass precursor materials and, on shock-impact melting of the precursor materials producing these glasses, the oxidized sulfur was reduced to predominately sulfide.

In order to further test this hypothesis, we have used microXANES to measure the valence states of vanadium in GRIM glasses from Lith A and Lith B to complement and compare with previous analogous measurements on Lith C [3,4] (note: 506 and 507 contain the largest amounts of martian atmospheric gases but the gas-contents in Lith C measured by [3,4] are unknown). Vanadium is ideal for addressing this redox issue because it has multiple valence states and is a well-studied element [3]. Ferrous-dominated iron valences determined by microXANES on the Lith A and Lith B glasses provide little redox sensitivity [2].

Vanadium valence measurements for impact glass in Lith C [3,4] at three different locations yielded valence values of 3.1, 3.2 and 3.4 with inferred  $fO_2$  val-

ues of IW-0.7, IW-0.1 and IW+0.7, respectively. This range of oxygen-fugacity values is understandable because the glasses are shock-molten impact glasses which are heterogeneous in nature. Oxygen fugacity values obtained from the analysis of Fe-Ti oxides [5] and Eu partitioning in pyroxenes [6] from EET79001 Lith A and Lith B (host lithologies) were in the range of IW+0.3 to IW+1.9 suggesting that V in the Lith C impact glass was reduced in the impact process [4].

Here, we examine whether the 506 from Lith A and 507 from Lith B GRIM glasses yield similar or different  $fO_2$  values from those of Lith C [3,4] using the vanadium K-edge microXANES technique.

**Methods:** Synchrotron microXANES (X-ray Absorption Near Edge Structure) spectroscopy measurements of V valence were obtained at the Advanced Photon Source (APS), Argonne National Laboratory, Beamline 13-ID, Consortium for Advanced Radiation Sources (CARS). A monochromatic (cryogenic, Si (111) double crystal monochromator) X-ray beam (2x2  $\mu\text{m}$ ) was produced using KB mirrors. Fluorescent vanadium K X-rays were measured (Vortex-ME4 SDD; SII NanoTechnology Inc.) as a function of incident X-ray energy in the vicinity of the V K absorption edge. The intensity of the V K pre-edge peak (~5470 eV) was used to infer valence and oxygen fugacity after calibration with various synthetic standards of known valence and  $fO_2$  of production, as described in [3]. An estimate of the liquidus temperature of the glass is required to infer  $fO_2$ , and a value of 1400°C was used here, analogous to that used for the Lith C determination [3,4]. Oxygen fugacity results are expressed in log units relative to the iron-wüstite (IW) buffer.

**Results:** Vanadium valence and inferred oxygen fugacity were determined for GRIM glass regions on thin sections of EET79001,506 (Lith A) and EET79001,507 (Lith B) (Figure 1).

*506 (Lith A).* Two regions in a glass vein were analyzed. At the first region, a line scan was done collecting XANES spectra in 4 micron steps across the vein. Vanadium valences ranged from 3.03 to 3.09 with a mean of  $3.06 \pm 0.03$  (i.e., close to pure V<sup>3+</sup>) with  $fO_2$  between IW-0.8 and IW-1.1 with a mean of  $IW-0.9 \pm 0.1$ . At the second region, 3 analyses were obtained at the center and two edges of the vein. Vanadium valences ranged from 2.86 to 2.96 with a mean of  $2.91 \pm 0.05$  and  $fO_2$  between IW-1.4 and IW-2.0 with a mean

of  $IW-1.7 \pm 0.1$ . Thus, Region 2 was slightly more reduced than Region 1. Combining the data for the two regions yields a mean valence of  $3.01 \pm 0.03$  and mean  $fO_2$  of  $IW-1.2 \pm 0.01$ . These results suggest that the glassy regions in 506 are dominated by  $V^{3+}$  with varying minor addition of either  $V^{4+}$  (Region 1) or  $V^{2+}$  (Region 2).

**507 (Lith B).** Three spots were analyzed on the 507 glass. Two glass regions with sulfur-rich blebs nearby gave V valences of 3.6 and 3.8 while a “bleb-free” glass region gave a valence of 3.4. The mean V valence for the three spots was  $3.59 \pm 0.06$  with mean  $fO_2$  of  $IW+1.4 \pm 0.2$ . Thus, all three 507 regions contained a mixture of  $V^{3+}$  and  $V^{4+}$ . Clearly, the 507 glass is more oxidized than the 506 glass with a slight tendency for the “bleb-rich” glass to be more oxidized than the “bleb-free” glass.

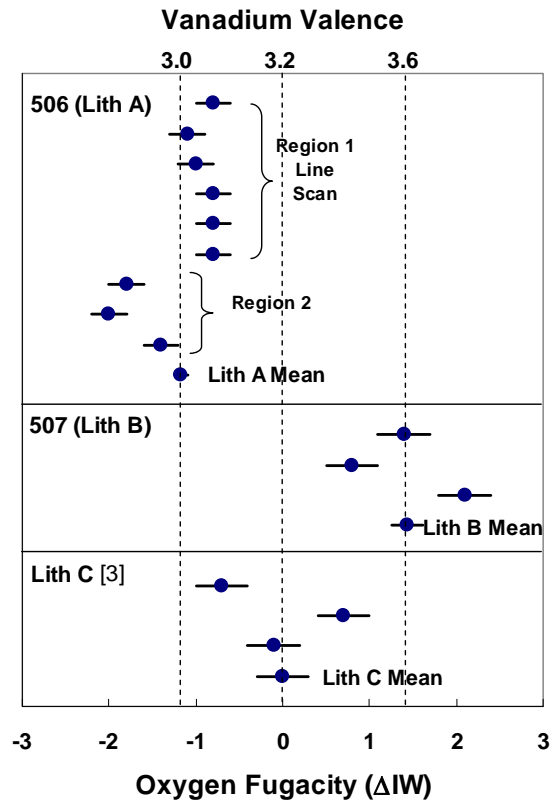
**Conclusions:** Compared to the previously reported Lith C glass vanadium results (mean valence of 3.2 and mean  $fO_2$  of  $IW$  [3,4]), 506 (Lith A) glass is about one log unit more reduced ( $V^{3+}$  dominated) and 507 (Lith B) glass is about one log unit more oxidized (roughly equal mixture of  $V^{4+}$  and  $V^{3+}$ ). Moreover, as both 506 and Lith C [3,4] belong to the same Lithology A, these results indicate that V reduction had taken place in 506 (with reference to Lith C [3,4]) presumably during impact-melting and quenching. The 507 Lith B glass  $fO_2$  inferred from V valence falls in the range of the values obtained from Fe-Ti oxide and Eu oxybarometry [5,6] whereas the inferred 506 Lith A glass  $fO_2$  is more reduced.

The existence of reduced sulfur in these glasses indicates that reduction of the precursor material, most likely sulfate-bearing regolith, probably occurred during the glass-producing impact event. If so, vanadium is also expected to have been reduced in this event. The vanadium results, therefore, represent lower limits (reduction limits) for the oxidation states of the impact melt precursor material. If the degree of impact reduction in the various glasses was comparable, the 507 glass derived from a more oxidized precursor than that producing the 506 glass. This interpretation is consistent with the petrology of the host rocks, Lith B being a more oxidized, pyroxene-phyric shergottite compared to the olivine-phyric Lith A [7].

The effect of impact reduction (in log units) remains to be fully calibrated. One measure of this effect is the total range observed from the highest  $fO_2$  value in Lith C measured by [3,4] (assumed to be compositionally equivalent to 506) to the lowest value of  $fO_2$  measured for 506 in this study, i.e., nearly 2 log units. This comparatively high degree of variability in  $fO_2$  as measured by variation in vanadium valence is fully consistent with impact reduction of some re-

golite-associated sulfates to sulfides thereby explaining the predominance of sulfides over sulfates observed in the GRIM glasses,

**References:** [1] Rao M. N. et al. (2004) *LPS XXXV*, #1501. [2] Sutton S. R. et al. (2008) *LPS XXXIX*, #1961. [3] Sutton S. R. et al. (2005) *GCA* 69, 2333-2348. [4] Karner J. M. et al. (2006) *Am. Min.* 91, 270-277. [5] Herd C. D. K. et al. (2001) *Am. Min.* 86, 1015-1024. [6] McCanta M.C. et al. (2004) *GCA* 68, 1943-1952. [7] Karner J. M. et al. (2007) *Am. Min.* 92, 1238-1241.



**Figure 1:** Vanadium K microXANES results for three impact glass samples from EET79001. 506 (Lith A) and 507 (Lith B) GRIM glass data are from this work. Lith C results are from [3]. The vertical dashed lines pass through the mean values for 506 (leftmost), 507 (rightmost) and Lith C (center).