Martian Regolith in EETA 79001 Shock Melts? – Evidence from Major Element Composition and Sulfur Speciation

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Introduction
Antarctic Martian meteorite Elephant Moraine (EETA) 79001 exhibits two lithologies (A and B), joined along an igneous contact. Lithology A is a basalt, consisting of relatively magnesian pyroxenes and plagioclase. Lithology A contains many megacrysts of highly magnesian olivine and low-Ca pyroxene, with common chromite inclusions. Lithology B is a sub-ophitic ferroan basaltic rock. Both lithologies are cut across by thin (~1–80 μm) black, glassy veins and larger (mm- to cm-size) pockets of glass + crystals, presumably formed during the impact event which also ejected the rock from the Martian surface into an eventual Earth-crossing trajectory. These veins and pockets are loosely referred to as ‘lithology C’ or shock veins and pockets to clarify their impact origin.

Studies documenting anomalously high S contents in lithology C glasses from electron microprobe (EM) measurements (Rao et al., 1999, 2004) cite Martian soil (SO3 5.9 wt%) as the source of excess sulfur. These studies describe a scenario in which plagioclase-enriched, fine-grained lithology A and Martian soil are mixed together during impact to produce lithology C. In turn, this inferred soil composition forms the basis of speculation about Martian weathering processes (e.g., fluid composition and environmental conditions). The interpretation that the composition of the glass in EETA 79001 reflects melting and incorporation of a regolith component has also been central to arguments supporting an injection mechanism for the formation of shock melts in Martian meteorites, where exogenous melt is forcibly and rapidly injected into their present locations in the rock.

In contrast, however, the melt pockets could have formed by in situ shock melting of local portions of the host rock. This formation mechanism is consistent with current understanding of shock dynamics in heterogeneous materials, where shock impedance (shock wave velocity x phase density) contrasts give rise to reflection and refraction of shock waves (Stöffler et al., 1991). Collapse of pore space in the host rock produces the highest dissipation of energy, supported by physical models, as well as shock recovery experiments (Heider and Kenkmann, 2003).
Here, we present a combination of petrographic observations, EM chemical analyses, and X-ray Absorption Near Edge Structure (XANES) spectroscopy measurements at the S k-edge on EETA 79001 lithology C to test for the possible presence of a Martian regolith component. Sulfur speciation will be important in assessing a Martian regolith component - the stable oxidation state at Mars’ surface is likely S$^{6+}$, based on the composition of the Martian atmosphere. We do not expect that sulfur speciation would be modified during shock following the experimental results of Wilke et al. (2003). The small volume melts considered here quench in milliseconds to seconds. A model for shock melt formation is proposed, expanding on ideas developed in previous work (Beck et al., 2007, Walton and Herd, 2007) – shock melts represent local, mineral-scale melts that incorporated primarily igneous components.

Figure 1. Thin section EETA 79001,73 investigated in this study. The section is half Lithology A (olivine megacryst is stained yellow; the other is low-Ca pyroxene) and half shock pocket.

**Theory and/or Method**

EETA 79001,73 was initially characterized using a JEOL 6301F Field Emission (FE) SEM at a working distance of 8 mm and an accelerating voltage of 20 kV in BSE imaging mode. Analyses of minerals and glasses were carried out using a JEOL 8900 EM equipped with five wavelength dispersive spectrometers (WDS). These studies incorporated elemental X-ray mapping, and quantitative analysis using WDS analysis. An accelerating potential of 15 or 20 kV and a beam current of 10 or 15 nA were used for WDS and X-ray mapping, respectively.

Bulk compositions of shock melts were obtained by averaging a total of 335, 360 and 300 defocused beam analyses for the vein, pocket glass and pocket glass + crystals, respectively. The resultant elemental abundances were normalized to EETA 79001 whole rock to analyze
fits. Xenolithic material in EET 79001 is heterogeneously distributed; three different melt compositions were therefore used in the normalization.

XANES spectra at the S K-edge were collected at the European Synchrotron Radiation Facility in Grenoble using the scanning X-ray microscope (SXM) of the ID21 (X-ray microscopy) undulator beamline. XANES spectra were taken by continuously scanning the monochromator over the desired energy range, which took about one minute. To achieve acceptable counting statistics multiple scans were stacked to yield one spectrum. The acquisition time for one spectrum varied between 20 and 40 min, corresponding to 2 and 4 s per energy point. The following samples were used as reference material for $S^{2-}$ and $S^{6+}$ species: terrestrial basalts (Lau Basin 1540-4), quenched synthetic glasses of basaltic composition that were either sulfide-saturated or sulfate-saturated and a pyrrhotite standard.

**Results**

XANES spectra are shown in figure 2. All spectra of EETA 79001 glass exhibited a broad peak (centered at 2.477 keV), which is interpreted as $S^{2-}$ dissolved in the glass. All of the glass spectra also exhibit a sharp peak at 2.471 keV, and small peaks at energies above 2.485 keV, which are characteristic of pyrrhotite and are commonly observed in sulfide-rich basalts. Our XANES analyses do not shown any evidence for sulfate in the shock glass, which would be apparent by a peak at 2.482 keV.

![Figure 2. XANES spectra for EETA 79001 shock glasses and several reference standards for $S^{2-}$ and $S^{6+}$](image)

Compared to the bulk composition of lithology A, chemical analyses of glasses do not show good fits with whole rock elements; they are enriched in Ca, Al, Na, K and S, and depleted in Fe, Mg, Ti, Mn, Cr and P. These data are nearly identical to the EMPA data presented by Rao et al., (1999, 2004); these authors attributed the enrichments to a Martian regolith component. However, the bulk composition of the pocket is not merely the average composition of its glass, but must include the crystals that grew from the melt. To retrieve the bulk pocket compositions,
one must add its quench pyroxene and olivine crystals in the proper proportions. Combining defocused glass + crystal analyses, the bulk composition that we calculate approaches that of the three compositions used to normalize the data. Slight enrichments in Ca, Al, Na and S compared to the bulk composition can be attributed to preferential melting of pyrrhotite and plagioclase by shock; this is well documented from ordinary chondrites and terrestrial impact structures as a result of its compressible crystal structure, which preferentially absorbs shock wave energy.

Conclusions
Our petrographic and chemical data give no support for the claim that the shock melts in EETA 79001 contain an exogenous, regolith component. Rather, our data are consistent with the shock melts forming in situ from locally derived materials. First, we see no sign that the shock pockets were injected from elsewhere; the analyzed melt veins and pockets are surrounded by shocked solids and the shock level increases toward the melt. Second, plagioclase and pyrrhotite are melted and mobilized farther from the melt pockets and veins (i.e., at a lower shock state) than are olivine and pyroxene. This is consistent with excess portions of plagioclase and pyrrhotite in the shock melts compared to the bulk rock, as is seen in our analyses. Rao et al. (1999, 2004) have interpreted these excess components (Ca, Al, S) as representing Martian regolith, but the excesses are equally well explained as arising from shock melting of local minerals. Third, bulk compositions of pockets cannot be taken merely as the glasses within them, because most have crystallized quench olivine and pyroxene. The glasses among these quench phases is necessarily enriched in Ca, Al and S, which can then be mis-interpreted as enrichment in Martian regolith. Fourth S-edge XANES analyses on lithology C glasses do not detect any oxidized sulfur, which we expect for a regolith signature. Our results are consistent with the formation of shock pockets by shock impedance contrasts, with collapsed void space in the target rock yielding the highest dissipation of energy. Large pockets melt higher proportions of the host rock and their bulk composition approaches that of the bulk lithology whereas smaller pockets reflect local mineralogy.

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References