ACID-SULFATE-WEATHERING ACTIVITY IN SHERGOTTITE SITES ON MARS RECORDED IN GRIM GLASSES.

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Introduction: Based on mass spectrometric studies of sulfur species in Shergotty and EET79001, [1] and [2] showed that sulfates and sulfides occur in different proportions in shergottites. Sulfur speciation studies in gas-rich impact-melt (GRIM) glasses in EET79001 by the XANES method [3] showed that S K-XANES spectra in GRIM glasses from Lith A indicate that S is associated with Ca and Al presumably as sulfides/sulfates whereas the XANES spectra of amorphous sulfide globules in GRIM glasses from Lith B indicate that S is associated with Fe as FeS. In these amorphous iron sulfide globules, [4] found no Ni using FE-SEM and suggested that the globules resulting from immiscible sulfide melt may not be related to the igneous iron sulfides having ~1-3% Ni. Furthermore, in the amorphous iron sulfides from 507 GRIM glass, [5] determined δ^{34}S values ranging from +3.5‰ to –3.1‰ using Nano-SIMS. These values plot between the δ^{34}S value of +5.25‰ determined in the sulfate fraction in Shergotty [6] at one extreme and the value of – 1.7‰ obtained for igneous sulfides in EET79001 and Shergotty [7] at the other. These results suggest that the amorphous Fe-S globules likely originated by shock reduction of secondary iron sulfate phases occurring in the regolith precursor materials during impact [7].

Sulfates in the regolith materials near the basaltic shergottite sites on Mars owe their origin to surficial acid-sulfate interactions. Below we examine the nature of these reactions by studying the composition of the end products in altered regolith materials. For the parent material composition, we use that of the host shergottite material in which the impact glasses are situated.

Ti-mass-balance procedure: To estimate the elemental gains and losses in the end product (w) resulting from weathering of the parent regolith material (p), we modeled the interactions of acid-sulfate fluids with basaltic material near shergottite sites on Mars using the following relation [8-10]:

$$T_{jw} = [(C_{jw} / C_{iw}) / (C_{jp} / C_{iw}) - 1] \text{ x } 100.$$

The term T_{jw} refers to the mass removal of an element (j) from the weathered regolith material (w) compared to its parent material (p) and is calculated relative to an immobile element (i) where C is the concentration of the particular element. The gains and losses of a mobile element are determined by referencing the mobile element to an immobile element such as Ti. Negative T_{jw} values indicate elemental loss, whereas positive values indicate elemental gain from a source other than the parent material.

For this purpose, we determined the elemental abundances in GRIM glasses EET79001, 507; Shergotty DBS, Los Angeles 748, Zagami H1 and QUE94201 by both raster and point modes along several line-traverses by EPMA and Fe-SEM methods and obtained the average composition for these glasses (S calculated as "SO_3").

The results for Ti–normalized major element abundances in these glasses are plotted in Fig.1 which shows that large amounts of "SO_3" are added to the weathered residue in these samples. Also, ~20–80% of MgO is removed from the weathered residue in these glasses. Moreover, these glasses show enrichment of CaO, Na_2O, Al_2O_3, and SiO_2 in the weathered residue suggesting addition of amorphous plagioclase (Na-feldspar) to the weathered residue. Further, ~10–50% of FeO seems to have been added in these glasses. These results are consistent with a scenario where moderately acidic acid-sulafte solutions percolated through the regolith materials containg poorly-crystalline basaltic glass [11,12] which is easily soluble in acidic solutions. As a result of the fluid-rock interactions, the Fe- and Mg- bearing phases in basaltic materials are leached at low pH, leaving behind the acid-resistant Ca-Na-feldspar and pyroxene. Also, some Fe seems to have been deposited as hydroxy-sulfate, as the pH of the solutions increased during interaction with the basalt [13].

Note that this scenario is based on the average of all measured abundances in these glasses assuming that the glass is homogeneous. However, these glasses are not. To examine whether this scenario holds good under heterogeneous conditions, we plot the abundances of SiO_2, FeO and MgO vs SO_3 obtained at individual spots in the glassy veins in Figs. 2 - 4.

Major Element Correlations: The SO_3 and SiO_2 abundances in EET79001 ,507 (typical example) and Meridiani [14] and Pathfinder rocks/soils [11] are plotted in Fig. 2, which shows anti-correlation between SO_3 and SiO_2. This suggests that as SO_3 increases in the weathered residue, SiO_2 decreases correspondingly because of the "closure" effect. This decrease becomes more pronounced when the dissolved silicate is removed by the percolating fluids from the system. Furthermore, the ,507 data in Fig.2 plot between the data-fields representing the heavily- weatherd Meridiani rocks as one end-member and moderately-weathered Pathfinder rocks/ soils as the other. These results indicate that the ,507 glass precursor materials near shergottite sites on Mars have undergone acid-sulfate weathering by solutions similar to that experienced by the weathered rock fragments and soil aggregates near Meridiani and Pathfinder sites. This weathering trend in ,507 data suggests that sulfur existed as sulfate in weathered regolith materials near shergottite sites.

In Figs. 3 & 4, FeO and MgO abundances in ,507 are plotted against SO_3 along with those from Pathfinder and Meridiani rocks/soils. In ,507, FeO and SO_3 correlate positively because both Fe and S occur in amorphous sulfide globules formed by shock reduction of Fe-SO_4 [7]. Note that the parent-material in Lith B (no olivine) has an Fe content of ~17.8%. The distribution of the data representing the FeO abundances measured at different spots in ,507 glass show that in some spots FeO is lower whereas in others it is higher than the FeO in the parental material. This indicates that both losses and gains of FeO might have occurred in the weathered residue comprising the glass precursor materials. This observation could be explained through the removal of Fe as Fe-SO_4 from the system at low pH in some cases and addition of Fe as Fe-hydroxysulfate at higher pH in others [13].

In Fig.4, MgO clearly shows no correlation with SO_3 suggesting that soluble $MgSO_4$ is removed from the system by the percolating acidic solutions. But, the MgO data of ,507 plotted may represent the residual acid-resistant pyroxene in the weathered residue. The Meridiani rocks /soils also show a similar trend. These results are consistant with our model, if the regolith at the basaltic shergottite sites contained basaltic glass [11,12] which dissolves in moderately acidic solutions preferentially leaving behind acid-resistant plagioclase and pyroxene. From these fluids, Fe is deposited or removed depending on the pH, wherer as the soluble $MgSO_4$ is mostly removed from the system. This observation is also supported by the addition of the plag-component (CaO-Al_2O_3-Na_2O-SiO_2) to the ,507 glass precursor materials as shown in Fig.1. These results show that impact-melted regolith is an integral component in the GRIM glasses and that moderately acidic sulfate fluids percolated through regolith materials near the basaltic shergottite sites on Mars.

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Figure Captions: **Fig.1.** Percent-change in the elemental ratios normalized to TiO_2 in GRIM glasses in shergottites. **Fig.2**. SO_3 and SiO_2 anti-correlation in ,507 glass and Meridiani/Pathfinder rocks/soils. **Fig.3**. SO_3 and FeO positive correlation in ,507 glass and Pathfinder rocks/soils. **Fig.4**. SO_3–MgO zero-correlation in ,507 glass and Meridiani rocks /soils.