

**EVIDENCE FOR MARS REGOLITH PRESERVED IN SHERGOTTITE EET79001: DIFFERENTIAL COMMUNITION AND CHEMICAL WEATHERING RECORDS.** M.N.Rao<sup>1</sup> and D.S.McKay<sup>2</sup>, <sup>1</sup>Lockheed Martin, 2400 NASA Road One, Houston. TX.77058, <sup>2</sup>NASA Johnson Spae Center, Houston. TX. 77058. (e-mail: david.s.mckay@Jsc.nasa.gov).

**Introduction:** Earlier, we pointed out that some shergottite impact melt glasses contain large abundances of Martian atmospheric noble gases and show large variations in <sup>87</sup>Sr/<sup>86</sup>Sr (initial) isotopic ratios. These samples likely contain Martian regolith fines (MRF) [1-3]. We showed that one of the characteristics of these MSF fractions is the simultaneous enrichment of felsic component and an associated depletion of the mafic component relative to the host phase in which these glasses are located. In several samples studied by us, the magnitude of enrichment and depletion is found to vary from one sample to the other. In addition, these samples show evidence for the occurrence of secondary sulfate mineral phases due to aqueous alteration near Mars surface. As the basaltic shergottites presumably originate from near-surface regions of young volcanic terrains such as Tharisis (Olympus Mons) or Elysium Mons [4], the MSF fraction embedded in these impact glasses likely provide clues regarding the physical and chemical weathering environment to which their precursor soils were exposed near the Martian uplands prior to the impact-melt generation.

We suggested earlier that the felsic enrichment and mafic depletion observed in these samples is related to the occurrence of the Martian regolith fine fraction in them [3]. These glasses contain varying amounts of the MRF fraction and the relative ratios of the coarse and fine fractions in these impact glasses determine the magnitude of the enrichment and depletion factors in these samples. On comparison of our results with those obtained in the laboratory simulation bombardment experiments on gabbro using projectiles with similar impact velocities on Moon/Mars by Horz et al. [5], we found that, though the patterns of enrichment and depletion of the element-oxides in the samples are similar, but their magnitudes are grossly different. In the Horz et al. experiments, the finer size fractions were enriched in AL2O3 relative to the starting composition and were depleted in FeO and MgO. If we assume that melt glass pocket ,507 originally consisted entirely of fine-grained regolith developed on the host rock represented by EET79001 (lithology B), can we explain the difference in chemistry entirely by differential comminution and mechanical concentration of the fines? When we compare the melt glass composition in EET79001 to the bulk rock composition, we find the same trends shown by Horz et al. [5], but they

are much more enhanced. If the regolith material which was the precursor to the melt glass originally consisted of fine-grained regolith, differential comminution concentration of the fines by mechanical fractionation could explain the trends, but not the magnitude of the chemical difference. Consequently we conclude that, while differential comminution and mechanical fractionation may have operated, there must be other processes operating on Mars responsible the significant difference in composition between the melt glass and the bulk rock. In this study, we examine this aspect in detail and show that these differences could be explained by chemical (acid-sulfate) weathering of the soil fines near the martian surface by aqueous solutions containing acidic volatiles such as SO<sub>2</sub> and H<sub>2</sub>O released in volcanic eruptions during the last few hundred million years on Mars [6,7].

**Experimental:** Several impact melt glasses in shergottites were studied by us using a Cameca SX100 state-of-the-art microbeam automated Electron Microprobe at JSC using standard analytical and calibration procedures described earlier [1-3]. We discuss below data obtained on an impact-melt glass inclusion ,507 from EET79001 and compare the results with those obtained on Shergotty glasses (sample provided by Don Bogard).

**Results and Discussion:** We studied earlier several veins and pods in impact-melt glass samples ,77 ,78 ,18 and ,20A in EET79001 and averaged all the data points in these veins. The average values are plotted in Fig.1 of [2] where we found significant enrichment of Al<sub>2</sub>O<sub>3</sub> and CaO relative to the bulk rock containing these melt pockets (Lith A) and much larger depletion of FeO and MgO relative to Lith A. SO<sub>3</sub> abundance varied from 0.4 to 1.6 showing modest enrichment relative to Lith A. These values represent averages of about 900 data points obtained in the line profiles across the veins. In the present study, we focuss our attention on the Electron Microprobe and SEM data gathered along several line profiles in the veins and pods of impact melt glasses of ,507 of EET79001 (Lith B).

The FeO & MgO as well as Al<sub>2</sub>O<sub>3</sub> & CaO abundances are plotted against SO<sub>3</sub> in Figs. 1 & 2 respectively. In Fig. 3, SiO<sub>2</sub> is plotted against SO<sub>3</sub>. At some analysis sites, we found SO<sub>3</sub> contents as high as ~16%, a value more than twice as high as the SO<sub>3</sub>

content of Viking and Pathfinder [8,9]. The  $\text{SO}_3$  vs FeO plot in Fig.1 where  $\text{SO}_3$  varies from about 0.6% to 16%, shows excellent positive correlation between the two elements. When we extrapolate the correlation line back to  $\text{SO}_3 = 0.5\%$ , the FeO content of the mineral assemblage in the glass turns out to be  $\sim 10\%$ . This indicates that the FeO content of the precursor soil fines in the impact glass is depleted by  $\sim 50\%$  relative to the host bulk rock. Further, in the  $\text{Al}_2\text{O}_3$  vs  $\text{SO}_3$  plot in Fig. 2, the data points show negative correlation between these elements. When we extrapolate the correlation line, as before, to  $\text{SO}_3 = 0.5\%$ , we find the  $\text{Al}_2\text{O}_3$  content in the starting materials to be  $\sim 20\%$ . This indicates that  $\text{Al}_2\text{O}_3$  is enriched by a factor of 2 relative to the host phase. If we consider that these enrichment and depletion factors are only due to comminution of basaltic rocks due to meteoroid bombardment, then the observed values found here are very high compared to those obtained by Hoerz et al. [5] in the simulation experiments on gabbro. These results suggest that there may be an additional process operating on these soil fines on Mars. The most likely candidate for such a process is chemical weathering of soil fines near Mars surface. We explore below the conditions and the consequences of acid-sulfate weathering of soil fines near Mars surface during the last few hundred Ma.

*Acidic Volatiles:* Based on the resurfacing rates on Mars, Tanaka et al.[10] estimated that the volcanic eruptions on Mars took place once in every  $10^4$  years during the last few hundred Ma. During these volcanic eruptions/emnations, huge amounts of volcanic gases consisting of water and sulfurous gases (among others) are released into the atmosphere where  $\text{SO}_2$  is oxidized, converted to  $\text{H}_2\text{SO}_4$  and deposited as aerosols on rock surfaces [6,7]. Because of the large surface area of the comminuted fine basaltic materials near the volcanic eruptions, these acidic volatiles chemically react with the constituent mineral components resulting in slow dissolution and chemical (acid-sulfate) weathering. Here, we examine the nature and conditions of dissolution and reprecipitation of secondary mineral phases during acid-sulfate weathering of ferromagnesian minerals and feldspars in the Martian regolith.

*Chemical Weathering :* To study the nature of chemical weathering effects on ferromagnesian minerals by acid-sulfate solutions, we use the FeO and MgO vs  $\text{SO}_3$  plot in Fig. 1. The Fe-Mg silicates rank highest in order of vulnerability of igneous minerals to chemical weathering reactions, with feldspars being

next in order [11]. When the pyroxenes are degraded by acid-sulfate solutions, the  $\text{Fe}^{+2}$  and  $\text{Mg}^{+2}$  go into solution along with silicic acid. It may be noted that the oxidation of  $\text{Fe}^{+2}$  to  $\text{Fe}^{+3}$  is extremely slow on Mars compared to Earth because of very cold temperatures near Mars surface. The excellent positive correlation between FeO and  $\text{SO}_3$  indicates that iron may be precipitated as ferric hydroxy sulfate which is relatively insoluble. Note that the potassium abundance in our samples is very low which does not favour the precipitation of K-jarosite /alunite in these samples [6, 7]. Also, note that sulfur predominantly exists as sulfate in these samples [2,12,13].

At low  $\text{SO}_3$  values, both FeO and MgO in this melted regolith (507) are highly depleted relative to the host rock (Lith B). This observation suggests that The chemical weathering appears to have been a three step process. First (step 1)  $\text{MgSO}_4$  and  $\text{FeSO}_4$  were formed as a result of acid-sulfate degradation of pyroxenes.. Second (step 2), the regolith was partially leached of these components; they were possibly removed from the system by transgressing aqueous solutions seeping into the top portions of Martian regolith, a process which decreased their concentration and increased the concentration of  $\text{Al}_2\text{O}_3$  in the residual soil. During step 2, some  $\text{SiO}_2$  is removed in solution. We hypothesize that as acid-sulfate solutions degrade pyroxenes and feldspars, some  $\text{SiO}_2$  goes into solution as  $\text{H}_2\text{SiO}_4$  and it is removed from the system by the transgressing solutions. Finally (step 3), a solution was reintroduced into the soil and precipitated the  $\text{SO}_3$  phase along with a considerable amount of FeO and a slight amount of MgO, presumably as sulfates. During step 3, some components such as  $\text{Al}_2\text{O}_3$  may also have been removed to a slight degree. The behaviour of feldspars in the soil precursors under these acidic conditions on Mars can be deciphered from the correlation lines in  $\text{Al}_2\text{O}_3$  and CaO vs  $\text{SO}_3$  plot in Fig. 2. Both  $\text{Al}_2\text{O}_3$  and CaO negatively correlate with  $\text{SO}_3$  suggesting that the dilution effect is significant in bothcases. The decrease of CaO with added  $\text{SO}_3$  can almost entirely be explained by the dilution effect (closure), but only about half of the decrease of  $\text{Al}_2\text{O}_3$  can be explained by dilution. Consequently, the data reflect a real decrease (removal) of  $\text{Al}_2\text{O}_3$  by weathering and transport during step 3. Further, in Fig. 3, we show good correspondence between  $\text{SO}_3$  and  $\text{SiO}_2$ . We find that as the  $\text{SO}_3$  content increases from 0.5% to  $\sim 16\%$ ,  $\text{SiO}_2$  decreases from  $\sim 50\%$  to  $\sim 40\%$ . Most of this variation of  $\text{SiO}_2$  can be explained by dilution.

Note that MgO remains relatively flat over the complete range of  $\text{SO}_3$ . Dilution alone would cause

MgO to decrease about 16% as SO<sub>3</sub> increases, but this decrease is not observed. Therefore, MgO is actually increasing slightly in step 3 with the introduction the SO<sub>3</sub>-rich material along with FeO. However, it had been partially dissolved and leached out in step 1 and 2.

**Model calculations :** We present a model based on the above results and carry out calculations ,under the assumptions discussed below. We start with shergottite basaltic composition of 56% pyroxene and 29% feldspar plus maskelynite for EET79001 [14]. This material is comminuted by meteoroid bombardment on Mars producing fine-grained regolith fractions where felsic component is slightly enriched and mafic component is depleted relative to the starting material. In our model, we use the enrichment and depletion factors given by Horz et al. [5]. We assume that all FeO and MgO in the solution results from the dissolution of pyroxenes and all Al<sub>2</sub>O<sub>3</sub> in the solution comes from the dissolution of feldspars. CaO is contributed equally by the dissolution of pyroxenes and feldspars into solution. In this model, the acid-sulfate solutions are generated from acidic-volatiles released in volcanic eruptions into the atmosphere[6, 11]. They interact with the enriched/depleted starting basaltic fine material by dissolving varying proportions of pyroxenes and feldspars depending on the acid-sulfate availability under restricted aqueous conditions. We consider three cases in our calculation : Case A = 8% pyroxene and 4% feldspar dissolved into the transgressing solutions where the resulting MgSO<sub>4</sub>, H<sub>2</sub>SiO<sub>4</sub>, and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> are removed from the system and an equivalent amount of iron sulfate is reintroduced and precipitated as insoluble Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> on the residual grains. Case B = 16% pyroxene and 8% feldspars dissolved (and the rest of the details are same as above). Case C = 32% pyroxene and 16% feldspar dissolved (and the rest of the details same as above). We assume that when iron dissolves it goes into solution as FeSO<sub>4</sub> and when it precipitates, it leaves the solution as Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. Using these model steps in dissolution and precipitation reactions, we calculate the composition of different element-oxides in the end products. We plot these calculated values (model-dependant) in Figs. 1, 2 and 3. The agreement between the experimental and calculated values is good. All trends generated by the model correspond to trends of the actual measured data. This observation indicates that these glasses contain locally-produced fine-grained Martian regolith which had undergone acid-sulfate weathering and fractionation under limited aqueous conditions.

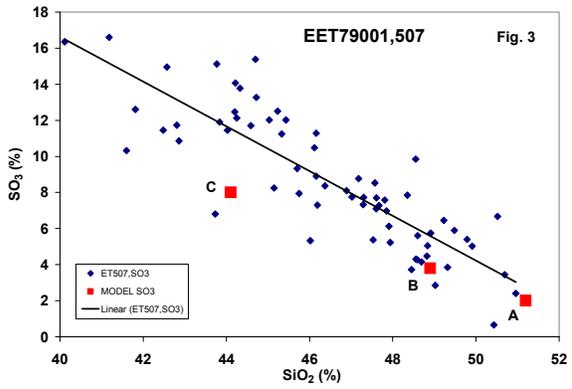
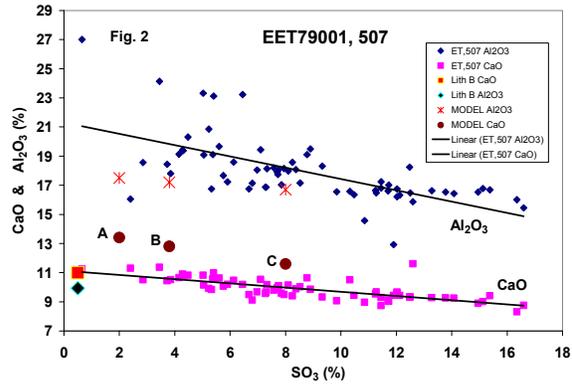
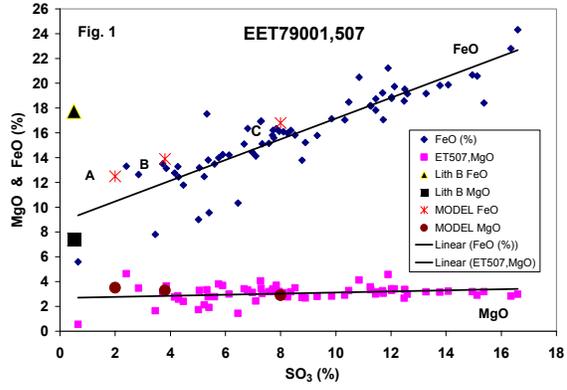
**Conclusions:** We find that the composition of the gas-rich melt inclusion (,507) shows systematic varia-

tions from the host rock (EET79001, Lith B) that can be explained by a multi-step history consisting of differential comminution with some chemical fractionation, acid/sulfate dissolution, removal of some components, and introduction of sulfates, mainly Fe but also minor Mg. This regolith was then melted and mixed with Lith B, trapping the gas-rich melt in pockets, presumably during the impact that ejected the sample from Mars. Similar chemical trends (not shown here) found in a gas-rich glass inclusion in Shergotty suggest that this weathering sequence may be repeated at other martian locations.

**References:** [1] Rao M.N. et al. (1999) *GRL*, 26, 3265-3268. [2] Rao M.N. and McKay D. S.(2002) "Unmixing the SNCs", *LPI Contribution No.1134*, pp.49-51. [3] Rao M.N. and McKay D. S.(2003) *LPS XXXIV*, #1252. [4] Nyquist L.E. et al. (2001) 'Chronology and Evolution of Mars', 96, 105-164. [5]. Horz et al. (1984) *Proc. LPSC. 15<sup>th</sup>, JGR, 89*, C183-C186. [6] Banin A. et al. (1997) *JGR, 102*, 13341-13356. [7]. Morris R.V. et al. (2000) *JGR, 105*, 1757-1817. [8]. Clark B.C. et al. (1982) *JGR, 87*, 10059-10067. [9] Rieder R. et al. (1997) *Science*, 278, 1771-1774. [10] Tanaka K.L. et al. (1992) *Mars* (eds. Kieffer, Jakosky, Snyder & Mathews) pp.345-352. [11] Burns R.G. (1993) *GCA*, 57, 4555-4574. [12] Gooding J.L. and Muenow D.W. (1986) *GCA*, 50, 1049-1060. [13] Clark B.C. and Van Hart D.C. (1981) *Icarus*, 45, 370-378. [14] McSween H.Y. Jr. and Jarosewich E. *GCA*, 47, 1501-1513. [15] McSween H.Y. Jr. and Keil K. (2000) *GCA*, 64, 2155-2166.

**Figure caption:** The FeO & MgO vs SO<sub>3</sub> plot (Fig.1) ; Al<sub>2</sub>O<sub>3</sub> & CaO vs SO<sub>3</sub> plot (Fig.2); SiO<sub>2</sub> vs SO<sub>3</sub> plot (Fig.3) for EET79001,507 (Lith B). The positive and negative correlations are striking. For the details about the model compositions used in Case A, Case B and Case C which had undergone acid-sulfate weathering under restricted aqueous conditions, see text. The solid lines are least square trend line fits to the data.

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