ACID- SULFATE WEATHERING ENVIRONMENT AT SHERGOTTITE PROVENANCE ON MARS. M.

N. Rao[1], L. E. Nyquist[2], D. K. Ross[3,4] and S. J. Wentworth[5], [1]SCI, Johnson Space Center, Houston. TX. 77058. (e-mail: sitarao@sbcglobal.net), [2]XI/NASA Johnson Space Center, Houston, TX. 77058, [3]Jacob JETS, NASA Johnson Space Center, Houston, TX. 77058 and [4]UTEP- CASSMAR., [5]HEPCO, Jacobs Engineering, Johnson Space Center, Houston. TX. 77058.

Introduction: In some impact melt (IM) glasses in the shergottites such as EET79001, Shergotty and Tissint, recently [1] showed that secondary mineral assemblages having large sulfur excesses cannot be produced *in-situ* by impact shock melting of the host rock constituents. Instead, these putative secondary minerals inferred to be present in IM glasses were produced somewhere else in the shergottite source region and were subsequently mobilized into the host rock voids (by lava erosion or aolian activity) prior to impact ejection. In this abstract, we examine the aqueous conditions (pH and water/rock ratios) under which the acid sulfate solutions could have interacted with the primary minerals in the basaltic rocks and precipitated the secondary minerals such as Fe-sulfates in some cases and Ca- and Al-sulfates in other cases under favorable conditions at the shergottite provenance on Mars.

The Model: The shergottite source region on Mars apparently consists of two different types of rock complexes, (a) One hosting olivine phyric types from which shergottites such as Tissint, DAG 476, EET79001, Lith A and others were launched. These rocks have olivine, pyroxene and feldspar as major primary minerals. (b) A second region consisting of pyroxene phyric types from which meteorites such as Shergotty, Zagami, EET79001, Lith B and others were derived. These rocks consist of pyroxene and feldspar (no olivine) as major primary minerals. The rocks were located near the Martian surface [1] and were pervasively covered with Martian soil/dust that had high sulfate content (~8% SO_3) and low chloride content (~0.7% Cl) [2-5].

The large overabundance of sulfur observed in Martian soils is generally attributed to chemical alteration caused by the interaction of sulfate-rich acidic fluids with rock and dust near the Martian surface [2-5]. The acid sulfate fluids originated from SO_2 emitted by volcanic activity into the Martian atmosphere where, after oxidation, it combined with water vapor producing H_2SO_4 aerosols. In turn, these aerosols rain down to the Martian surface and mix with water available there. If there is little water in some regions (low water to rock ratios), the pH of the solutions remain highly acidic (pH= 0 to 1). On the other hand, if more water is available at some other places (higher water to rock ratios), the pH of the solutions becomes moderately acidic (pH= 3 to 5).

In the shergottite source region, the acid sulfate solutions percolating through the rocks initiate mineral dissolution where easily soluble mineral phases dissolve first and go into solution preferentially leaving behind relatively refractory minerals chemically unaffected [4,5,12]. In the case of olivine phyric rocks, the easily soluble mineral olivine first goes into solution releasing the major cations Fe and Mg into solution. On the other hand, when such fluids flow through the pyroxene phyric rock complexes, feldspar goes into solution preferentially (no olivine in this case) by releasing major cations Ca and Al into solution [4-6].

The occurrence of jarosite has not been reported in the shergottite impact melt glasses studied so far [1,7.8,9] , thus making the highly acidic low pH, (i.e.,~ 0 to 1) and low water to rock ratio sulfate solutions less likely to have percolated through the overlying Martian soil at the shergottite provenance. Alternatively, the pH of the solutions that interacted with the rocks in this region could have been moderately high, i.e., ~3 to 5 (with high water to rock ratios) as another possibility.

Secondary Minerals – Olivine phyric rocks: From moderately acidic (pH = ~3 to 5) sulfate solutions that interacted with the shergottite rocks, secondary minerals such as Fe^{3+} hydroxy sulfates (olivine dissolution) and Al – hydroxy sulfates together with gypsum (feldspar dissolution) likely precipitated as poorly crystalline aggregates because of limited interaction time between fluid and rock. This deposition is dependent on the saturation state of the particular ion concentration under consideration with respect to the specific mineral phase. The highly insoluble poorly-crystalline minerals deposited near the shergottite source region presumably serve as mineral reservoirs from which the altered materials were subsequently mobilized and incorporated into the host rock voids.

Dissolution of olivine by the moderately acidic fluids releases Fe and Mg along with other soluble chlorides of Na and K into solution. When Fe concentration levels exceed the solubility product constant, the highly insoluble Fe- hydroxy sulfates precipitate. [8] reported the occurrence of copious amounts of Ferric sulfates mixed with phosphates in a vug in QUE 94201. This result is consistent with the Fe sulfate deposition discussed above. Also, the highly soluble mineral phases such as Mg-sulfate and chlorides of Na and K brought into solution remained without precipitating.

Thus the soluble mineral phases were decoupled from the insoluble ones and were ion-transported away from the reaction sites to other locations as these fluids flowed down the topographic lows in this region. This inference is consistent with the result that we found no $MgSO_4$ added into the #507 glass precursors as shown in Fig.4A given in [1]. Also, the chloride contents in EET79001, Shergotty and Zagami impact melts determined by EPMA are found to be close to the detection limits [10].

The Solutions: In Fig.3 given in [1], the FeO-SO_3 plot shows positive correlation whereas Al_2O_3 -SO_3 shows a corresponding negative correlation. On close examination of each data point in the plot, one notices that when the Fe^{3+} content is high the Al^{3+} content is correspondingly low, and vice-versa in #507, suggesting an inverse elemental relation between Fe^{3+} and Al^{3+} in this sample. It is likely that this feature indicates substitutive solid solution behavior in this system and was possibly established during the hydroxy sulfate precipitation. In the case of alunite–jarosite sub-group minerals belonging to the recently altered volcanic deposits of Cerro Negro, significant solid solution mixing between Fe^{3+} and Al^{3+} occurred during precipitation from acid sulfate solutions at pH = ~0 to 1 [12]. A similar solid solution mixing between Fe and Al could have also occurred when the glass precursor minerals of EET79001,507 precipitated from acid sulfate solutions at pH= ~3 to 5 at the shergittite source region.

Elemental Ratios: The Fe/S (atomic) ratios determined in the Fe- S bearing mineral phases in the IM glass precursors likely provide clues regarding their characterization although these inferences are not uniquely definitive because of unknown structural parameters associated with the constituent mineral grains because they were subjected to impact shock deformation [11]. To learn about the composition of Ferric sulfates, we determined the Fe/S ratios in blebs in EET79001, 507 and Tissint IM glasses. They range from 1.04 to 1.12 indicating that they are not related to either jarosite (Fe/S = 1.5) or schwertmanite (Fe/S = 8). The Fe-S blebs also are not related to pyrrhotite (Fe/S=0.92). In this context, note that [11] studied several secondary ferric sulfate minerals in Paso Robles class soils at Gusev and suggested a chemical formula of the type $(Fe^{3+})_2$ $(SO_4)_3$. nH_2O for them. It is likely that , at the shergottite source region also, similar kind of ferric sulfates could have precipitated from the acid sulfate solutions. Thus, the Fe sulfates in #507 glass precursors discussed could be Ferric hydroxy sulfates (Fe/S=1) admixed with small amounts of goethite or hematite.

Moreover, the occurrence of silica and Fe-sulfates (proxy for SO_3) together in #507 glass precursors as indicated by the anti-correlation shown in Fig. 2 of [1] suggests that acid sulfate solutions with moderate pH interacted with the shergottite rocks because SiO_2 is highly soluble if the pH of the solutions is 0 to 1 and it won't precipitate from these fluids [13].

Pyroxene-phyric rocks: When acid-sulfate solutions attack pyroxene phyric rocks, feldspar preferentially dissolves releasing the major cations Ca and Al into solution [4,5,12,13]. Here, the precipitation of gypsum from these solutions is pH independent whereas Al-hydroxy sulfate precipitation is pH dependent [6, 13]..

When the ion activity product (IAP) exceeds the solubility product constant (SP) for the given phase of interest (e.g., $CaSO_4$), Ca precipitates as gypsum or anhydrite. The gypsum / anhydrite deposition is accompanied by the precipitation of Al as Al – hydroxy sulfate from the acid sulfate solutions at pH = ~ 3 -5 [5]. Both these insoluble precipitates were left behind on the pyroxene phyric rocks as the acid sulfate solutions moved away from the reaction sites transporting the soluble ions. The poorly crystalline minerals gypsum and Al – hydroxy sulfates precipitated here were later mobilized by aeolian activity into the host rock voids (e.g. EET79001). This inference is consistent with the finding that the impact- melt glasses #506, #27 and #54 in EET79001, Lith A show positive correlation between CaO and SO_3 (indicating Ca sulfates) as well as Al_2O_3 and SO_3 correlation (indicative of Al - hydroxy sulfates) as shown in Fig.5 given in [1].

Conclusions: The results presented here and in [1] suggest that acid sulfate solutions of moderate pH (with high water/rock ratios) percolated through rocks and soil in the shergottite source region more recently than ~180 Myr ago, the time of shergottite crystallization.

References: [1] Rao M.N. et al. (2018) *Meteoritics & Planet. Sci., 53,* No.12. [2] Clark B.C. et al. (2005) *EPSL*, *240*, 73 – 94. [3] Newsom H. E. et al. (1999*) J. G. R.*, 104, 8717-8728. [4] Tosca N. J. et al. (2004) *J.G.R.* 109, doi: 10.1029/2003JE002218. [5] Hurowitz J.A.etal.(2005)*J.G.R.*,110,doi:10.1029/2004JE 002391. [6] Golden D.C.etal.(2005)J.G.R.*110*,doi: 10.1029 / 2005JE002451. [7] Gooding J. L. et al. (1988) G. C. A. 52, 909-915. [8] Wentworth S. J. et al. (2005) *Icarus, 174, 383-395*. [9] Schrader C. M. etal. (2016) MAPS,51,663-680.[10]RaoM.N.etal.(2008)J.G.R. *113*, doi:10.1029/2007JE002958.[11]YenA.S.etal.(2008)*J. G.R.,*113,doi:10.1029/2007JE002798.[12]McCollomT. M. et al.(2013)*J.G.R.,118,*doi:10.1002/jgre.20044. [13] Bigham J. M. and Nordstrom D. K. (2000) *Rev. Mineral. 40*, 351 – 453.