

SHOCK EXPERIMENTS ON BASALT - FERRIC SULFATE MIXES AT 21 GPa & 49 GPa AND THEIR RELEVANCE TO MARTIAN METEORITE IMPACT GLASSES. M.N. Rao¹, D.K. Ross¹, T.H. See¹, L.E. Nyquist², S. Sutton³, P.D. Asimow⁴, ¹SARD/ESCG, NASA Johnson Space Center, Houston, TX 77058 (thomas.h.see@nasa.gov), ²ARES, NASA Johnson Space Center, Houston, TX 77058, ³APS CARS & Dept. of Geophysical Sciences, Univ. of Chicago, Chicago, IL 60439, ⁴Div. of Geological and Planetary Sciences, Caltech, Pasadena, CA 91125.

Introduction: Large abundance of Martian atmospheric gases and neutron-induced isotopic excesses as well as Rb-Sr isotopic variations [1-3] determined in some impact glasses in basaltic shergottites (*e.g.*, Shergotty #DBS, Zagami #H1 and EET79001 #27, #8 and #104) provide definitive evidence for the occurrence of a Martian regolith component in their constituent mineral assemblages. Some of these glasses, known as gas-rich impact-melts (GRIM), contain numerous micron-sized iron sulfide blebs along with minor amounts of iron sulfate particulates. As these GRIM glasses contain a Martian regolith component and as iron sulfates (but not sulfides) are found to occur abundantly on the Mars surface, we suggested that the sulfide blebs in GRIMs were likely generated by shock-reduction of the parental iron sulfate bearing regolith material that had been incorporated into the cavities / crevices of basaltic host rock prior to the impact event on Mars [4]. To test whether the sulfates could be reduced to sulfides by impact shock, we carried out laboratory shock experiments on a basalt plus ferric sulfate mixture at 49 GPa at the Caltech Shock Wave Laboratory and at 21 GPa at Johnson Space Center (JSC) Experimental Impact Laboratory. The experimental details and the preliminary results for the Caltech 49 GPa experiment were presented at LPSC last year [5]. Here, we report the results for the 21 GPa experiment at JSC and compare these results to obtain further insight into the mechanism of the bleb formation in the GRIM glasses.

21 GPa experiment:

The 21 GPa experiment was carried out in the Flat-Plate Accelerator, a 20 mm smoothbore, horizontal powder propellant gun located in the Experimental Impact Laboratory at JSC [6]. The target consists of moderately compressed disc of powder [Columbia River Basalt (CRB) and ferric sulfate $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, 65 μm grain size, ~45% porosity] that was placed in a 9 x 0.8 mm sample well in a stainless steel (SS) target assembly. The assembly was, in turn, pressed into a SS target holder and the face of the combined assembly was machined flat. The target was then impacted with a 304 SS flyer plate travelling at 1.01 km/s. The resulting impact generated a planar shock wave of 21 GPa in the sample mix [6]. The SS assembly was then machined open to recover the shocked sample material that was subsequently prepared as a thin section for petrographic and FE-SEM investigations.

There are several regions in this polished thin section that show no evidence of melting which suggests that the temperature increase due to shock in these spots was relatively low. The lowest temperature minerals in the shocked sample are apatites in the CRB and the $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ which we had added to the target mixture.

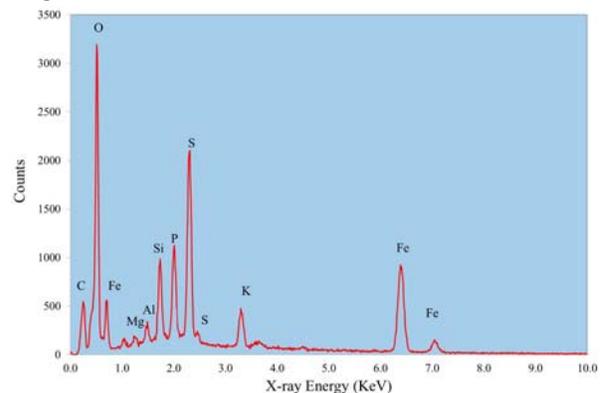


Figure 1. Typical EDS spectrum of the amorphous regions in the 21 GPa sample that shows cracking pattern shown in Fig. 2. Note the large S and P peaks.

FE-SEM examination of the amorphous material in this sample reveals that the prominent peaks are due to Fe and O signals along with those of S and P (Fig. 1). Here, it appears that ferric sulfate and apatite preferentially melted and the molten phases readily mixed with each other resulting in an amorphous material on quenching. No indication of immiscibility of fluids was found in this sample. In other regions bearing amorphous material, one obtains FE-SEM spectra showing Fe, S, and O peaks (but no P signal) indicating melting of only iron sulfate but no apatite (figure not shown). Moreover, we did not find any rounded Fe-sulfate or Fe-sulfide blebs that would have suggested fluid immiscibility between silicate and sulfide phases. These results indicate that significant inhomogeneities occurred in melting due to shock heating of the sample. The elemental abundances of Fe, S, and O deduced for the amorphous phases do not indicate formation of any pure mineral phases of known chemical composition.

Several amorphous regions in the 21 GPa sample display exhibit a cracking pattern that is typical thermal contraction (Fig. 2); this feature was not observed in the 49 GPa experiment. This thermal cracking could be the result of excessive temperature differences within a sample and its surroundings. During shock wave reverberation and decompression [7], the gases trapped

in the parent charge might have escaped from the cracked surface without interacting with the surrounding materials.

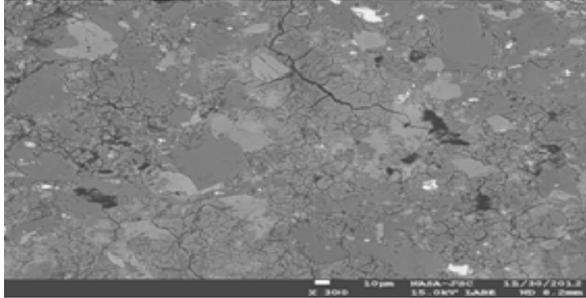


Figure 2. Thermal contraction cracking pattern in 21 GPa JSC shock experiment on basalt-ferric sulfate mix.

49 GPa shock experiment:

The experimental details and the preliminary results obtained in the 49 GPa experiment were reported earlier [5]. Note that the CRB plus ferric sulfate mixed charges shocked at 49 GPa and 21 GPa are aliquots from the same sample mixture. The 49 GPa sample was exposed to CO as a reducing agent prior to shock whereas, the JSC 21 GPa sample was not. We carried out detailed FE-SEM examination of the sulfide and sulfate blebs in the 49 GPa experiment and report an update of the new results obtained here.

We determined the Fe/S (atomic) ratios in different S-bearing phases (blebs) such as Fe-sulfate and Fe-sulfide in the shock-molten sample (shown in Figs. 1-4 of [5]). One finds dominant Fe, S, and O peaks in rounded blebs as well as incipiently-molten grains in several S-bearing phases in the quenched melt indicating the presence of sulfate. These blebs yield an Fe/S atomic ratio of $\sim 1.02 - 1.09$ (range) indicating a 1:1 relationship between Fe and S. This result suggests the occurrence of ferrous sulfate (FeSO_4), presumably derived from ferric sulfate by reduction due to the high-velocity shock at 49 GPa. At this stage, only Fe^{3+} was reduced to Fe^{2+} , whereas the sulfate anion seems to have remained unaffected because sulfate involves more energetic reduction to sulfide (as discussed below in steps II, IIa, and III). Ideally, one expects to find a Fe/S (atomic) ratio of 0.67, if no shock-reduction had taken place in the parent $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ in the sample.

There is another group of rounded blebs that display dominant Fe and S peaks (but no O peak) and yield an Fe/S (atomic) ratio of 0.93 indicating that these blebs contain FeS [8]. These blebs presumably formed by the reduction of FeSO_4 to FeS into an immiscible sulfide fluid that on quenching and dispersion gave rise to numerous FeS blebs (discussed below in Steps IV and IVa). Minetti *et al.* [9] and Therkelsen *et al.* [10] carried out high velocity shock experiments on

kaerusitites (35 GPa) and on individual minerals plagioclase (plag), pyroxene (pyx), and olivine (38 GPa), respectively, and showed that Fe^{3+} is reduced to Fe^{2+} by shock.

Based on the results from the 49 GPa experiment, below we present a generalized model involving the step-wise chemical processing reactions during impact shock wave heating of the regolith bearing materials on the Martian surface. Step I: Near the Martian surface, the H_2O present in the sample is likely to become supercritical at temperatures $>350^\circ\text{C}$ on impact heating and dissociates into H^+ and OH^- providing hydrogen as the reducing agent. However, in the 49 GPa experiment, the CO that was mixed into the sample prior to impact acts as the reductant. Step II: The Fe^{3+} in the ferric sulfate gets reduced to Fe^{2+} by the reaction $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ involving one electron transfer. Step IIa: Due to shock, ferric sulfate undergoes chemical transformation and reduction to ferrous sulfate by the reaction $\text{Fe}_2(\text{SO}_4)_3 \rightarrow 2\text{FeSO}_4 + (\text{SO}_4)^{2-}$. Here, one mole of ferric sulfate yields two moles of ferrous sulfate and one mole of sulfate $(\text{SO}_4)^{2-}$. Step III: Under moderate reduction conditions, this additional sulfate $(\text{SO}_4)^{2-}$ gets reduced to $\text{SO}_2\uparrow$ by the reaction $(\text{SO}_4)^{2-} + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{SO}_2\uparrow + 2\text{H}_2\text{O}$ (involving 2 electrons transfer) and SO_2 gas escapes from the molten charge. Step IV: On more energetic reduction, the sulfate is reduced to sulfide (S^{2-}) by the reaction $(\text{SO}_4)^{2-} + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{S}^{2-} + 4\text{H}_2\text{O}$ (involving 8 electrons transfer). Step IVa: Finally, Fe^{2+} combines with S^{2-} to form FeS by the reaction $\text{Fe}^{2+} + \text{S}^{2-} \rightarrow \text{FeS}$. The resulting FeS forms into an immiscible fluid which on quenching and dispersion produces numerous micron-size blebs observed in the impact melts.

In summary, in the case of 21 GPa experiment, the shock wave interaction in the CRB + ferric sulfate mix seems to be limited to the surface where no iron sulfate reduction took place. But, in the 49 GPa experiment, the shock wave interaction occurred all over the sample and the ferric sulfate is reduced to ferrous sulfate by moderate shock reduction in several areas and to iron sulfide blebs by energetic reduction in other locals.

References: [1] D.D. Bogard and P. Jhonson, *Science*, 221, 651, 1983 [2] M.N. Rao *et al.*, *JGR*, 116, E08006, doi:10.1029/2010JE003764, 2011 [3] L.E. Nyquist *et al.* 75th *MetSoc Meeting at Cairns (Austr.)* (abs.) #5262, 2012. [4] M.N. Rao *et al.*, *LPSC XXXV* (abs.) #1501, 2004: GRL, [5] M.N. Rao *et al.*, *LPSC XXXIII* (abs.) #2102, 2011 [6]. T.H. See *et al.*, *LPSC XXXII* (abs.) #1807, 2001. [7] P. Beck *et al.* *Nature*, 435, 1071, 2005. [8] J.P. Lorand *et al.* *Meteorit. Planet. Sci.* 40, 1257, 2005. [9] M.E. Minitti *et al.* *EPSL*, 266, 288, 2008. [10] J.P. Therkelsen *et al.*, *LPSC XXXIII* (abs.) #1696, 2002.