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 Fe$_2$(SO$_4$)$_3$, 9H$_2$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 Fe$_2$(SO$_4$)$_3$, 9H$_2$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.](https://ntrs.nasa.gov/search.jsp?R=20130009928)
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 re-

sults 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 sul-

fide 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 indicat-

ing the presence of sulfide. These blebs yield an Fe/S

atomic ratio of ~1.02 – 1.09 (range) indicating a 1:1

ratio of ~1.02 – 1.09 (range) indicating a 1:1

atomic ratio. This result suggests the presence of sulfate . These blebs yield an Fe/S (atomic) ratio of 0.93 indicating that the-

blebs contain FeS [8]. These blebs presumably

resulted from the reduction of FeSO₄ to FeS by the reaction Fe²⁺ + S²⁻ \rightarrow FeS. The resulting FeS forms

kaerosiitites (35 GPa) and on individual minerals plag,

pyx, and olivine (38 GPa), respectively, and showed that Fe²⁺ is reduced to Fe²⁺ 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 su-

face, the H₂O present in the sample is likely to become

superheated at temperatures >350°C on impact heating

dissociates into \( \text{H}^+ \) and \( \text{OH}^- \) providing hydrogen

as the reducing agent. However, in the 49 GPa ex-

periment, the CO that was mixed into the sample prior to

impact acts as the reductant. Step II: The Fe³⁺ in the

ferric sulfate gets reduced to Fe²⁺ by the reaction Fe³⁺ + e⁻ \rightarrow Fe²⁺ involving one electron transfer. Step IIa:

Due to shock, ferric sulfate undergoes chemical trans-

formation 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 \( \text{SO}_2 \) by the reaction \((\text{SO}_4)^{2-} + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{SO}_2 + 2\text{H}_2\text{O} \) (involving 8 electrons transfer) and \( \text{SO}_2 \) gas escapes from the molten charge. Step IV:

On more energetic reduction, the sulfate is reduced to

double sulfide \((\text{S}^{2-})\) by the reaction \((\text{S}^{2-}) + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{S}^{2-} + 4\text{H}_2\text{O} \) (involving 8 electrons transfer). Step IVa:

Finally, Fe²⁺ combines with \( \text{S}^{2-} \) to form FeS.

The resulting FeS forms

into an immiscible fluid which on quenching and dis-

persion produces numerous micron-size blebs ob-

served 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 sam-

ple 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 lo-

cals.
