SULFUR ISOTOPES IN GAS-RICH IMPACT-MELT GLASSES IN SHERGOTTITES.

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Introduction: Large impact melt glasses in some shergottites contain huge amounts of Martian atmospheric gases and they are known as gas-rich impact-melt (GRIM) glasses. By studying the neutron-induced isotopic deficits and excesses in ^{149}Sm and ^{150}Sm isotopes resulting from ^{149}Sm (n,γ) ^{150}Sm reaction and ^{80}Kr excesses produced by ^{79}Br (n,γ) ^{80}Kr reaction in the GRIM glasses using mass-spectrometric techniques, it was shown that these glasses in shergottites EET79001 and Shergotty contain regolith materials irradiated by a thermal neutron fluence of ~10^{15} n/cm^2 near Martian surface [1,2]. Also, it was shown by [3,4] that these glasses contain varying amounts of sulfates and sulfides based on the release patterns of SO$_2$ (sulfate) and H$_2$S (sulfide) using stepwise-heating mass-spectrometric techniques. Furthermore, EMPA and FE-SEM studies in basaltic-shergottite GRIM glasses EET79001, LithB (,507& ,69), Shergotty (DBS I &II), Zagami (,992 & ,994) showed positive correlation between FeO and "SO$_3$" (sulfide + sulfate), whereas those belonging to olivine-phyric shergottites EET79001, LithA (,506, & ,77) showed positive correlation between CaO / Al$_2$O$_3$ and "SO$_3$" [5,6].

S K-XANES studies: To record the spatial distribution of sulfate and sulfide in these glasses, we studied the S K- XANES spectra obtained in ,506 and ,507 samples using the Synchrotron X-ray Microprobe at the Argonne National Laboratory [7]. The ,507 spectra showed abundant iron sulfide (FeS) signals and less abunduant signals due to sulfate. In the ,506 sample, sulfide was again dominant but more likely dominated by Ca coordination with only minor FeS. This reduced sulfur was mixed with varying proportions of oxidized sulfur with more oxidized sulfur near the host silicate contact. These results indicate that oxidized sulfur is more abundant in ,506 than in ,507. In these regolith-associated samples, the sulfur-bearing species are expected to be sulfates because the Martian surface is oxidizing. However, both reduced and oxidized sulfur species exist in these glasses and the reasons are examined below.

Fe/Ni ratios: To study the sulfur chemistry in these glasses, we determined the Fe-S-Ni abundances in several S-bearing sites [8] using the FE-SEM at MPI (Mainz). In ,506, Ni concentrations varied between 0.4 and 11% in igneous sulfide grains. The average Fe/Ni ratio of ~50 in these grains is only slightly larger than the ratio of ~31 found in Lith A sulfides [9]. Note

that [10] determined a FeO/NiO ratio of ~420 in two other GRIM glasses ,27 and ,54 in Lith A by INAA. This value is somewhat similar (factor of 2) to the Fe/Ni ratio of ~800 determined by us in the sulfide-free vesicular glassy areas in ,506 where sulfate presumably mixed with molten silicate. On the other side, in ,507, sulfur is present as FeS (sometimes as FeSO$_4$) occuring mostly as secondary micron-size globules with amorphous texture. We found the Ni content here to be close to the detection limit. The Fe/Ni ratio in the globules is ~150- 900 much higher than in Lith A sulfides [9]. These results suggest that the Ni abundances in secondary sulfur-bearing species in these glasses are different from those found in igneous sulfides in EET79001.

S-isotopes by Nano-SIMS: To study the origin of the sulfur components in GRIM glasses, we determined the sulfur isotopic ratios, i.e. δ^{34}S values relative to CDT (Canyon Diablo troilite) in ,506 and ,507 using the Nano-SIMS at MPI (Mainz). A Cs$^+$ beam (100 nm, < 1pA) was rastered (2μm x 2μm) over selected pyrrhotite grains in ,506 and ,507 and negative secondary ions of ^{32}S and ^{34}S were measured in multi-collection mode. In ,506 and ,507, we could easily identify FeS grains in the SEM but not sulfates. The results of δ^{34}S obtained for typical sulfide grains in ,506 with reference to CDT are shown in Fig.1. The weighted average is $-$ 1.15 ± 0.25 ‰ (1σ). If one considers 2σ errors, the δ^{34}S values obtained in ,506 agree with those determined by [11] for EET79001, Lith A (mean:─1.9 ‰). The sulfide grains in ,506 are ~8-30μm, rounded and crystalline. On the otherhand, the sulfide grains in ,507 are 1-2 μm and rarely up to ~ 7μm. The δ^{34}S values determined for typical ,507 sulfides are given in Fig.1. The weighted average for ,507 sulfides is +0.03 ± 0.61‰. The large error for the mean is because of the small size of the individual grains. The δ^{34}S value for largest grain (7μm) is +1.4± 0.6‰. This value is considered to be different from the mean of ─1.7‰ given by [11] for EET79001, Lith B sulfides.

To examine the sulfate – sulfide relation in GRIM glasses, we need to know the δ^{34}S values for sulfates in ,506 and ,507. In the GRIM glasses, sulfides are easily found in the SEM whereas crystalline sulfates are difficult to spot as they turned glassy during shock-melting and quenching. Hence, they could not be measured in the Nano-SIMS. So, we rely on the sulfur isotope data obtained for Shergotty by [12] using

controlled sequential-leaching of different S-bearing components by selected chemical solvents in the powdered meteorite. The sulfides (AVS) studied by [12] in Shergotty and those studied by [13] in EET79001, Lith B yielded δ^{34}S values of −0.01‰ and −0.019‰ respectively. These values agree with the δ^{34}S value of +0.03 ± 0.61 ‰ determined by us for ,507 (Lith B) sulfides. We assume that this agreement for sulfides can be extended to sulfates in these two basaltic shergottites. We consider that the δ^{34}S values for sulfates in Shergotty and EET79001, 507 are similar because their GRIM glasses show several similarities [5,6]. Farquhar et al. [12] found a δ^{34}S value of +5.25‰ for the sulfate fraction in Shergotty and , by analogy, we assume the same δ^{34}S value for the sulfates in EET79001, 507.

The δ^{34}S value of +5.25‰ for the sulfate in ,507 is heavy compared to the sulfide (FeS). Such large δ^{34}S values are usually attributed to volcanic exhalation of SO_2 on Mars similar to Earth [11,14,15]. Because volcanic exhalations of SO_2 on Mars is a favored mechanism to explain the high sulfur contents found in Martian soils, a large surface source of isotopically heavy sulfur on Mars is a possibility [11,14]. Clearly, such large +δ^{34}S values for sulfates cannot be produced by the oxidation of sulfides (δ^{34}S ~ −2‰) in 507 [16-18]. In non-equilibrium oxidation of sulfides (kinetic), the sulfates might show δ^{34}S values somewhat lower than those of the sulfides [15-18].

It appears that most of the sulfides in these glasses are secondary. They are presumably produced by high temperature reduction of sulfates during shock-melting and quenching on Mars. A possible reductant in the thermochemical sulfate reduction at high temparatures is H_2 as the ferrous minerals in the matrix generate H_2 locally by the reaction $FeO + H_2O \rightarrow Fe_2O_3 + H_2$ [17]. The resulting molten silicate liquid accommodates only a limited amount of FeS. Hence, the excess S became immiscible with the silicate melt and was purged out as secondary FeS globules [4,19]. On quenching, they produced amorphous textures. In this context, on the Earth, during basalt-seawater interactions, the sulfate is reduced to pyrrhotite at temperatures > 300 ℃ [17]. Here, Ohmoto and Rye [17] showed that during the reduction of sulfate to sulfide at high temperature in the circulating fluid systems through underlying volcanics, seawater with a δ^{34}S value of +20‰ produces H_2S between +20‰ and − 5 ‰ depending on the degree of reduction. We suggest that a similar type of reduction at high temperature could have taken place in shergottite GRIM glasses during shock-melting (~1000 ℃) and quenching. As a result, the sulfates in ,507 assumed to have δ^{34}S ~ 5.3‰ would have been reduced to sulfides with δ^{34}S

values ranging between +5.3‰ and − 2.0‰ during shock-melting and quenching. Independent evidence for the occurrence of reduction in these glasses is provided by vanadium which was shown to have reduced from the +4 state to the +3 state in these glasses using V K-XANES spectra obtained by us recently [20].

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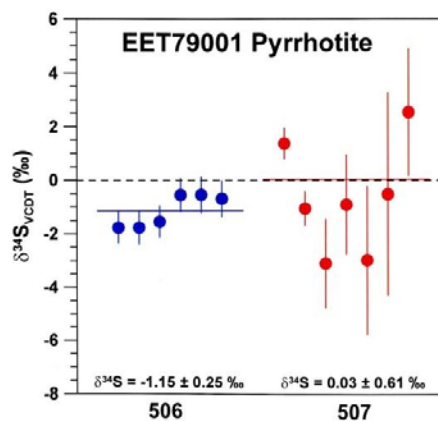

Fig.1. δ^{34}S for sulfides in GRIM glasses in basaltic shergottite (,507) and olivine-phyric shergottite (,506). In ,507, 1-2 μm (red) grains have large errors. Larger (red) grains have smaller errors. Raster size is 2x2 μm². The ,506 (blue) grains are ~8-30 μm.