

Geochemical Constraints on the Evolution of Ancient Water Reservoirs on Mars from Sulfur Speciations in Impact Glasses of Shergottites

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Geological observations of Mars exploration imply that ancient Mars had a great amount of water, in contrast to the cold and arid environment at present. The loss of water due to the selective dissipation of hydrogen to the space induced the surface oxidation by oxygen left behind. The progressive oxidation of Martian surface resulted in the formation of sulfate (SO_4^{2-}) and perchlorate (ClO_4^-) minerals. Such geochemical information is expected to be recorded in Martian meteorites originated from the Martian surface. In particular, redox sensitive element of sulfur (valence state of -2 to +6) is a promising tracer for constraining the oxidation process. Since the Martian mantle is highly reduced, sulfur is considered to have been supplied to the Martian surface as sulfide (H_2S and $\text{Fe}_{(1-x)}\text{S}$), which are then oxidized to form sulfate minerals. Although Mars exploration missions showed the widespread distribution of sulfate minerals, no clear evidence for the presence of sulfate minerals in shergottites was reported.

This study examined sulfur speciation in impact glasses of three basaltic shergottites (Martian meteorites), Elephant Moraine (EETA) 79001, Larkman Nunatak (LAR) 06319, and Dhofar 019, using X-ray absorption near-edge structure (XANES) spectroscopy. The measured XANES spectra were classified into four types: (Type-1) FeS, (Type-2) highly reduced sulfide, (Type-3) mixture of sulfide and sulfate, and (Type-4) sulfate. The Type-1 and -3 were observed from EETA79001 and LAR 06319, while the Type-2 spectra were obtained only from EETA79001. The Type-1 and -2 are distinguished by the absence of the first peak at 2468.5 eV, suggesting a low $f\text{O}_2$ condition ($\sim\text{IW}+1$) of the Type-2 sulfide. All the sulfate spectra (Type-3) from EETA79001 and LAR 06319 are accompanied with sulfide. The coexisting sulfate and sulfide in the impact glasses should have possibly originated in Mars because impact glasses were formed by shock on the surface of Mars. In addition, the presence of the highly reduced sulfide (Type-2) suggests that the impact glasses in EETA79001 would not have experienced alteration/weathering on the oxic Earth's environment after the fall. On the other hand, Dhofar 019 showed only Type-4 spectra. Rare earth element patterns of bulk rock and maskelynites of Dhofar 019 show a Ce anomaly that is induced by the oxidation of Ce followed by the interaction with water. However, Dhofar 019, found in the desert, is expected to have less alteration by terrestrial water. Further studies are necessary to discuss the cause of sulfate signature for Dhofar 019. Thus, the following discussion focuses on LAR 06319 and EETA79001.

The Type-3 spectra obtained in this study indicate the existence of sulfate as a minor precursor phase of impact glasses. Geochemical signatures of volatile elements (e.g., D/H, C, and halogens) in impact glasses of EETA79001 and LAR 06319 imply the alteration of their host rocks by Martian subsurface fluid. Alteration parts of the meteorites are thought to have experienced local melting and quenching by shock and resulted in impact glasses because they have lower melting temperature than the surrounding primary silicate phases (pyroxene+plagioclase+/-olivine). We propose two possible scenarios for the formation of sulfate species to the shergottite host-rocks: (i) oxidation of sulfide minerals by subsurface oxic water and (ii) precipitation of sulfate ion derived from subsurface water. The difference among these models is the source of S(VI) species, whether it originated in (i) magmatic sulfide in shergottite or (ii) sulfate ion in the subsurface water/ice. These models supposing water-rock interaction indicate that the

ancient water reservoir might have already been oxic. Either model requires post-magmatic water-rock interaction that participated in the formation of impact glass in Martian basalt of shergottites.

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