

SULFUR K-EDGE XANES ANALYSES OF SHERGOTTITES: IMPLICATION FOR AQUEOUS ALTERATION PROCESSES ON MARS. M. Shidare¹, R. Nakada², T. Usui³, M. Tobita¹, and T. Yokoyama¹, ¹Dept. of Earth & Planet. Sci., Tokyo Inst. Tech., 2-12-1 Ookayama, Meguro, Tokyo 152-8551, Japan (shidare.m.aa@m.titech.ac.jp), ²JAMSTEC, 200 Monobe, Nankoku, Kochi 783-8502, Japan, ³ELSI, Tokyo Inst. Tech., 2-12-1 Ookayama, Meguro, Tokyo 152-8551, Japan

Introduction: The Martian geology and geomorphology indicate that there was a large body of liquid water on the surface [1], while the surface of Mars today is relatively dry. The loss of water was induced by the selective dissipation of hydrogen, and oxygen left behind has progressively oxidized the Martian surface [2]. The surface oxidation resulted in the formation of highly oxidized minerals such as perchlorate (ClO_4^-) and sulfate (SO_4^{2-}). Mars exploration missions indicate that perchlorate and sulfate minerals are globally distributed on the surface [e.g., 3, 4].

Sulfur is appropriate for constraining the oxidation process because of its redox sensitivity and high abundance in rocks and soils (~5–10 wt.% SO_3 , [5]). Sulfur is thought to have been supplied as sulfide (H_2S and FeS) from highly reduced mantle (~IW+1), which was oxidized to form sulfate minerals on the Martian surface [3]. Previous studies on Martian meteorites reported the existence of sulfate minerals in grain boundaries [6, 7], yet most of them have been suspected of terrestrial contamination because of their occurrences [7]. Thus, we focus on impact glasses that definitely formed on the surface of Mars to search for indigenous Martian sulfate components in meteorites.

X-ray absorption near-edge structure (XANES) analysis uniquely provides a means to analyze the sulfur speciation in amorphous impact glass. Our preliminary XANES study developed a new methodology to effectively search for sulfate in impact glasses based on X-ray fluorescence (XRF) maps of sulfide and total-sulfur [8]. The superposition of these two maps visualized distribution of sulfur species (as $\text{S}^{2-}/\Sigma\text{S}$ ratio) and enabled us to obtain XANES spectra indicating sulfate signatures from impact glasses of two Martian meteorites [8]. This study conducts systematic XANES analyses of three shergottites (Larkman Nunatak (LAR) 06319, Elephant Moraine (EETA) 79001, and Dhofar 019). We selected these meteorites because they have distinct Mars ejection ages (i.e., derived from different launching sites), aiming at less biased information on Martian surface environment.

Samples and methods: LAR 06319 is an olivine-phyric shergottite with crystallization and cosmic ray exposure (CRE) ages of 193 ± 20 Ma and 3.3 Ma, respectively [9, 10]. EETA79001 is a shergottite meteorite that was crystallized at 173 ± 3 Ma and has a CRE age of 0.73 ± 0.15 Ma [11, 12]. Dhofar 019 is an oli-

vine-phyric shergottite found in the desert of Oman [13] with crystallized and ejected ages of 575 ± 7 Ma [14] and 19.8 ± 2.3 Ma [15], respectively. We employed an indium-mounted polished section of LAR 06319, 50 [16], a thin section of EETA79001, 20 from lithology C, and a thin section of Dhofar 019.

Sulfur K-edge (2472 eV) XANES analyses were performed at BL27SU of SPring-8 (Hyogo, Japan). The X-ray beam was focused using a K-B mirror to a final spot size of 15 (vertical) \times 15 (horizontal) μm^2 . The X-ray energy was calibrated with peak maximum of haüyne at 2480 eV. Prior to the XANES measurements, XRF maps (scanned in 8 μm step) were obtained to determine analytical spots with referring to back scattered electron and X-ray images. Following the preliminary study [8], two XRF maps were obtained for each analytical area at 2480 eV (peak maximum of S(VI)) and at 2468 eV (peak maximum of S(-II)).

Results and discussion: Ten analytical spots of impact glasses in LAR 06319 and EETA79001 showed

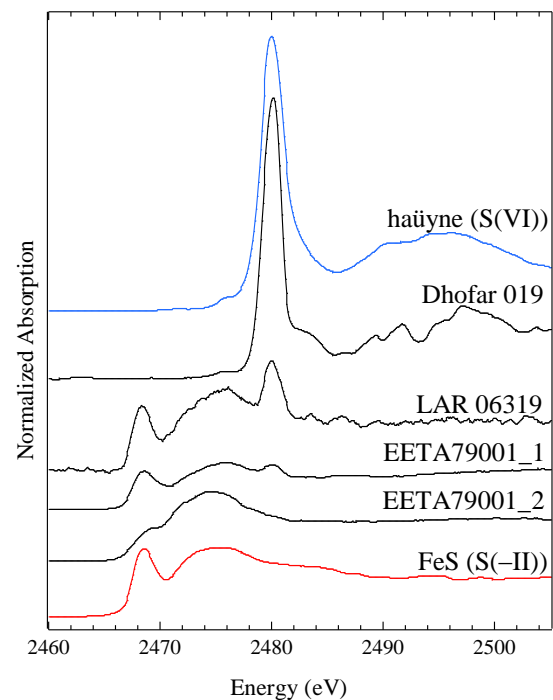


Figure 1. Representative spectra of Dhofar 019, LAR 06319, and EETA79001 with reference materials of haüyne and FeS.

XANES spectra that have characteristics for both S(-II) and S(VI), and all the others showed only S(-II) spectra (Fig. 1). The contribution of S(VI) was calculated by linear combination fitting of reference materials and confirmed to be less than 12%. As for Dhofar 019, only S(VI) spectra were observed (Fig. 1).

A previous study on the S K-edge XANES analysis of EETA79001 only showed the occurrence of S(-II) species in the impact glass [17], in contrast to the current study and our preliminary analyses [8]. The discrepancy can be related to the heterogeneous distribution and low abundance (<12%) of S(VI) species. Since superimposed XRF maps show that S(VI) species are strongly localized in the EETA79001 impact glasses, the previous study using large X-ray beam ($200 \times 200 \mu\text{m}^2$, [17]) could not observe S(VI) signature.

Because the impact glass was formed on the surface of Mars, both S(VI) and magmatic S(-II) signatures found in the individual impact glasses of LAR 06319 and EETA79001 indicate a mixing of non-terrestrial sulfide and sulfate phases on the Martian surface. If the observed S(VI) signature is a result of oxidation process on Earth, heterogeneous distribution of S(VI) species and existence of highly reduced S(-II) (EETA79001_2 in Fig. 1) in the impact glass cannot be explained.

In contrast, the XANES spectra of two impact glasses of Dhofar 019 only showed S(VI) signatures. 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 [18]. However, Dhofar 019, found in the desert, is expected to have less alteration by terrestrial water. Thus, the following discussion focuses on LAR 06319 and EETA79001.

The XANES spectra obtained in this study indicate the existence of sulfate as a minor precursor phase of impact glasses. A previous study on hydrogen isotope suggested that the impact glasses of LAR 06319 and EETA79001 records the interaction with subsurface water [16]. We propose three possible scenarios for the formation of S(VI) species to the shergottite host-rocks: (A) oxidation of sulfide minerals by subsurface oxic water, (B) precipitation of sulfate ion derived from subsurface water, and (C) incorporation of sulfate minerals in Martian regolith. The difference among these models is the source of S(VI) species, whether it originated in (A) magmatic sulfide in shergottite, (B) sulfate ion in the subsurface water/ice, or (C) sulfate minerals in the regolith. 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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References: [1] Ehlmann B. L. and Edwards C. S. (2014) *Ann. Rev. EPS*, 42, 291-315. [2] Zahnle K. et al. (2008) *JGR*, 113, E1104. [3] Bibring J.P. et al. (2006) *Science*, 312, 400-404. [4] Vaniman D. T. et al. (2014) *Science*, 343, 6169. [5] Clark B. C. et al. (1982) *JGR*, 87, 59-67. [6] McCubbin F. M. et al. (2009) *GCA*, 73, 4907-4917. [7] Hallis L. J. and Taylor G. J. (2011) *MAPS*, 46, 1787-1803. [8] Shidare M. et al. (2017) *ILVIII*, Abst #1973. [9] Shafer J. T. et al. (2010) *GCA*, 74, 7307-7328. [10] Nagao K. and Park J. (2008) *71st Ann. Met. Soc. Mtg.*, Abst #5200. [11] Debaille V. et al. (2008) *nature geosci.*, 2, 548-552. [12] Nyquist L. E. et al. (2001) *Space Sci. Rev.*, 96, 105-164. [13] Taylor L. A. et al. (2000) *MAPS*, 35, A155. [14] Borg L. E. et al. (2001) *XXXII*, Abst #1144. [15] Shukolyukov Y. A. et al. (2000) *MAPS*, 35, A147. [16] Usui T. et al. (2015) *EPSL*, 410, 140-151. [17] Walton E. L. et al. (2010) *GCA*, 74, 4829-4843. [18] Taylor L. A. et al. (2002) *MAPS*, 37, 1107-1128.

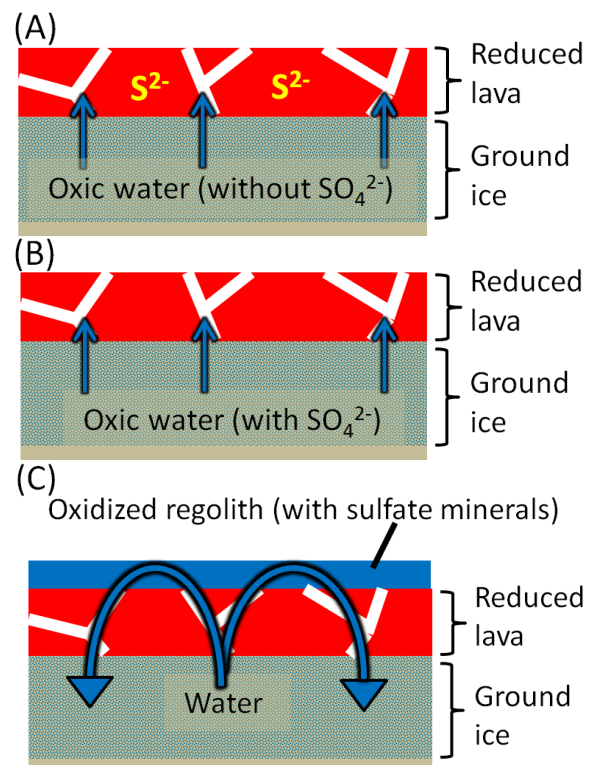


Figure 2. Three models for the formation of sulfate-bearing impact glass in shergottite. (A) Oxidation of magmatic sulfide, (B) incorporation of sulfate from ground water aquifer, (C) transportation of regolith sulfate.