DETECTION OF MARTIAN SULFATE FROM IMPACT GLASSES IN SHERGOTTITES BY X-RAY ABSORPTION NEAR-EDGE STRUCTURE ANALYSIS. M. Shidare¹, R. Nakada², T. Usui³, K. Shimizu⁴, T. Yokoyama⁵, Y. Takahashi⁶, ¹Dept. of Earth & Planet. Sci., Tokyo Inst. Tech., 2-12-1 Ookayama, Meguro, Tokyo 152-8551, Japan (shidare.ma@mi.titech.ac.jp), ²JAMSTEC, 200 Monobe, Nankoku, Kochi 783-8502, Japan, ³ELSI, Tokyo Inst. Tech., 2-12-1 Ookayama, Meguro, Tokyo 152-8551, Japan, ⁴Dept. of Earth & Planet. Sci., The University of Tokyo, 7-3-1 Hongo, Bunkyo, Tokyo 113-0033, Japan

Introduction: The geology and geomorphology of Mars indicate that there was a large body of liquid water on the surface [1]. In contrast to the ancient watery environment, the surface of Mars today is relatively dry. Since the loss of water due to atmospheric escape to space has induced the selective dissipation of hydrogen, oxygen left behind has progressively oxidized the Martian surface [2]. The progressive surface oxidation resulted in the formation of highly oxidized minerals such as perchlorate (ClO₄⁻) and sulfate (SO₄²⁻). Mars exploration missions (e.g. Mars Express and MSL) indicate that perchlorate and sulfate minerals are globally distributed on the surface [e.g., 3, 4]. On the other hand, no clear evidence for the presence of these oxidized phases in shergottites has been reported. For example, a X-ray absorption near-edge structure (XANES) study of impact glasses in Elephant Moraine (EETA) 79001 did not find any sulfate (S(VI)) signatures [5], although these impact glasses are known to have trapped surficial and atmospheric components [6, 7]. This study conducted a systematic survey of sulfate in impact glasses of shergottites based on X-ray fluorescence (XRF) maps of sulfide and total-sulfur prior to the XANES measurements. The incorporated XRF maps visualized the potential occurrence of sulfate components and enabled us to observe S K-edge XANES spectra of Martian sulfate-bearing components in impact glasses of EETA79001 and Larkman Nunatak (LAR) 06319.

Samples and Methods: This study focuses on impact glasses of two shergottites, EETA79001 and LAR 06319. EETA79001 consists of three lithologies (A: olivine phyr; B: basaltic; C: glass). These lithologies have identical crystallization ages of 173±3 Ma [8]. Impact glass occurs dominantly in Lithology-C. LAR 06319 is an olivine-phyr shergottite with a crystallization age of 193±20 Ma [9]. This meteorite also has impact glass pockets. Previous studies indicated that the impact glasses of these two meteorites contained Martian surface components [6, 7]. We employed a thin section of lithology C (EETA79001, 20; Fig. 1) and a polished rock chip embedded in indium metal (LAR 06319, 50; Fig. 2).

The samples were carbon coated and analyzed using an electron probe micro analyzer (JEOL JXA-8530F) at Earth-Life Science Institute (ELSI). Mineral and glass compositions were determined using a 15 kV accelerating voltage, a 40 nA beam current (5 nA for glasses), highly focused beam diameter (5 μm for glasses), and standard ZAF correction for all phases.

Sulfur K-edge (2470 eV) XANES analyses were performed at BL27SU of SPring-8 synchrotron radiation facility (Hyogo, Japan). The white beam from an undulator was monochromatized using a Si(111) double crystal monochromator. The X-ray beam was focused using a K-B mirror to a final spot size of 15 (vertical) × 15 (horizontal) μm². The X-ray energy was calibrated with peak maximum of haüyne at 2480 eV. Prior to the XANES measurements, XRF mapping (scanned in 8 μm step) were obtained to determine analytical spots with referring to the BSE images (Figs. 1 and 2).

Figure 1. BSE and XRF images of impact glass of EETA79001. A: BSE image. Impact glass is located within the yellow dashed lines. Green crosses indicate XANES points shown in Fig. 3. B: Superimposed XRF (blue: sulfide; red: total S) image of Fig. 1A.

Figure 2. BSE and XRF images of impact glass of LAR 06319. A: BSE image. Impact glass is located within the yellow dashed lines. Green crosses indicate XANES points shown in Fig. 3. B: Superimposed XRF (blue: sulfide; red: total S) image of Fig. 2A.
1A and 2A). In this study, 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)). The superposition of the two XRF maps shows the area where S(VI) is expected to exist (Figs. 1B and 2B).

**Results and discussion:** Major element compositions of impact glasses in EETA79001 and LAR 06319 are characterized by high Al2O3 (~7 wt.% and ~17 wt. % for EETA79001 and LAR 06319, respectively) and Na2O (~1 wt.% and ~3 wt.% for EETA79001 and LAR 06319, respectively) contents, as well as moderate mafic mineral components (e.g., ~17 wt.%FeO and ~10 wt.%FeO for EETA79001 and LAR 06319, respectively), reflecting melting of major constituent phases of olivine, pyroxene, and maskelynite. In addition, the impact glasses are enriched in minor elements of phosphorous (~0.1 wt.% and ~0.1 – 3 wt.% for EETA79001 and LAR 06319, respectively) and sulfur (~1 wt.% and ~0.1 wt.% for EETA79001 and LAR 06319, respectively). The enrichment of phosphorous and sulfur indicate the incorporation of non-silicate phases such as merrillite and sulfide (and possibly sulfate) during the shock-induced melting by impact.

The S K-edge XANES spectra of impact glasses are shown in Fig. 3 along with those of the reference materials of S(-II) and S(VI). The shapes of the spectra revealed a clear distinction between sulfide and sulfate. The S(-II) presents a sharp peak at 2468 eV and a broad peak at around 2475 eV. A synthetic experiment showed that under reducing condition at QFM-1.4 the S(-II) peak at 2468 eV becomes small [10]. The presence of S(VI) is suggested by a sharp peak at 2480 eV. In our analysis, only S(-II) species were observed from spot-2 of LAR 06319, and spots-2 and -3 of EETA79001. Spot-3 of EETA79001 is likely to have formed under more reducing condition than the others.

On the other hand, we clearly observed the peak corresponding to the presence of S(VI) species at spot-1 of LAR 06319 and less evidently at spot-1 of EETA79001. Although only a small peak was observed from EETA79001, our XRF mapping and XANES measurements successfully indicated the incorporation of sulfate mineral(s) in impact glasses. Because the impact glass was formed on the surface of Mars, both S(-II) (magmatic) and S(VI) (surficial) signatures found in individual impact glasses indicate mixtures of non-terrestrial sulfide and sulfate minerals on Mars.

Water is essential for the formation of sulfate minerals. High δD values (~1500 – 2000 ‰), suggestive of ancient (~4 Ga) Martian surface components [11], were observed from impact glasses of these meteorites [6]. The presence of both Martian hydrogen and S(VI) components in the impact glasses suggest that the bedrocks of these meteorites were partially altered by crustal fluids with δD values lower than the present Martian atmosphere (~5000 ‰) [6]. The crustal fluids should have preferentially altered grain boundaries and voids to form alteration veins and pods. These altered areas are prone to melt by impact relative to the other silicate parts, resulting in impact glasses as observed in EETA 79001 and LAR 06319. This scenario is consistent with a weathering experiment that demonstrated that sulfate phases (gypsum and hexahydrate) are produced by the interaction of water with reduced magmatic phases of olivine, pyroxene, and pyrrhotite [12].


**Figure 3.** XANES spectra of impact glasses of EETA79001 and LAR 06319 in Figs. 1 and 2, except for spot 3 of EETA79001. Peaks on the dot lines are typical for the spectra of S(-II) and S(VI). Both S(-II) and S(VI) were observed apparently at spot 1 of both meteorites.