MICRO-XANES DETERMINATION OF OXIDATION STATES OF V AND Fe IN OLIVINE-HOSTED GLASS INCLUSION AND GROUNDMASS GLASSES OF YAMATO 980459. R. Nakada[1], T. Usui[2], M. Ushioda[3], and Y. Takahashi[4], [1] Kochi Institute for Core Sample Research, JAMSTEC, Japan (nakadar@jamstec.go.jp), [2] Department of Solar System Sciences, ISAS, JAXA, Japan, [3]Geological Survey of Japan, AIST, Japan, [4]Department of Earth and Planetary Science, the University of Tokyo, Japan.

Introduction: The redox condition, or oxygen fugacity (fO_2), of a magma controls the stability and composition of crystallizing and volatile phases in a magma, and provides information on the genesis, differentiation, and a source region of the mantle. A knowledge on the evolution of the Martian interior has been acquired by the analysis of the Martian meteorites. Mineralogical oxybarometers have been conventionally used to estimate the fO_2 of Martian magmas (e.g., [1–5]). Partitioning of redox sensitive elements has been more recently used to evaluate the fO_2, combined with laboratory experiments (e.g., [6–10]).

These previous studies did not pay much attention to glassy compounds. Meanwhile, olivine-hosted glass inclusion and groundmass glasses are generally crystallized out at the earliest and latest stages of the formation of basaltic rocks, respectively. This fact means that the investigation of these contrasting glass phases has the potential to provide information on the transition or evolution of the fO_2 condition from the initial basaltic magma generation to the final solidification stages. X-ray absorption near edge structure (XANES) analysis on the redox sensitive elements can be the best method to estimate the fO_2 condition of glass in Martian meteorite because XANES is applicable to amorphous glass, which is impossible to analyze using X-ray diffraction.

This study performed micro-XANES (μ-XANES) analysis on V and Fe in both inclusion and groundmass glasses of a Martian meteorite (Yamato 980459; Y98) to estimate fO_2 condition and evolution of Martian magma. The determination of the oxidation states of V and Fe can offer reasonable clues with which to estimate fO_2 condition, taking into account the facts that these elements are highly redox sensitive to reflect various oxidation states over a wide range of fO_2 experienced by planetary basalts [11].

Sample: Y98 is an olivine-phyric shergottite, displaying a porphyritic texture with olivine megacrysts. Since Y98 represents a primary melt composition that evolved in a close-system [12, 13], Y98 is an ideal meteorite sample to directly determine the oxidation states of redox sensitive elements in the inclusion and matrix glasses based on the XANES analysis.

Analysis: A polished thin section of Y98 (#51-2) was used in this study. The V K-edge (5465 eV) μ-XANES analyses were performed using the undulator beamline BL05XU of SPring-8 (Hyogo, Japan). The X-ray beam was focused using a K-B mirror to a final spot size of 1.0 (vertical) × 1.0 (horizontal) μm^2. The Fe K-edge (7111 eV) μ-XANES spectra were measured using the bending magnet beamline BL-4A of Photon Factory (PF; Tsukuba, Japan), where the X-ray beam was focused using a K-B mirror to a final spot size of 4.5 (V) × 4.0 (H) μm^2. Prior to the μ-XANES measurements, X-ray fluorescence (XRF) mapping which was scanned in 5 μm step were obtained to determine the analytical spot with referring to the backscattered electron images [13]. The μ-XANES measurement were carried out at 2 analytical spots of 2 different inclusion glass (4 spots in total), and 8 analytical spots for groundmass glass.

The oxidation state of Fe was calculated by analyzing the pre-edge features [14], and the fO_2 condition of the analytical spot was estimated by the pre-edge feature of V [15]. Silicate glasses which have the same composition with that of Y98 were synthesized under three different fO_2 conditions; relative to the iron-wüstite (IW) buffer (IW±0), 0.7 log unit more oxic than IW (IW+0.7), and IW+2.2. These glass standards were used for calibration.

Results & Discussion: The V K-edge XANES spectra of synthesized glasses shows that the pre-edge peak intensity at around 5467 eV becomes larger with increasing fO_2 (Fig. 1). In contrast, the maximum absorption peak at around 5483 eV becomes smaller with increasing fO_2. The V K-edge XANES spectra of 2 inclusion and 2 groundmass glasses are also presented in Fig. 1. A comparison of XANES spectra shows that the pre-edge peak intensities of the inclusion glasses are smaller than those of groundmass glasses, suggesting that the inclusion glass was formed under more reducing condition than groundmass. A mean fO_2 value of inclusion glass is IW±0.0 (±0.2), whereas that of groundmass glass is IW±0.8 (±0.3). The oxidation state of Fe varied from 1.89 to 1.97 for the inclusion glasses, whereas 2.01 to 2.36 for the groundmass glasses, which is strongly correlated with fO_2 condition (Fig. 2). The current study based on direct V and Fe μ-XANES analyses on inclusion and groundmass glasses shows consistent fO_2 values with previous studies reporting redox conditions of Y98 [7, 8, 13, 16].

The μ-XANES analysis clearly shows different redox condition between inclusion and groundmass glass, representing the earliest and the latest stage of the magma crystallization. This result reasonably indicates that groundmass glass showed more oxidizing condition than the inclusion glass. The fO_2 increase during magma evolution is also reported for lithology A of Elephant Moraine 79001, North West Africa 1068/1110, and Larkman Nunatak 06319 based on different mineralogical oxybarometers [17–19]. Although the mineralogical oxybarometer is a reliable method to estimate the redox condition, it requires more than two mineral phases to determine the fO_2 condition. In this respect, the best merit on performing the XANES analysis is that it can be applied to a single phase of glassy compounds. This fact means that redox condition of volcanic rocks is more easily determined even if they do not crystallize out several kinds of minerals. This is the prime reason why the current study showed the fO_2 increase of Y98 that represents a primary melt composition and contains only olivine, pyroxene, and chromite [12, 13].

This fO_2 difference indicates that the redox condition of the Y98 parent magma evolved during magma ascent and emplacement. Since Y98 is believed to have evolved in a closed system, our finding suggests that fractional crystallization and/or ascent of magma potentially induced the fO_2 increase. This study shows that the μ-XANES technique enables us to determine the fO_2 condition by only measuring a single phase of glassy compounds, and thus, it is useful to discuss the redox condition of volcanic rocks even if they do not crystallize out a pair of phases utilized for conventional oxybarometers.

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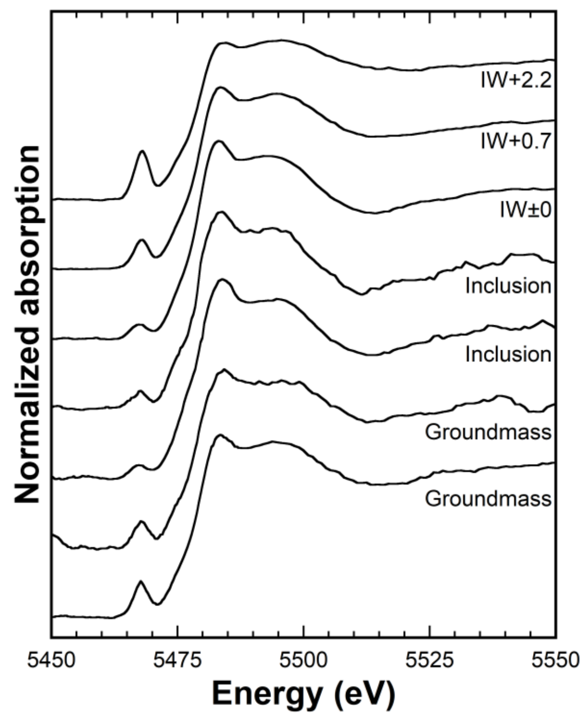

Figure 1. Vanadium K-edge XANES spectra of synthesized glasses under three different fO_2 conditions, inclusion glass, and groundmass glass.

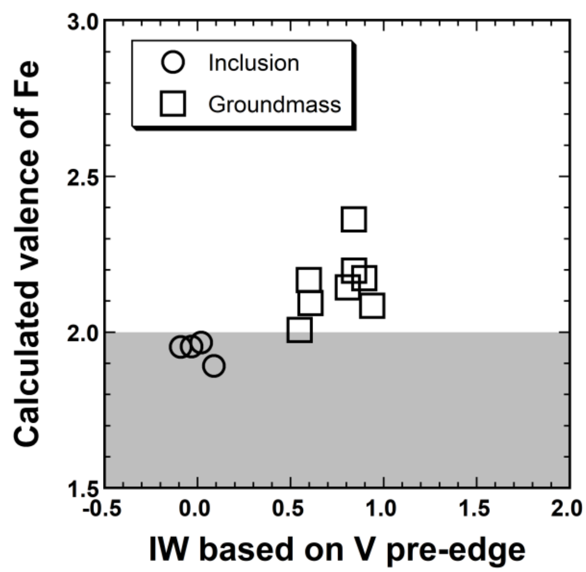

Figure 2. Relationship between fO_2 condition estimated by V pre-edge and averaged oxidation states of Fe.