

Supplementary Information

Vanadium micro-XANES determination of oxygen fugacity in olivine-hosted glass inclusion and groundmass glasses of martian primitive basalt Yamato 980459

Ryoichi Nakada ^{a,b*}, Tomohiro Usui ^{b§}, Masashi Ushioda ^c, Yoshio Takahashi ^d

^a Kochi Institute for Core Sample Research, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Monobe 200, Nankoku, Kochi 783-8502, Japan

^b Earth-Life Science Institute, Tokyo Institute of Technology,
Meguro, Tokyo 152-8550, Japan

[§]Present address: Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, 3-1-1 Yoshinodai, Sagami-hara, Kanagawa 252-5210, Japan

^c Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology (AIST), Central 7, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8567, Japan

^d Department of Earth and Planetary Science, The University of Tokyo,
Hongo 7-3-1, Bunkyo, Tokyo 113-0033, Japan

SUPPLEMENTARY SAMPLES AND METHODS

Micro-XANES measurements

Chromium K-edge XANES. The Cr K-edge (5989 eV) μ -XANES analyses were performed using the bending-magnet beamline 10.3.2 at the Advanced Light Source (ALS),

Lawrence Berkeley National Laboratory, California. The white beam from a bending magnet 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 3.3 (vertical) $\mu\text{m} \times 2.8$ (horizontal) μm . The measurements were conducted at ambient pressure and temperature. The spectra of reference materials, such as metal foil, CrCl_2 (Sigma-Aldrich, St. Louis, USA), Cr_2O_3 (Wako), and Na_2CrO_4 (Wako) reagents for Cr were measured in transmission mode, whereas those of Y98 were acquired in fluorescence mode. In the latter mode, XRF signals of the sample placed at 45° to the incident beam were obtained using a single element SDD positioned 90° to the incident beam. The spectrum of Cr-spinel was obtained from the ALS reference database. Prior to the μ -XANES measurements, XRF mapping that was scanned in 5 μm steps was obtained to determine the same analytical spot with reference to the XRF map obtained at SPring-8. The X-ray energy was calibrated by defining the first peak in the first derivative spectrum of Cr foil as 5989.2 eV, as in the previous studies (Berry and O'Neill, 2004).

Iron K-edge XANES. The Fe K-edge (7111 eV) μ -XANES spectra were measured at the BL-4A of Photon Factory (PF; Tsukuba, Japan) at ambient pressure and temperature. The white beam from a bending magnet 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 4.5 (V) $\mu\text{m} \times 4.0$ (H) μm . As in the cases of V and Cr, the spectra of reference materials (fayalite, magnetite, and hematite) were measured in the transmission mode, whereas those of Y98 were acquired in the fluorescence mode as described above. The XRF mapping was collected prior to the μ -XANES measurement scanned in 5 μm steps. The comparison between the two XRF maps collected at SPring-8, ALS, and PF enabled the measurement of

the Fe K-edge μ -XANES at the same analytical spot as those of V and Cr XANES.

The Fe K-edge XANES spectra of olivine and pyroxene grains in the thin section of Y98 were also measured. Since compositional zoning was reported for these grains in Y98 (Usui et al., 2008), measurements were performed at semi-micro beamline at BL-15A1 of PF at ambient pressure and temperature. The white beam was monochromatized using a Si(111) double-crystal monochromator and the X-ray beam was focused to a final spot size of about 15 (V) μm \times 15 (H) μm using a K-B mirror. The analytical spots were determined after obtaining the XRF map to find out the compositional zoning. Furthermore, Fe K-edge XANES spectra of Fe foil and synthesized terrestrial (N-MORB) and martian (Y98) basaltic glass were measured at BL-12C of PF at ambient pressure and temperature.

In the measurement at BL-12C and BL-15A1, Fe K-edge XANES spectrum of hematite was also obtained in transmission mode as performed at BL-4A. The comparison of hematite spectrum obtained in each beamline enabled us to calibrate the X-ray energy. In this study, the incident X-ray energy of the encoder was calibrated at each beamline using a hematite pre-edge peak maximum of 7111 eV. In the analytical process, the X-ray energy was further calibrated with the peak maximum of hematite at 7130 eV to compare each spectrum obtained at different beamlines, because the measurement interval of the step scan caused a slight (less than 0.25 eV) difference in the X-ray energy.

The pre-edge peak was analyzed to determine the average oxidation state of Fe followed by previous studies (Wilke et al., 2001, 2007; Giuli et al., 2002; Nakada et al., 2014). The contribution of the pre-edge structure was extracted from a raw spectrum by subtracting the background using a spline function. After the subtraction, the normalized pre-edge was fitted with a combination of three Gaussian functions, and the centroid position of the pre-

edge peak was defined as the intensity-weighted average of the three centroid energies of the Gaussian functions. Three Fe-bearing minerals, fayalite (divalent), magnetite (average oxidation state of 2.67), and hematite (trivalent), were used as standard materials to define a calibration curve for the centroid position against the oxidation state (Supplementary Fig. 10). The pre-edge centroid position of Y98 samples were plugged into the regression function to calculate the average oxidation state of Fe.

RESULTS

Micro-XANES measurements

A careful observation for the Cr K-edge XANES spectra is necessary because those of the analyzed glasses showed a feature similar to that of chromite and Cr-spinel (Supplementary Fig. 11). All the measured glasses showed maximum absorption peaks around 6009 eV, and most of the spectra have a second maximum around 6020 eV (Supplementary Fig. 11B, 11C). In addition, some spectra showed a third absorption peak at around 6062 eV, where spectra of chromite and Cr-spinel also exhibit absorption peaks (Supplementary Fig. 11A). These XANES features indicate that Cr K-edge XANES spectra of analyzed glasses are largely affected by the contribution from Cr-bearing minerals, possibly due to irradiation of Cr-bearing minerals.

The valence state of Fe based on the pre-edge centroid energy analysis was 1.94 on average for inclusion glass, which was smaller than those of groundmass glass (2.15; Table 1). Since the calibration curve was determined using fayalite, magnetite, and hematite, an oxidation state smaller than 2 was obtained by the extrapolation of the calibration curve. The averaged Fe valence state of glass synthesized at IW+1 condition was 2.08, while that

of QFM glass was 2.38 (Nakada et al., 2017). Fe K-edge XANES obtained from groundmass especially in GM 2 and 3, showed two-humped peaks, which is characteristic of pyroxene and chromite (Supplementary Fig. 12). In contrast, XANES spectra of synthesized glasses show a broader absorption peak at around 7123 eV (Supplementary Fig. 12A), though such a characteristic is not observed from analytical spots of Y98 samples. Although the averaged valence of Fe was below two for analytical spots in inclusion glasses, XANES spectra of these two spots did not show large absorption at around 7218 eV. This fact means that the contribution of metallic-Fe is not significant. However, taking into account the fact that the oxidation state of Fe in the inclusion glass was 1.94, a subtle contribution (<5%) of metallic Fe that was small enough to affect the XANES spectrum might be possible. The oxidation state of Fe is well correlated with that of V (Fig. 5). The most reduced Fe was observed from an inclusion glass, whereas the highest Fe redox state was observed from groundmass glass in GM 2, which is also the same trend as that of V.

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