Redox States of Geochemically-Enriched Shergottites as Inferred from Fe Micro-XANES Analysis of Maskelynite and Plagioclase.
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Introduction:

Shergottite is the largest group of Martian meteorites that crystallized at 160-550 Ma near the Martian surface as shallow intrusions or thick lava flows [e.g., 1]. Recent petrological and isotopic studies have revealed that shergottites show obvious correlations between oxidation state and geochemical characteristics, and such correlation must have important information about their mantle sources and are directly relevant to Martian evolution [e.g., 2]. The difference in such geochemical characteristics can divide them into three subgroups: depleted, enriched and intermediate shergottites [e.g., 3]. Enriched shergottites shows high La/Yb, low Sm/Nd, and high $^{87}Sr/^{86}Sr$ value. Enriched shergottites crystallized under the oxidized environment about oxygen fugacity (fO_2) of log fO_2=QFM-1.0 by Fe-Ti oxide oxybarometer [e.g., 2].

However, redox states of many enriched shergottites have not been estimated. This is partly because Fe-Ti oxides of these enriched shergottites are not in equilibrium. In our previous study we indicated that NWA 4468, Zagami, NWA 1068 and RBT 04262 were derived from an oxidizing reservoir(s) by using synchrotron radiation (SR) Fe X-ray Absorption Near Edge Structure (XANES) measurement of maskelynite [4]. This result is consistent with the observation that they are geochemically-enriched shergottites [5, 6]

In this study, we estimated redox states of additional four enriched shergottites whose redox states have not been measured by SR XANES analysis and discussed the origin of enriched shergottites.

Samples and methods:

We studied polished thin sections of four geochemically-enriched shergottites (NWA 856, Dhofar 378, Shergotty and LAR 06319). We first observed them by an optical microscope, and analyzed them by electron microprobe (JEOL JXA-8900L) at University of Tokyo. We also employed SR Fe-XANES analysis (BL-4A Photon Factory, KEK, Tsukuba, Japan) to measure $Fe^{3+}/\Sigma Fe$ ratios of maskelynite and plagioclase. The analyzed areas are about ~5 μm in size. We used kaersutites with known $Fe^{3+}/\Sigma Fe$ ratios determined by wet chemistry as standards because they show a linear relationship between centroid energy positions of XANES pre-edge spectra and the $Fe^{3+}/\Sigma Fe$ ratio. Based on the linear relationship, we estimated the $Fe^{3+}/\Sigma Fe$ ratio of analyzed samples [7].

Results and Discussion:

Optical microscopy of analyzed samples shows that plagioclase in Shergotty, NWA 856 and LAR 06319 is completely transformed to isotropic glass (maskelynite). Dhofar 378 contains not only maskelynite but also partially recrystallized plagioclase. The FeO abundance of maskelynite and plagioclase is 0.7 wt% in Shergotty, 0.6-0.8 wt% in NWA 856, 0.8-0.9 wt% in LAR 06319 and 0.6-0.7 wt% in Dhofar 378 (Table 1). The maskelynite and plagioclase composition are An_{62-63} in Shergotty, An_{40-60} in NWA 856, An_{51-57} in LAR 06319, and An_{37-51} in Dhofar 378, respectively.

The $Fe^{3+}/\Sigma Fe$ ratios of maskelynite in Shergotty, NWA 856 and LAR 06319 are estimated to be about 0.7. The $Fe^{3+}/\Sigma Fe$ ratios of maskelynite in Dhofar 378 are estimated to be about 0.7, too (Figs. 1 and 2, Table 1). The pre-edge peak position seems to be shifted by a few eV, respectively, but the estimated $Fe^{3+}/\Sigma Fe$ ratio usually bears 10% error. Therefore, we conclude that $Fe^{3+}/\Sigma Fe$ ratios of maskelynite and plagioclase in all samples have nearly the same value.

Our XANES analysis revealed that Shergotty, NWA 856, LAR 06319 and Dhofar 378 crystallized under oxidized environment as NWA 4468, Zagami, NWA 1068 and RBT 04262. Because the $Fe^{3+}/\Sigma Fe$ ratios of maskelynite in NWA 4468, Zagami, NWA 1068 and RBT 04262 are 0.6-0.9 [e.g., 4], three enriched shergottites (Zagami, Los Angeles and Shergotty) crystallized under similar oxidized environment (log fO_2=QFM-1.0) [4]. Thus, all six enriched shergottites (NWA 856, LAR 06319, Dhofar 378, NWA 4468, NWA 1068 and RBT 04262) may have crystallized under oxidized environment with similar fO_2 (fO_2=QFM-1.0).

There are two ideas for the origin of enriched shergottites. One is that enriched shergottites may be produced from the mantle-derived reduced magmas that were affected by early and extensive hydrothermal alteration of the Martian crust [8]. Another idea is that enriched shergottites may be produced from the residual melt of magma oceans [3, 9]. This study is not able to clarify the validity of two ideas at present, but it is important to estimate the fO2 of available shergottites more accurately. We are currently working on synthetic experiments of plagioclase in shergottite magma because we may be able to establish a shergottite oxybarometer by measuring $Fe^{3+}/\Sigma Fe$ ratios in plagioclase that synthetically crystallizes under controlled redox conditions in the laboratory and compare this result with natural samples.

References:

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Table 1. The result of EPMA and XANES analysis.

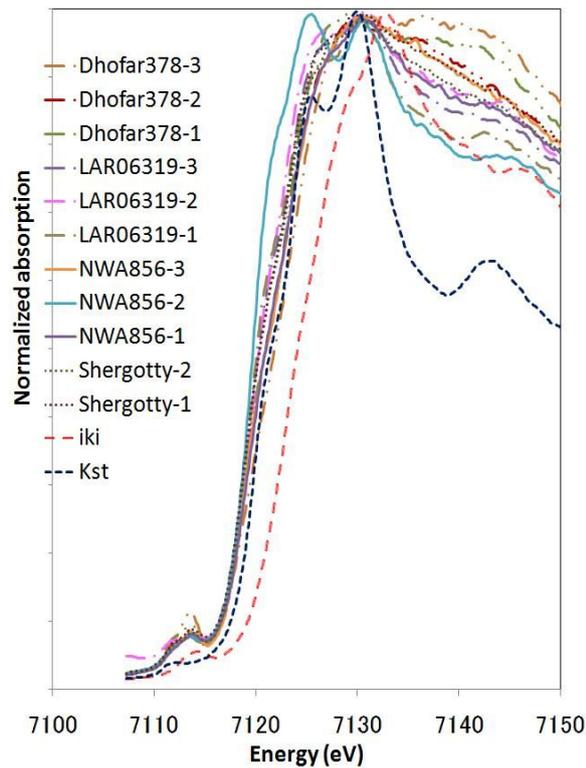| Smaple	FeO (wt%)	$Fe^{3+}/\Sigma Fe$
Shergotty-1	0.6	0.7
Shergotty-2	0.6	0.7
NWA856-1	0.6	0.7
NWA856-2	0.8	0.7
NWA856-3	0.6	0.7
LAR06319-1	0.9	0.7
LAR06319-2	0.8	0.7
LAR06319-3	0.8	0.7
Dhofar378-1	0.6	0.7
Dhofar378-2	0.7	0.7
Dhofar378-3	0.6	0.7

Fig. 1. SR Fe-XANES spectra of plagioclase in Dhofar 378 and maskelynite in LAR06319, NWA 856 and Shergotty with standard amphiboles (KST: kaersutite from Kaersut, Greenland ($Fe^{2+}/\Sigma Fe$=0.01) and IKI: kaersutite from Iki, Japan ($Fe^{2+}/\Sigma Fe$=0.93)). The SR beam size was about 5 μm in diameter.
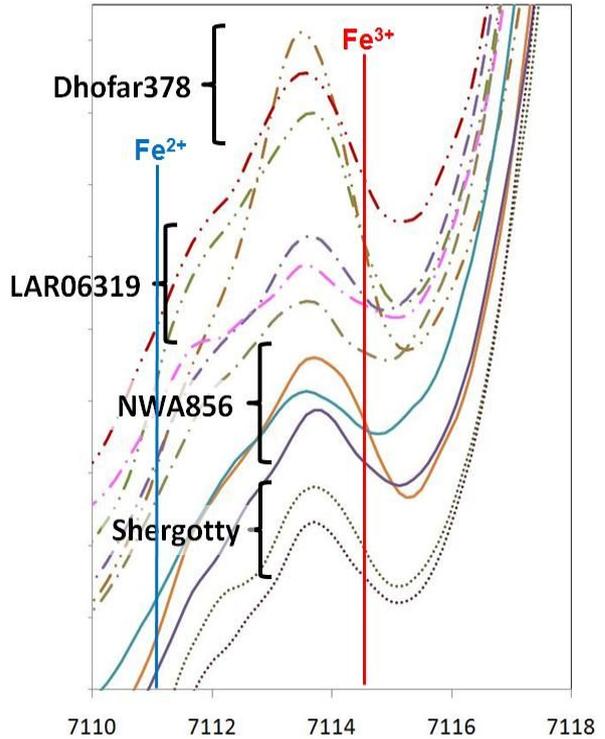

Fig. 2. Enlarged portion of Fig. 1 in the energy range of 7110 eV – 7118 eV, corresponding to the pre-edge peak positions. The pre-edge peak position was used to estimate the $Fe^{3+}/\Sigma Fe$ ratios of each sample.