COMPARISON OF REDOX STATES BETWEEN GEOCHEMICALLY-INTERMEDIATE AND ENRICHED LHERZOLITIC SHERGOTTITES. W. Satake, T. Mikouchi, J. Makishima, and M. Miyamoto, Department of Earth and Planetary Science, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan, (E-mail: satake@eps.s.u-tokyo.ac.jp).

Introduction: Lherzolitic shergottites show similar mineralogy and ages [e.g., 1,2], and are widely believed to have originated from the geochemically-intermediate reservoir having distinct trace element and isotopic compositions [e.g., 3,4]. RBT04262 and NWA4468 are recently discovered new shergottites that contain pyroxene oikocrysts enclosing olivine and chromite, and petrographically similar to previously known lherzolitic shergottites [e.g., 1,5]. Their geochemical studies revealed that they originated from geochemically-enriched reservoir(s) and are distinct from previously known lherzolitic shergottites [e.g., 5-7], although they can be classified as lherzolitic shergottites by petrology and mineralogy. The discovery of these geochemically-enriched lherzolitic shergottites has provided the information about the variation of Martian magma reservoirs, and generated the necessity to rename this group [8]. Although REE abundances of RBT04262 and NWA4468 have been measured [e.g., 5-7], their redox states have not been estimated yet. Thus, it is not clear whether these samples also fit to the geochemical-redox state relationship widely observed in shergottites [e.g., 3]. In this study, we tried to estimate redox state of both geochemically-intermediate and enriched lherzolitic shergottites by applying oxybarometers using Fe-Ti oxide compositions. We also tried to determine the $Fe^{3+}/\Sigma Fe$ ratio of kaersutite and ulvöspinel in these samples by using the synchrotron micro-XANES analysis to compare redox states between geochemically-intermediate and enriched samples.

Samples and Methods: We analyzed two geochemically-intermediate (ALH77005 and LEW88516) and two enriched (RBT04262 and NWA4468) lherzolitic shergottites. We first observed them by optical and scanning electron microscopes, and analyzed them by electron microprobe. The obtained Fe-Ti oxide compositions were used to estimate oxygen fugacity by using Ca-QUIlF program [9] and the model by Ghiorso and Evans [10]. We employed synchrotron radiation (SR) Fe-XANES analysis (BL-4A, Photon Factory, KEK, Tsukuba, Japan) to measure $Fe^{3+}/\Sigma Fe$ ratios of kaersutite and ulvöspinel. XANES analysis for standard kaersutites with known $Fe^{3+}/\Sigma Fe$ ratio shows 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 samples [11].

Results: We carefully selected areas where ulvöspinel and ilmenite coexist and their compositions are almost uniform near the boundary. We could not find suitable areas in our LEW88516 sample. The Ca-QUIlF program result shows that equilibration temperature and the oxygen fugacity of RBT04262 are T=504-547 °C and log fO_2=QFM-1.8~3.0, respectively. The Ghiorso and Evans model gave higher temperature, but similar fO_2: 666-800 °C and QFM-1.8~3.0. NWA4468 is estimated to be QFM-3.8~4.9 at 374-441 °C by Ca-QUIlF. The Ghiorso and Evans model gave QFM-4.2~6.3 at 488-622 °C for NWA4468. We could not obtain reasonable results for ALH77005.

Optical and scanning electron microscope observations show that ALH77005 and RBT04262 contain kaersutites in magmatic inclusions in pyroxene oikocrysts, but we could not find them in either LEW88516 or NWA4468 in our samples. Fe-XANES results show that the $Fe^{3+}/\Sigma Fe$ ratio of ALH77005 kaersutites is estimated to be about 0.4-0.6, and RBT04262 kaersutites is estimated to be about 0.5 (Fig. 1). In a similar way, we could obtain Fe-XANES of ulvöspinel in four samples (Fig. 2). The $Fe^{3+}/\Sigma Fe$ ratio of RBT04262 ulvöspinel is estimated to be about 0.5, and that of NWA4468 ulvöspinel is estimated to be about 0.3-0.4. The $Fe^{3+}/\Sigma Fe$ ratio of ALH77005 ulvöspinel is estimated to be about 0.2, which is clearly lower than those in RBT04262 and NWA4468. The $Fe^{3+}/\Sigma Fe$ ratio of LEW88516 ulvöspinel is estimated to be about 0.3.

Discussion and Conclusion: The obtained oxygen fugacities of RBT04262 and NWA4468 by two different oxybarometers using Fe-Ti oxide compositions gave wide ranges and the values are too low, which extends to below the IW buffer. These results suggest that the employed Fe-Ti oxide pairs were not appropriate to apply these oxybarometers although we checked whether ulvöspinel and ilmenite are in equilibrium by using the Mg/Mn partitioning test from [12]. It is clearly necessary to employ another oxybarometer (e.g., olivine-pyroxene-spinel oxybarometer [3]) to properly estimate their oxygen fugacities.

We found that there is no clear difference in $Fe^{3+}/\Sigma Fe$ ratio of kaersutite between ALH77005 and RBT04262. Because kaersutite is present only in pyroxene oikocrysts as magmatic inclusions, it should have crystallized at some early stages. Therefore, this result may suggest that there is no oxygen fugacity difference between the geochemically-intermediate reser-

voir and the enriched reservoir. However, this is unlikely because clear oxygen fugacity difference of these magmas has been known [e.g., 3]. Therefore, we think that the oxygen fugacity estimate of kaersutite by using Fe-XANES analysis could not provide enough resolution to detect subtle oxygen fugacity difference between geochemically-intermediate and enriched lherzolitic shergottites. In contrast, we could find that the $Fe^{3+}/\Sigma Fe$ ratio of ulvöspinel shows difference between geochemically-intermediate and enriched lherzolitic shergottites, and geochemically-enriched samples show higher $Fe^{3+}/\Sigma Fe$ ratios consistent with the geochemical characteristics [e.g., 3]. Because the difference is small (ALH77005 and LEW88516: $Fe^{3+}/\Sigma Fe$=0.2-0.3, RBT04262 and NWA4468: $Fe^{3+}/\Sigma Fe$=0.3-05), more careful analysis combined with another oxybarometer is necessary to conclude this observation.

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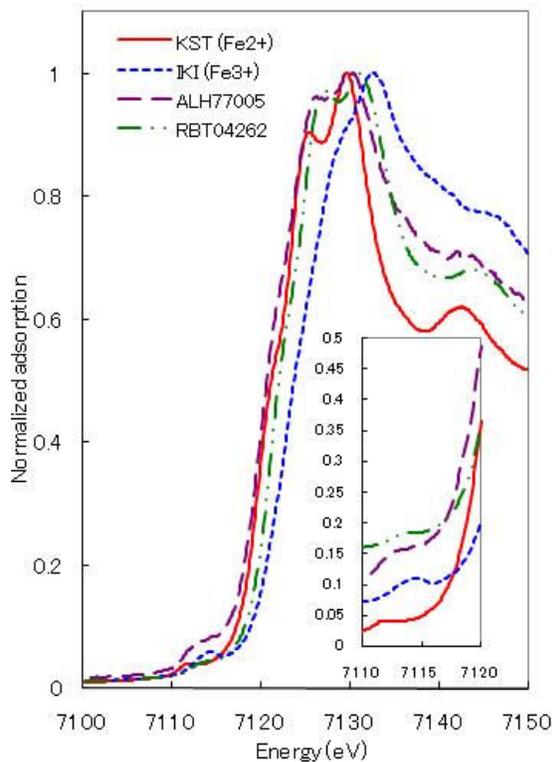

. 1 SR Fe-XANES spectra of kaersutites in ALH77005 and RBT04262 with standard kaersutites (KST: Kaersut, Greenland, $Fe^{3+}/\Sigma Fe$=0.01 and IKI: Iki Island, Japan, $Fe^{2+}/\Sigma Fe$=0.93). The SR beam size was about 5 µm in diameter. The inset diagram shows the pre-edge peak region, which was used to estimate the $Fe^{2+}/\Sigma Fe$ ratios of ALH77005 and RBT04262 kaersutites.
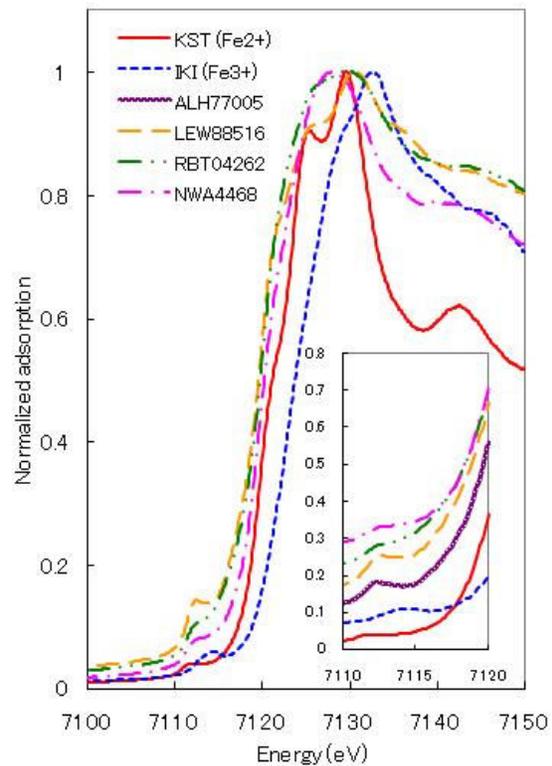

Fig. 2 SR Fe-XANES spectra of ulvöspinel in ALH77005, LEW88516, RBT04262, and NWA4468 with standard kaersutites (same as Fig. 1). The SR beam size was about 5 µm in diameter. The inset diagram shows the pre-edge peak region, which was used to estimate the $Fe^{2+}/\Sigma Fe$ ratios of ulvöspinel in ALH77005, LEW88516, RBT04262, and NWA4468.