

**CHARACTERISTICS OF TITANIUM-RICH KAERSUTITES IN MARTIAN METEORITES AND TERRESTRIAL ROCKS.** A. Monkawa<sup>1</sup>, K. Makino<sup>2</sup>, T. Mikouchi<sup>1</sup>, E. Koizumi<sup>1</sup>, T. Ishii<sup>3</sup>, M. Miyamoto<sup>1</sup>, <sup>1</sup>Dept. of Earth and Planet. Science, Graduate School of Science, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan (monkawa@space.eps.s.u-tokyo.ac.jp), <sup>2</sup>Dept. of Geology, Shinshu University, Asahi, Matsumoto, Nagano 390-8621, Japan, <sup>3</sup>Ocean Res. Inst., University of Tokyo, Minamidai, Nakano-ku, Tokyo 164-8639, Japan.

**Introduction:** Amphibole has been widely recognized in mantle xenoliths that are entrained in both alkali basalts and kimberlites. Although amphibole is nearly absent in meteorites, kaersutites occurs in magmatic inclusion in martian meteorites. The presence of kaersutite in the martian meteorites has been important in understanding water contents in martian magmas and mantle. Martian kaersutites are more Ti-rich than terrestrial one and poorer in OH<sup>-</sup> [1]. It has been reported that there are two types of Ti incorporation into amphibole in general. (1) The deficiency of H has an effect on site preference of Ti in the octahedral site of amphibole. Ti preferentially occupies the M1 site in the H-deficient kaersutite [2,3]. Ti replacement associated with O<sup>2-</sup> for OH<sup>-</sup> occurs in Ti-rich amphibole. (2) Ti-poor amphibole holds Ti essentially in the M2 site because of its small ionic radius [4-6], and is considered implicitly to be solid solution of Ti tschermakite. Although (1) is common for Ti-rich and OH-poor kaersutites, some kaersutites [7,8] suggest (2), because dehydrogenation is not observed by infrared absorbance. The purpose of this study is to clarify the relationship of Ti, Fe<sup>3+</sup>/ΣFe ratio, and OH contents in kaersutites based upon the observation of two types of zoned and five types of homogeneous terrestrial kaersutites. Furthermore, we estimated Fe<sup>3+</sup>/ΣFe ratios of kaersutites in three martian meteorites (Zagami, LEW88516, NWA856) by electron microprobe, and further discussed the relationship of Ti, Fe<sup>3+</sup>, and OH contents.

**Analytical Method:** Fig. 1 shows X-ray spectra of both almandine and aegirine recorded in the region from 16.761 to 18.050 Å by steps of 0.0096 Å. We employed three methods to estimate Fe<sup>3+</sup>/ΣFe ratio by electron microprobe. (1) Peak intensity method [9]: Measurement of the change in Lα and Lβ X-ray emission peak intensity ratio (Lβ/Lα). (2) Peak shift method [10]: Measurement of the shift in Lα peak position. The time required for a single peak search was 60 s. We estimated the change in Lα peak position by using a peak search software. (3) Flank method [11]: The flank method is a hybrid of (1) and (2) by measuring intensity ratio of certain portions of the peak flanks. The obtained spectra from both Fe<sup>2+</sup>-rich sample (almandine) and Fe<sup>3+</sup>-rich sample (aegirine) (peak profiles) are plotted in Fig. 1. We obtained difference spectra by subtracting aegirine from almandine. Maximum value (17.515 Å -17.524 Å) and minimum value (17.285 Å -17.294 Å) obtained from the difference

spectra were determined from the measurement points. Then, we constructed calibration curve based upon both Fe<sup>3+</sup>/ΣFe ratio determined by wet-chemical analysis and Lβ/Lα ratio obtained by electron microprobe analysis, and estimated Fe<sup>3+</sup>/ΣFe ratio of kaersutites by using the obtained calibration curve.

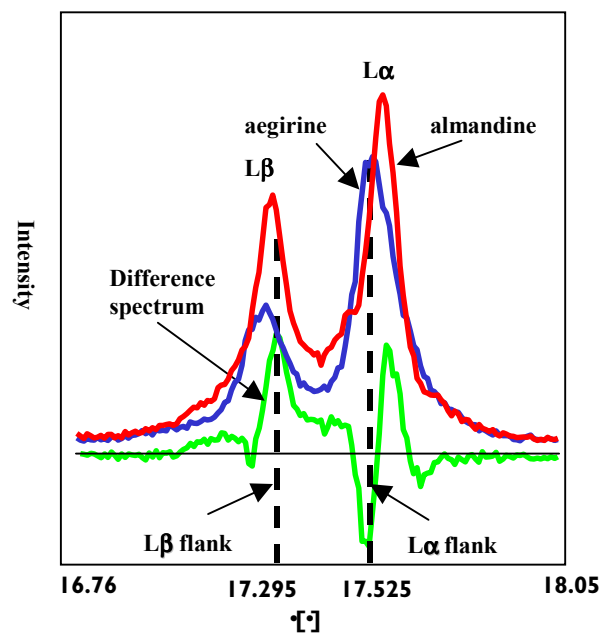


Fig. 1. Difference spectra (green curve) of FeL emission spectra of the almandine (Fe<sup>3+</sup>/ΣFe =1) and aegirine (Fe<sup>3+</sup>/ΣFe =0). The vertical lines show measuring positions of the flank method.

**Results and Discussion:** The Fe<sup>3+</sup>/ΣFe ratio of the LEW88516 kaersutite (0.72) is similar to terrestrial one (Dougho: 0.64). However, kaersutites in Zagami and NWA856 meteorites have higher Fe<sup>3+</sup>/ΣFe ratio (0.84) compared with terrestrial one. Nevertheless, it is interesting that their Fe<sup>3+</sup> pfu are nearly equal (Fe<sup>3+</sup> pfu: ~0.4). The correlation between Ti and OH in three martian kaersutites and terrestrial kaersutites is shown in Fig. 2a. Although the Red Hill kaersutite shows no correlations between Ti and OH, the Shionomisaki kaersutite shows negative correlations between them. Fig. 2b shows correlation between Fe<sup>3+</sup> and OH (OH value in three meteorites is quoted from [2]). The Shionomisaki kaersutite shows no correlations between Fe<sup>3+</sup> and OH. Moreover, both Shionomisaki and martian kaersutites have similar abundance of Fe<sup>3+</sup> pfu, although their OH contents are variable. This trend is

clearly distinct from the zoning trend of the Iki kaersutite that shows both deoxygenation and hydrogenation. According to these results, kaersutite without dehydrogenation is expressed as (1)  $\text{Ti} + \text{Al}^{IV} = \text{Al}^{VI} + \text{Si}$  (*Ti pargasite substitution*; e.g., Red Hill). On the other hand, kaersutite with dehydrogenation is expressed as (2)  $\text{Ti} + \text{O}^{2-} = \text{Al}^{VI} + \text{OH}^-$  (*kaersutite substitution*; e.g., Shionomisaki). Therefore, it is presumed that Ti is incorporated into the M2 site in *Ti pargasite substitution* (without dehydrogenation). In contrast, Ti will be accommodated in the M1 and M3 sites in *kaersutite substitution* (with dehydrogenation). However, Ti could be also incorporated into the tetrahedral site. Thus, accurate structural refinement by X-ray and neutron diffraction techniques is required to resolve this issue.

Fig. 2 also suggests that kaersutite in martian meteorites is distinctly Ti-rich and OH-poor compared with terrestrial ones. Martian kaersutite appears to be an end member in *kaersutite substitution*. As is discussed above, Fig. 2b shows that the  $\text{Fe}^{3+}$  contents in the analyzed martian kaersutites are constant in spite of their small amounts of OH during *kaersutite substitution*. In other words, it suggests that *kaersutite substitution* is related to both Ti and OH, not to the oxidation of  $\text{Fe}^{2+}$ . Ti-rich composition (Ti: >1.0 pfu) of kaersutites in martian meteorites is unusual with the terrestrial standards. In the terrestrial kaersutites, the Ti content in the octahedral site never exceeds 0.8 pfu in both synthetic and naturally terrestrial amphibole [12]. The high Ti content in martian kaersutites is may be due to their low OH contents in magma that promoted incorporation of Ti into kaersutite.

We are planning to employ other micro-beam techniques (TEM-EELS and XANES) to estimate more precise  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio of martian kaersutites and will check validity of the estimate by electron microprobe.

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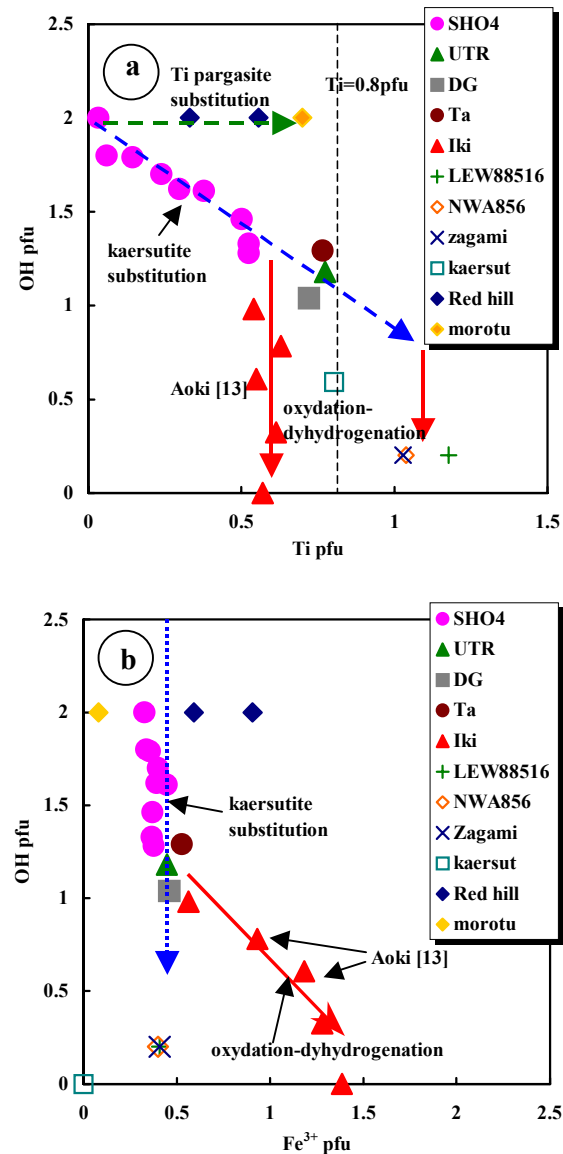


Fig. 2. (a) The relationships of Ti and OH and (b)  $\text{Fe}^{3+}$  and OH in kaersutites in three meteorites and terrestrial samples. SHO4; zoned kaersutite from Shionomisaki, Japan. UTR; Utruyou island, Korea. DG; Oki Dougo, Japan. Ta; Touge, Japan. Iki; Iki island, Japan. Kaersut; Kaersut, Greenland. Red Hill; New Hampshire, USA. Morotu; Sakhalin, Russia.