REDOX STATES OF SOME HED METEORITES AS INFERRED FROM IRON MICRO-XANES ANALYSES OF PLAGIOCLASE. W. Satake[1], P. C. Buchanan[2], T. Mikouchi[1], and M. Miyamoto[1], [1]Dept. of Earth and Planetary Science, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan, (E-mail: satake@eps.s.u-tokyo.ac.jp), [2]Kilgore College, 1100 Broadway, Kilgore, Texas 75662-3204, USA.

Introduction: HED (Howardite, Eucrite and Diogenite) meteorites are the largest group of achondrites and are widely believed to have originated on 4Vesta [e.g., 1]. The Dawn spacecraft is presently exploring this large asteroid and the connection to HED meteorites will hopefully soon be clarified. Vesta is an important example of early differentiation in the solar system, and, thus, HED meteorites may offer substantial information about igneous differentiation on Vesta [e.g., 2]. Eucrites are mainly composed of pyroxene and plagioclase and are considered to have been derived from the crust of the asteroid, whereas diogenites contain orthopyroxene and chromite and may have been derived from the mantle.

The oxidation state of magmas is one of the most significant factors in controlling crystallization and is relevant to the redox state of the parent body. In most cases, an oxybarometer using chemical compositions of Fe-Ti oxides is employed to estimate oxygen fugacity (fO_2). However, Fe-Ti oxides are late-crystallization minerals, and thus may not reflect redox states of early crystallization. In our previous studies, we employed Fe micro-XANES analysis of plagioclase in four eucrites (ALH 76005, EETA 87520, Petersburg and Piplia Kalan) using synchrotron radiation (SR) to estimate the relative redox states of eucrites showing variable grain sizes due to different cooling rates [3]. The results showed that plagioclases in ALH 76005, Petersburg and Piplia Kalan have nearly identical $Fe^{3+}/\Sigma Fe$ ratios (~0.2), but the $Fe^{3+}/\Sigma Fe$ ratio of EETA 87520 plagioclase differs greatly between individual grains with two grains having $Fe^{3+}/\Sigma Fe$ ratios exceeding 0.8. Because EETA 87520 has a moderately coarse-grained texture and apparently represents an igneous rock that crystallized in a shallow magma chamber, some oxygen may have been retained [3]. In this study, we analyzed plagioclase in two additional eucrites and one diogenite by SR XANES to determine whether other HED meteorites might also show these effects.

Samples and Methods: We analyzed thin sections of two eucrites (Padvarninkai and Moore County) and one diogenite (Y-75032). We first carefully observed the samples by optical and scanning electron microscopes, and analyzed them by electron microprobe in order to select representative plagioclase grains. SR Fe-XANES was performed at BL-4A, Photon Factory, KEK in Tsukuba, Japan to measure the $Fe^{3+}/\Sigma Fe$ ratio of plagioclase [4]. The SR beam size was 5 x 6 μm. The XANES analyses for standard kaersutites with known $Fe^{3+}/\Sigma Fe$ ratios shows a linear relationship between centroid energy position of XANES pre-edge spectra and the $Fe^{3+}/\Sigma Fe$ ratio. Based on this linear relationship, we estimated the $Fe^{3+}/\Sigma Fe$ ratio of samples studied [4]. The XANES results are known to be influenced by crystal orientation. In order to minimize this effect, we selected elongated plagioclase grains and located the samples so that the elongation was always horizontal against the SR beam. In spite of this consideration, the error of the estimated $Fe^{3+}/\Sigma Fe$ ratio is approximately ±10% [4].

Results: Optical and scanning electron microscope observations indicate that plagioclase abundances of both eucrites are generally 10-30 vol.%. In contrast, the Y-75032 diogenite is almost entirely composed of orthopyroxene and there is only one plagioclase grain in the thin section studied.

Padvarninkai is highly shocked and some plagioclase grains are completely transformed to maskelynite. It has a fine-grained texture composed of plagioclase and pyroxene with impact melt veins. We selected a big plagioclase grain (~300x500 μm) for SR-XANES (Fig. 1). The plagioclase composition in Padvarninkai is An_{95} and the FeO abundance is 0.14 wt%. The obtained XANES spectrum suggests that its $Fe^{3+}/\Sigma Fe$ ratio is almost 0 (Fig. 2).

Moore County is a cumulate eucrite showing a coarser-grained texture and plagioclase is commonly larger than 1 mm (Fig. 1). We selected three large plagioclase grains with no visible effects of weathering. The plagioclase composition of Moore County is An_{95} and the FeO abundance is 0.08-0.13 wt%. Its $Fe^{3+}/\Sigma Fe$ ratio is estimated to be 0.7-0.9 (Fig. 2).

Y-75032 is a ferroan diogenite and Mg# of orthopyroxene is 67-70 [5]. Its grain size is larger than 1 mm. We could find only one plagioclase grain (Fig. 1), which shows a fine-grained feather-like texture probably formed by recrystallization [6]. The plagioclase composition is An_{95} and the FeO abundance is 0.06-0.08 wt%. The pre-edge peak positions suggest that its $Fe^{3+}/\Sigma Fe$ ratio is 0-0.1 (Fig. 2).

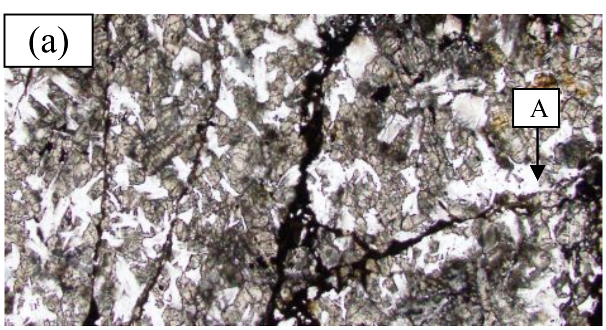
Discussion and Conclusion: The $Fe^{3+}/\Sigma Fe$ ratio of plagioclase in the two eucrites studied shows contrasting values (0 *vs*. 0.9). It is important to note that the $Fe^{3+}/\Sigma Fe$ ratio of Moore County is high (0.7-0.9). Such a high $Fe^{3+}/\Sigma Fe$ ratio is similar to that of EETA 87520 ($Fe^{3+}/\Sigma Fe$ >0.8) [3,7]. Both Moore County and EETA 87520 are cumulate eucrites with coarse-grained textures. This result may suggest that there is a relatively more oxidized environment in the deep crust of Vesta.

Because plagioclase in fine-grained eucrites (e.g., Padvarninkai) shows low $Fe^{3+}/\Sigma Fe$ ratios [3], suggesting crystallization under relatively reduced conditions, the crust of Vesta may show redox zoning from oxidized deep portions to reduced shallow portions. Monomict brecciated eucrite Stannern contains some metals [8] and its W isotope composition revealed that it was derived from a different part of Vesta's crust from other eucrites (Camel Donga, Juvinas, Bereba, Bouvante and Ibitira) [9]. This may be related to the heterogeneous redox environment of Vesta's crust.

It is unclear whether Vesta's mantle has a similar oxidized environment, but the low $Fe^{3+}/\Sigma Fe$ ratio of plagioclase in Y-75032 diogenite (0-0.1) suggests that the mantle has a reduced environment. The difference in values of eucrite and diogenite might be consistent with diogenites as residual materials from the removal of eucritic melts [10].

It is necessary to analyze plagioclase in many more HED meteorites in order to clarify these issues. For example, the Serra de Mage cumulate eucrite is an interesting sample because it contains quartz veins, suggesting the presence of liquid water [11]. Serra de Mage is estimated to have crystallized at 8 km depth [12], and its plagioclase may show a high $Fe^{3+}/\Sigma Fe$ ratio similar to Moore County and EETA 87520.

References: [1] McCord B. T. et al. (1970) *Science*, *168*, 1445-1447. [2] Takeda H. (1997) *Meteoritics & Planet. Sci., 32,* 841-853. [3] Satake W. et al. (2011) *LPSC XLII*, Abstract#2590. [4] Monkawa A. et al. (2006) *Meteoritics & Planet. Sci., 41,* 1321-1329. [5] Yamaguchi A. et al. (2009) *LPSC XLII*, Abstract#1547. [6] Mikouchi T. et al. (2002) *Meteoritics & Planet. Sci., 37,* A100. [7] Delaney J. S. et al. (1992) *LPS XXIII*, 299-300. [8] Harlow G. E. and Klimentidis R. (1980) *LPSC XI*, 1131-1143. [9] Kleine K. et al. (2005) *EPSL, 231,* 41-52. [10] Righter K. et al. (1997) *Meteoritics & Planet. Sci., 32,* 929-944. [11] Treiman H. et al. (2004) *EPSL, 219,* 189-199. [12] Miyamoto M. et al. (1994) *EPSL, 122,* 343-350.



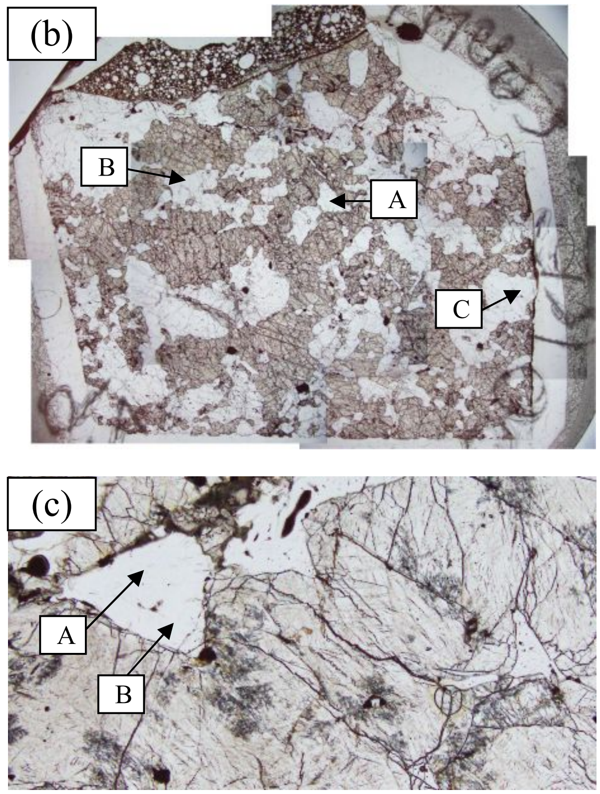


Fig. 1 Optical photomicrographs of (a) Padvarninkai, (b) Moore County and (c)Y-75032. A, B, and C shown in each image are analyzed plagioclase grains by SR-XANES. (a) and (c) are about 3 x 7 mm and (b) is about 14 x 16 mm in size.

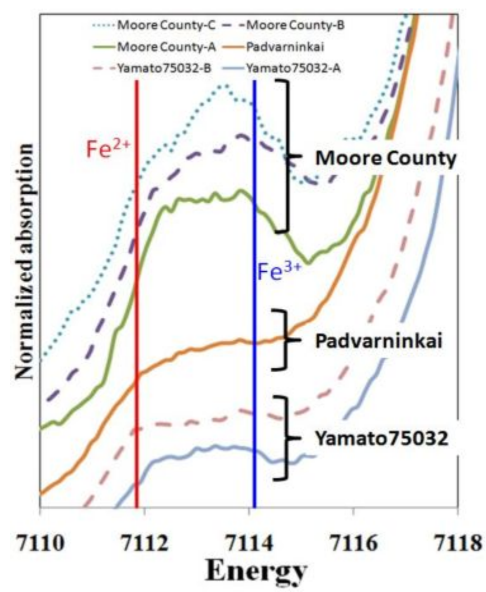


Fig. 2 Pre-edge peaks of Fe K-edge SR-XANES spectra of plagioclase in Padvarninkai, Moore County and Y-75032.