

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

**Introduction:** The eucrites are the largest group of achondrites and are widely believed to have originated on 4Vesta [e.g., 1]. At present, the Dawn spacecraft is approaching 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 to understand igneous differentiation on Vesta [e.g., 2]. 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 (especially, maskelynite) using synchrotron radiation (SR) to estimate the relative redox states of achondrites [3,4]. We have analyzed shergottites, lunar mare meteorites, angrites and primitive achondrites whose  $\log fO_2$  range from 5 orders of magnitude lower than the Quartz-Fayalite-Magnetite (QFM) buffer to 1 order of magnitude lower than QFM. We found that the obtained  $Fe^{3+}/\Sigma Fe$  ratios range from 0 to 1, and showed that Fe micro-XANES is a powerful tool to estimate their relative redox states. In this study, we focused on eucrites with variable grain sizes that were formed by different cooling histories, and analyzed plagioclase by SR XANES to discuss their redox states during crystallization.

**Samples and Methods:** We analyzed thin sections of four eucrites, ALHA76005, EETA87520, Petersburg and Piplia Kalan. We first carefully observed our samples by optical and scanning electron microscopes, and analyzed them by electron microprobe in order to select the representative plagioclase grains for SR Fe-XANES.

SR Fe-XANES was performed at BL-4A, Photon Factory, KEK, Tsukuba, Japan to measure the  $Fe^{3+}/\Sigma Fe$  ratio of plagioclase. The SR beam size was  $5 \times 6.5 \mu m$ . 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 [5]. The XANES results are known to be influenced by crystal orientation. In order to minimize this effect, we picked elongated plagioclase grains and located the samples so that the elongation was always horizontal against the SR beam. In spite of this consid-

eration, the error of the estimated  $Fe^{3+}/\Sigma Fe$  ratio is approximately 10% [5].

**Results:** Optical and scanning electron microscope observations show that all samples are mainly composed of pyroxene and plagioclase. The plagioclase abundance in these eucrites is generally 10-30 vol.%.

ALHA76005 is a polymict eucrite that contains significant proportions of unequilibrated clasts along with a few coarse-grained eucrite clasts. There are a couple of small clasts with fine-grained textures that appear to be unequilibrated in the thin section, and we selected them for SR-XANES. The grain size of plagioclase in these clasts is 125-225  $\mu m$  although a few grains reach 500  $\mu m$ . EETA87520 is a magnesian eucrite showing a coarser-grained texture and plagioclase is commonly larger than 1 mm (Fig. 1). Petersburg is a polymict eucrite. We studied clasts whose grain sizes are intermediate between the previous two (about 500  $\mu m$ ). Piplia Kalan is a genomict brecciated eucrite that contains a variety of different clasts that all have similar chemical compositions (Fig. 1). We selected two clasts with distinct textures. One is fine-grained similar to ALHA76005 whereas the other is coarse-grained similar to EETA87520 (Fig. 1).

Plagioclase in all analyzed samples has similar major-element compositions ( $An_{95-90}$ ). However, the FeO abundance shows some variations (ALHA76005: 0.1-0.4 wt%, EETA87520: 0.1-0.4 wt%, Petersburg: 0.1-0.7 wt%, Piplia Kalan: 0.05-0.6 wt%).

As Fig. 2 shows, all plagioclase grains analyzed display pre-edge peaks in the obtained XANES spectra. The  $Fe^{3+}/\Sigma Fe$  ratio of ALHA76005 is estimated to be 0.19-0.24, Petersburg is 0.19-0.24, and Piplia Kalan is 0.14. Thus, plagioclase in these three eucrites has nearly identical  $Fe^{3+}/\Sigma Fe$  ratios. However, the  $Fe^{3+}/\Sigma Fe$  ratio of EETA87520 plagioclase shows large differences from one grain to another. Although the  $Fe^{3+}/\Sigma Fe$  ratios of some EETA87520 plagioclase grains (A and D) are 0.33, two other grains (B and C) have clearly higher  $Fe^{3+}/\Sigma Fe$  ratios of 0.81 and 1.04 because their pre-edge peak positions are located at clearly higher energy positions.

**Discussion and Conclusion:** Surprisingly, the  $Fe^{3+}/\Sigma Fe$  ratio of plagioclase in eucrites studied shows a wide range (0.14-1.04) although they show basically similar mineralogy and petrology. Except for two plagioclase grains (B and C) in EETA87520, the obtained  $Fe^{3+}/\Sigma Fe$  ratios are 0.14-0.33, which is generally consistent with [6]. In comparison with our previous study [3,4], these  $Fe^{3+}/\Sigma Fe$  ratios are similar to achondritic

plagioclase formed at around the iron-wüstite (IW) buffer. This is consistent with the general idea that eucrites formed at such reducing condition.

Therefore, the anomalous spectra from two plagioclase grains (B and C) in EETA87520 showing clear pre-edge peaks at higher energy positions (Fig. 2) are quite unusual because they suggest formation under relatively oxidizing conditions near the QFM buffer [3,4]. Similar high  $\text{Fe}^{3+}$  ratio has been also suggested for EETA87520 plagioclase by [7]. There are two possible explanations for these features. One is that the high  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios were caused by terrestrial alteration. EETA87520 is an Antarctic meteorite, and thus it could be affected by terrestrial alteration during residence in Antarctica. However, EETA87520 shows a coarse-grained texture and we selected large clear plagioclase grains with no visible effects of weathering. Because we have never come across the effects of terrestrial weathering when we analyzed Antarctic Martian meteorites [3,4], we consider that terrestrial weathering is unlikely. The other possibility is that the presence of  $\text{Fe}^{3+}$  is originally related to the formation of EETA87520 on Vesta. EETA87520 shows a moderately coarse-grained texture and apparently represents an igneous rock that crystallized in a shallow magma chamber. In contrast, the other analyzed samples are apparently fragments of lavas that were extruded onto or close to the surface of Vesta. Perhaps some oxygen is lost from a lava that is exposed on the surface of an asteroid without atmosphere, but, would be retained if it was under pressure in the underground environment. If this is the case, it would explain the fact that the volcanic samples have lower apparent  $f\text{O}_2$  than the intrusive one. In order to clarify this issue, we need to analyze more eucrites with coarse-grained textures.

**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. (2010) *LPS XXXI*, Abstract #1902. [4] Satake W. et al. (2010) *Meteoritics & Planet. Sci.*, 45, #5232. [5] Monkawa A. et al. (2006) *Meteoritics & Planet. Sci.*, 41, 1321-1329. [6] Dyar M. D. et al. (2001) *LPS XXXII*, Abstract #1065. [7] Delaney J. S. et al. (1992) *LPS XXIII*, 299-300.

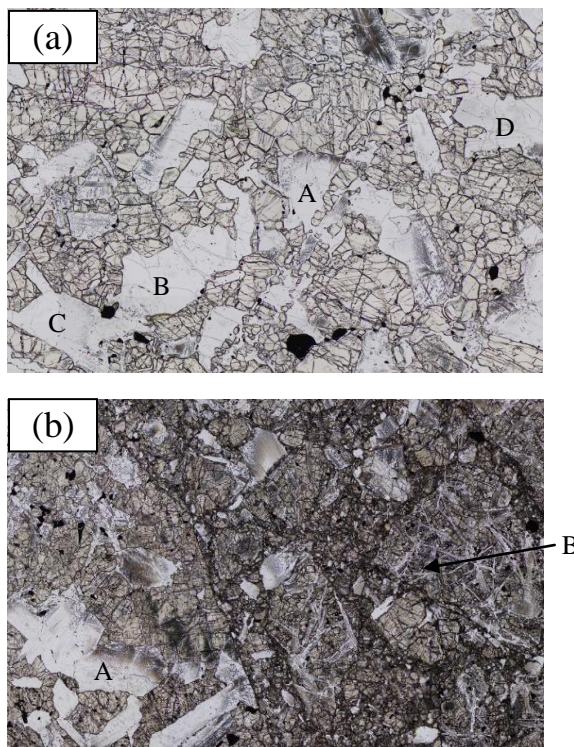


Fig. 1 Optical photomicrographs of (a) EETA87520 and (b) Piplia Kalan. A, B, C and D shown in each image are analyzed plagioclase grains by SR-XANES. Both images are about 4 x 6 mm in size.

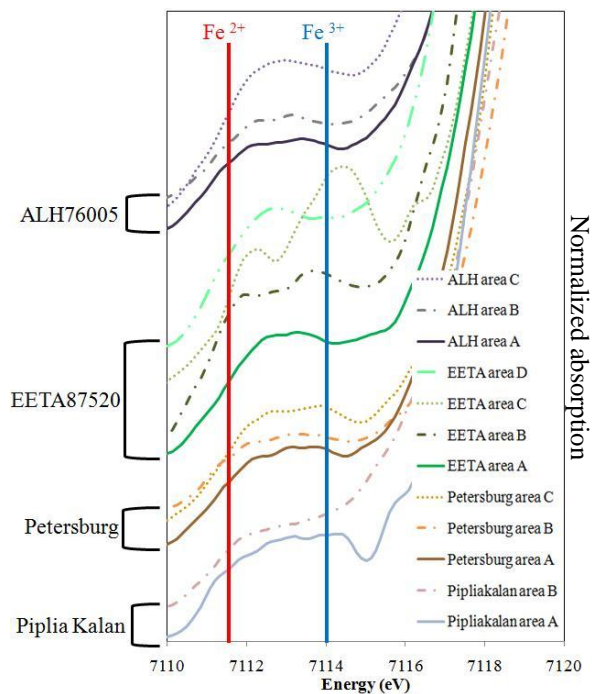


Fig. 2 Pre-edge peaks of Fe K-edge SR XANES spectra SR of plagioclase in ALHA76005, EETA87520, Petersburg, and Piplia Kalan. Note the apparent  $\text{Fe}^{3+}$  presence in two grains (B and C) of EETA87520.