FORMATION PROCESSES OF ZIRCONS IN BASALTIC EUCRITES: EVIDENCE FROM Zr/Hf RATIOS AND REE ABUNDANCES.

M. K. Haba[1], A. Yamaguchi[2], K. Horie[2] and H. Hidaka[3], [1]Geochemical Research Center, Graduate School of Science, University of Tokyo, Tokyo 113-0033, Japan (kikuchi@eqchem.s.u-tokyo.ac.jp), [2]National Institute of Polar Research, Tokyo 173-8515, Japan, [3]Department of Earth and Planetary Systems Science, Graduate School of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan.

Introduction: Most eucrites have basaltic composition, and some represent lavas or shallow intrusions from a differentiated parent body, possibly Asteroid 4 Vesta [1,2]. Many isotopic studies have been conducted using long- and short-lived chronometers to better understand the processes of accretion, core formation, mantle differentiation, and formation of the first basalts on the parent body. However, a majority of basaltic eucrites have experienced complex thermal histories due to metamorphic events [3,4]. The metamorphic events could have modify the original chemical compositions and isotopic systems in most constituent minerals, resulted in persistent unanswered questions regarding the precise timing and duration of the magmatic activity on the parent body. To address this issue, *in situ* U–Pb and ^{182}Hf–^{182}W analyses of the zircons (ZrSiO$_4$) found in basaltic eucrites have been performed by secondary ion mass spectrometry (SIMS) [5,6]. The U–Pb system suggests that the formation of zircons occurred within 20 million years after calcium-aluminum-rich inclusions formation (4568 Ma [7]), and that the U–Pb isotopic system was hardly disturbed subsequently during metamorphic events on the parent body. Furthermore, ^{182}Hf–^{182}W analysis revealed that the eucritic zircons quickly crystallized within 6.8 Ma after the metal–silicate differentiation. These previous studies indicate that the zircons from basaltic eucrites are some of the important minerals for providing chronological constraints on the mechanism of evolution of a protoplanet. However, the major and trace element characteristics of zircons from basaltic eucrites have not yet been reported sufficiently.

Here we present major and trace elements concentrations of zircons found in six basaltic eucrites. Then, we discuss geochemical characteristics and formation processes of zircons in the parent body based on Zr/Hf ratios and REE abundances.

Samples and analytical methods: Six basaltic eucrites (Yamato [Y-] 75011, Y-792510, Y-82082, Asuka [A-] 881467, Juvinas, and Stannern) were used in this study. The samples were mounted in an epoxy resin disk and polished with 1/4 μm diamond paste. The thick sections were examined using an electron microprobe analyzer (EPMA; JEOL JXA 8200) at the National Institute of Polar Research, Tokyo (NIPR). Zircon was identified by elemental mapping of zirconium and silicon using the EPMA. In addition, quantitative analyses were conducted using the EPMA to determine the chemical compositions of the zircons.

Ttwelve relatively large zircon grains (>10 μm) from Y-792510, A-881467, and Stannern were selected for *in situ* REE isotopic analysis using a sensitive high resolution ion microprobe (SHRIMP) at NIPR and Hiroshima University. The high-resolution method [8] and energy-filtering method [9] have been used for *in situ* REE analysis by SHRIMP to suppress unresolvable complex molecular fragments. Here we analyzed SL13 standard zircon using these two methods to select the most appropriate method for the *in-situ* REE analysis of the zircons from basaltic eucrites. The mass resolution was set to greater than 8800 (M/ΔM at 1 % of peak height) for the high-resolution method. In both methods, the masses of ^{96}Zr, ^{139}La, ^{140}Ce, ^{141}Pr, ^{143}Nd, ^{146}Nd, ^{147}Sm, ^{149}Sm, ^{151}Eu, ^{153}Eu, ^{155}Gd, ^{157}Gd, ^{159}Tb, ^{161}Dy, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{167}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu, ^{178}Hf, and ^{180}Hf were scanned. Measured REE count rates were referenced to mass 96 (^{96}Zr) derived from the matrix component of zircon and calibrated using 91500 standard zircon.

Results and discussion: The clasts of Y-75011 (i.e., the least metamorphosed basaltic eucrite) contain zircons of a few μm and complex shapes. However, the highly metamorphosed basaltic eucrites (Y-792510 and A-881467) contain some large (>10 μm) sub-rounded zircon grains. The zircons observed in this study indicate that the average and maximum sizes depend on metamorphic grade. This result suggests that the mechanism of formation of the zircons in the metamorphosed basaltic eucrites is related to metamorphic events.

The average Zr/Hf ratios of zircons from each sample are higher than the chondritic value (Zr/Hf = 36.3 [10]). The ratio of Zr and Hf partition coefficients (D_{Hf}/D_{Zr}) between ilmenite and lunar mare basalts is D_{Hf}/D_{Zr} = 1.2 [11]; this value indicates that ilmenite incorporates Hf in preference to Zr and leads to a high Zr/Hf ratio in the residual melt. Therefore, it is assumed that most of the zircons from the six basaltic eucrites formed after the crystallization of ilmenite. The Zr/Hf ratios of the zircons from Y-82082, Juvinas, and Stannern exhibit large variations compared to those from Y-792510 and A-881467: this observantion indicates that the melt conditions during the formation of the zircons, such as cooling rates and temperatures, could have varied among the basaltic eucrites. In

Stannern, the Zr/Hf ratios were observed to be lower than the chondritic value in some zircons, which cannot be explained by a simple formation process of zircon during initial crystallization. Because ilmenite incorporates Hf rather than Zr, ilmenite has a lower Zr/Hf ratio compared to the chondritic value. According to a heating experiment conducted on a basaltic eucrite [12], the mesostasis regions containing ilmenite, phosphate minerals, and silica are preferentially melted around the subsolidus temperature (1060 °C). Stannern was heated to temperatures just above melting, perhaps by a shock event [13]. Therefore, some zircons in Stannern might have formed or recrystallized in the melt derived from the mesostasis region that contains the dissolved ilmenite during the short metamorphic event.

The REE abundances in the zircons from Y-792510 and A-881467 are La = $0.1 \times$ CI and Lu = $1000 \times$ CI and exhibit marginal variation. However, the zircons from Stannern exhibit a higher and more variable REE abundances (La = $0.1–1 \times$ CI and Lu = $1000–10000 \times$ CI) than those from Y-792510 and A-881467. Although positive Ce anomalies were observed in the analyzed zircons, it can be attributed to isobaric interference on the mass spectrum from surrounding pyroxene. The most reliable data from the large zircon (>20 μm), which does not exhibit a contact with pyroxene, shows no Ce anomaly and a negative Eu anomaly. Therefore, it can be assumed that the zircons in these basaltic eucrites formed under reducing conditions, where Ce^{3+} is stable.

The melt compositions that were in equilibrium with the zircons from A-881467 and Stannern can be estimated using the zircon/melt REE partition coefficients. The REE patterns of the melt for A-881467 are shown in Fig. 1 for reference. The REE patterns of the estimated melts indicate LREE-enriched trends. Because the zircons are assumed to have form during the later stages in case of the fractional crystallization, the residual melt compositions after crystallizations of plagioclase and pyroxene were calculated. The REE abundances of the calculated residual melts are clearly higher than those of the melts coexisting with the zircons in A-881467 (Fig. 1(a)) and Stannern. Even if REE in the residual melt were removed by crystallization of phosphate minerals before formation of the zircons during the initial crystallization, the REE patterns of the melt coexisting with the zircons cannot be reproduced. Conversely, phosphate minerals could carry most of the REEs in the melt derived from partial melting during metamorphic events [14]. Then, the REE abundances of this melt were calculated by assuming that all REEs in the melt were sourced from phosphate minerals. The melts coexisting with the zircons can be reproduced by assuming that such melts contained the

dissolved merrillite at concentrations of 0.18 wt.% for A-881467 (Fig. 1(b)) and 0.03–0.15 wt.% for Stannern. These results suggest that (i) the zircons from A-881467 and Stannern larger than 10 μm formed or recrystallized in the melt during the metamorphic events, and (ii) the melt could be derived from the preferential partial melting of mesostasis region containing phosphate minerals.
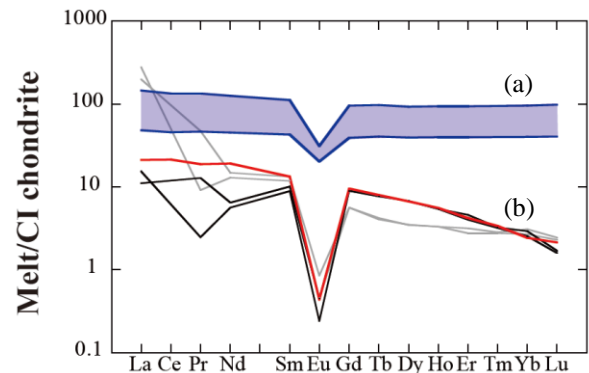

Figure 1: Chondrite-normalized REE patterns of the melts coexisting with the zircons from A-881467. Two types of data estimated by the partition coefficients of zircon/melt from [15] and [16] are shown as solid black lines and gray lines, respectively. Ce abundance is not described because the partition coefficient for Ce is assumed to be considerably different between terrestrial and asteroidal zircons. The blue area shows the REE compositions of the residual melt after the fractional crystallizations of plagioclase and pyroxene. The ratios of crystallized plagioclase and pyroxene to the total mass are set from 80 wt.% to the actual abundances (93.58 wt.% [17]). The red line indicates the REE compositions of the melt containing dissolved phosphate minerals. The reference data of CI chondrite are from [18].

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