**Isotopic and Geochemical Studies of Sr and REE in Eucrites and Diogenites.** K. Sera<sup>1</sup>, H. Hidaka<sup>1</sup> and S. Yoneda<sup>2</sup>, <sup>1</sup>Department of Earth and Planetary Systems Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan, <sup>2</sup>Department of Science and Engineering, National Museum of Nature and Science, Tsukuba 305-0005, Japan.

## Introduction:

Howardite, eucrite, and diogente (HED) are considered to be originated from the second largest asteroid 4 Vesta. HEDs provide useful information to understand the early differentiation processes of solar planetary materials. Application of radiogenic isotope systematics to HEDs put temporal constraints on mantle differentiation processes. Although many isotopic studies have been performed on eucrites by several kinds of geochronometers using decay systems with long-lived and short-lived radioisotopes to understand the processes of accretion, core formation, mantle differentiation, and the formation of primary basalts on the eucrite parent body [1-4], the exact time-scales for eucrites petrogenesis are still unclear.

The determination of REE abundance patterns of HEDs may provide additional data to discuss the geochemical differentiation processes in association with igneous activities.

In this study, systematic isotopic analyses of Sr, Nd, Sm and Gd, and the determination of REE abundances were performed on HED samples for better understanding of the timing of early differentiation on their parent body. The aim of Sr and Nd isotopic works is to search for isotopic evidence of early differentiation of solar planetary materials from the difference of <sup>87</sup>Rb-<sup>87</sup>Sr, <sup>147</sup>Sm-<sup>143</sup>Nd and <sup>146</sup>Sm-<sup>142</sup>Nd decay systems of HEDs. The purpose of Sm and Gd isotopic measurements is to evaluate cosmic-ray exposure history of individual samples from the isotopic shifts caused by neutron capture reactions, <sup>149</sup>Sm(n, $\gamma$ )<sup>150</sup>Sm and <sup>157</sup>Gd(n, $\gamma$ ) <sup>158</sup>Gd.

## Samples and experiments:

Eight noncumulate eucrites (Juvinas, Millbillillie, Stannern, DaG 380, Dag 391, DaG 411, DaG 443, and DaG 480), one cumulate eucrite (Y 980433), and six diogenites (Bilanga, NWA 5480, Tatahouine, Y 002875, Y 74013, and Y74097) were used in this study. It is known that most of cumulate eucrites are unbrecciated, while most of noncumulate eucrites and diogenites are brecciated. A few unbrecciated diogenites were found. Y 002875, Y 74013, and Y 74097 are unbrecciated diogenites.

About 1 g of each powdered sample was decomposed by treatment with HF- $HClO_4$  with heating. Then, the samples were taken to dryness and redissolved in 10 mL of 2M HCl. The solution was divided into two portions: the main portion for isotopic measurements by TIMS and the rest for the

determination of elemental abundances of REE by ICP-MS. To determine the precise elemental abundances of Rb and Sr for chronological work,

Each solution for the isotopic study was loaded onto a cation exchange resin packed column (Bio-Rad AG50WX8, 200-400 mesh, H<sup>+</sup> form, 50 mm length  $\times 4.0$  mm diameter). The column was washed with 2 M HCl for Sr elution. Next, the column was washed with 6M HCl for REE elution. The solution was then evaporated to dryness and redissolved in a drop of 0.1 M HCl. The Sr fraction was purified using a quartz column packed with Sr-specific resin (Eichrom, Sr resin, particle size of 100-150  $\mu$ m, 100 mm length  $\times 2.5$  mm diameter). The REE fraction was loaded onto a second column packed with lanthanide-specific resin (Eichrom, LN resin, particle size of 100-150  $\mu$ m, 100 mm lengthimes2.5 mm diameter) to separate Nd, Sm and Gd using 0.15, 0.25, 0.35 and 0.5 M HCl, respectively [5].

A thermal ionization mass spectrometer (Triton Plus) equipped with nine Faraday cup collectors was used for the isotopic measurements of Sr. Nd. Sm. and Gd. Sr was measured on single Re filament with Instrumental isotopic mass  $Ta_2O_5$  activator. fractionation was corrected by the exponential law using <sup>88</sup>Sr/<sup>86</sup>Sr= 8.375209 as a normalizing factor. Nd, Sm and Gd were measured on double Re filaments. For their isotopic measurements, <sup>146</sup>Nd/<sup>144</sup>Nd=0.7219, <sup>147</sup>Sm/<sup>152</sup>Sm=0.56081, 156Gd/160Gd=0.9361 were used to correct for instrumental mass fractionation using the exponential law. When the isotopic depletions of <sup>155</sup>Gd were found in the analyses, the Gd isotopic data sets were normalized by  $(^{155}Gd+^{156}Gd)/^{160}Gd=1.61290$ . Nd, Sm and Gd were measured as mono-atomic ions (M<sup>+</sup>).

Another minor aliquot of each sample solution was once evaporated to dryness, and redissolved using 5 mL of 0.5 M HNO<sub>3</sub>. A 0.05 g quantity of a 10 ppb indium solution was added to the individual sample solutions as an internal standard element to optimize the analytical conditions for REE measurements. An ICP-MS (Agilent 7500cx) was used for determination of the elemental abundances of Sr and REE.

## **Results and Discussion:**

CI chondrite-normalized REE abundance patterns of all 15 samples used in this study are shown in Fig. 1. Noncumulate eucrites show relatively flat REE patterns and high abundances (CIx10~25), while cumulate eucrites and diogenites show significant depletions of LREE and low abundances (CIx0.01~0.3 for LREE). The data of noncumulates eucrites are quite consistent with those of previous studies [6-8]. However, some of diogenites data such as Bilanga and Tatahouine show significant differences from previous data [9], which is suggested by diversity of their parent melts.



Figure 1. CI chondrite-normalized REE abundance patterns of 8 noncumulate eucrites (Juvinas, Millbillillie, Stannern, DaG 380, Dag 391, DaG 411, DaG 443, and DaG 480), 1 cumulate eucrite (Y 980433), and 6 diogenites (Bilanga, NWA 5480, Tatahouine, Y 002875, Y 74013, and Y74097) used in this study.

Isotopic works of cumulate eucrite and diogenites are still in progress. Here, preliminary data of the noncumulate eucrites are reported in this paper.

<sup>87</sup>Sr includes radiogenic component from the decay of <sup>87</sup>Rb, and its isotopic variation correlates with Rb/Sr elemental ratios. In order to estimate the initial <sup>87</sup>Sr/86Sr of the eucrite parent body, namely basaltic achondrite best initial (BABI) [10], from our Rb-Sr data, precise determination of Rb/Sr elemental ratios by isotope dilution method were also performed together with the Sr isotopic works. The fit of the data points from three non-desert eucrites to a straight line is consistent with the eucritic isochron given by previous study [10], while the data points from five desert eucrites are randomly deviated from the eucritic isochron probably due to terrestrial contamination.

On the other hand, the data points from 8 noncumulate eucrites including desert eucrites lie on a single isochron of <sup>147</sup>Sm-<sup>143</sup>Nd isotopic systematic with a slope of 4.567 Ga. The isotopic deviations of <sup>142</sup>Nd of noncumulate eucrites show slightly negative to zero values relative to terrestrial standard materials ( $\epsilon^{142}$ Nd=-0.2 to 0), and no positive values which are observed in typical cumulate eucrites having high Sm/Nd elemental ratios. These results are consistent with previous study [11].

Sm isotopic compositions of the eucrites show the depletions of  $^{149}$ Sm and excesses of  $^{150}$ Sm caused by neutron capture reactions due to cosmic rays irradiation. These Sm isotopic shifts correspond to the neutron fluences ranging from 3.2 to  $6.1 \times 10^{15}$  n cm<sup>-2</sup>. The estimated neutron fluences are almost consistent with their cosmic-ray exposure ages, suggesting no strong evidence of initial cosmic-ray irradiation on the surface of EPB. The isotopic shifts of Sm are caused by the cosmic-ray irradiation after release from the EPB. The variation of <sup>157</sup>Gd-<sup>158</sup>Gd isotopic shifts also show the consistency with that of <sup>149</sup>Sm-<sup>150</sup>Sm.

Systematic isotopic data obtained in this study provide a hint to understand the differentiation processes of HEDs. We are now applying this technique for the analyses of cumulate eucrites and diogenites.

## **References:**

[1] Lugmair G.W. and Shukolyukov A. (1998) Geochim. Cosmochim. Acta, 62, 2863-2886. [2] Misawa K., Yamaguchi A. and Kaiden H. (2005) Geochim. Cosmochim. Acta, 69, 5847-5861. [3] Srinivasan G., Whitehouse M.J., Weber I. and Yamaguchi A. (2007) Science, 317, 345-347. [4] Quitté G. et al. (2011) Geochim. Cosmochim. Acta, 75, 7698-7706. [5] Hidaka H. and Yoneda S. (2007) Geochim. Cosmochim. Acta, 71, 1074-1086. [6] Consolmagno G.L. and Drake M.J. (1977) Geochim. Cosmochim. Acta, 41, 1271-1282.[7] Makishima A. and Masuda A. (1993) Chem. Geol., 106, 197-205. [8] Yamaguchi A. et al. (2009) Geochim. Cosmochim. Acta, 73, 7162-7182. [9] Barrat J.A. et al. (2008) Meteorit. Planet. Sci., 43, 1759-1775. [10] Papanastassiou D.A. and Wasserburg G.J. (1969) Earth Planet. Sci. Lett., 5, 361-376. [11] Boyet M. and Carlson R.W. (2005) Science, 309, 576-581.