

Crystallization Ages of Zircons on Eucrite Parent Body from Hf-W systematics. G. Srinivasan<sup>1</sup>, M.J. Whitehouse<sup>2</sup>, I Weber<sup>3</sup> and A. Yamaguchi<sup>4</sup>. <sup>1</sup>Department of Geology, University of Toronto, Toronto, ON Canada. <sup>2</sup>Laboratory for Isotope Geology, Swedish Museum of Natural History, SE-104 05 Stockholm, Sweden. <sup>3</sup>Department of Planetologie, University of Munster, Munster, Germany. <sup>4</sup>Antarctic Meteorite Research Center, NIPR, Tokyo 173-8515.

The accretion of planetary bodies like Earth, Moon, Mars, Vesta and other meteorite parent bodies (diameter > 50 kilometers) was quickly followed by melting and metal-silicate differentiation resulting in core formation. The decay of <sup>182</sup>Hf [half-life ( $T_{1/2}$ ) ~ 9 million years (Ma)] to <sup>182</sup>W has proved to be a very useful relative chronometer to determine the core formation and silicate differentiation time scales. The refractory lithophile Hf and siderophile W present in near chondritic proportions in planetary bodies undergo significant fractionation during metal-silicate fractionation prior to core formation. Evolution of the mantle through silicate differentiation causes further fractionation because W is more incompatible compared to Hf [1]. Eucrites, howardites and diogenites (HEDs) are a group of differentiated meteorites that possibly originated on asteroid 4 Vesta. The eucrites have <sup>182</sup>W excess [2]] indicating a very early differentiation process on Vesta. The early differentiation of Vesta is consistent with the inferences derived from other short-lived radionuclides <sup>26</sup>Al [half-life ~ 0.7 ma], <sup>53</sup>Mn [half-life ~ 3.5Ma] [3].

Zircon is an ideal mineral for determining the <sup>182</sup>Hf abundance at the time of its formation. It has a high concentration of Hf (1-2%) and significantly low abundance of W. Previous measurements on Hf-W systematics carried out using SHRIMP, SHRIMP-RG and Cameca ims 4f [4] were limited in measurement quality and precision. These measurements were carried out using either single detector system, high mass resolution ranging from ~7000 to 11,000 or energy filtering which resulted in severe loss of signal and increased measurement time. The signal strengths constrained by meteorite zircon size (~ 10-20 $\mu$ m) limit the counting statistics and the measurement precision.

In this abstract we report the new <sup>182</sup>Hf-<sup>182</sup>W evolution systematics and  $\delta^{183}$ W composition of several zircons from A881388 eucrite. We also report the data the <sup>182</sup>Hf-<sup>182</sup>W evolution systematics for A881467 zircons which was reported previously [5] but have been corrected for their ionization efficiency following the prescription for the same as followed by [6]. These measurements were carried out using the multi-collector Cameca ims1270 large geometry ion microprobe (NORDSIMS) at the Swedish Museum of Natural History. These measurements have attempted to overcome the difficulties of the

earlier work [4]. The Hf-W measurements were carried out using the multi-detector assembly at a nominal mass resolution of ~ 7500. The W isotopes were measured as metal [14].

A881388 and A881467 [previous abstract] have unbrecciated non-cumulate eucrites and has a crystalline rock texture. In A881467 the all minerals meet at triple junction and therefore the texture reveal to be not a product of a primary product from a magma. A881388 contains zircons with sizes of up to 10 $\mu$ m in size. The Ca-low pyroxenes with a composition En~35Fs50-60Wo5-10 show thin exsolution lamellae (~1-5 $\mu$ m). In the augites (En~30Fs~30Wo~40) no exsolution lamellae are visible. Plagioclase composition varies from pure anorthite to Ab~11An~89. Silica, metal, and chromite-troilite assemblages are minor minerals.

The Cameca ims1270 ion microprobe at the Swedish National Museum, Stockholm, Nordic facility for secondary ion mass spectrometry (NORDSIMS) was used to determine the Hf-W composition of the A881467 and A881388 zircons and <sup>207</sup>Pb/<sup>206</sup>Pb of the A881467 zircons. The multi-collector detector assembly consists of five movable detectors. The Hf-W measurements were carried out using the multi-detector assembly at a nominal mass resolution of ~ 7500 using the narrowest available exit slit of 150  $\mu$ m. W isotopes were measured as metal.

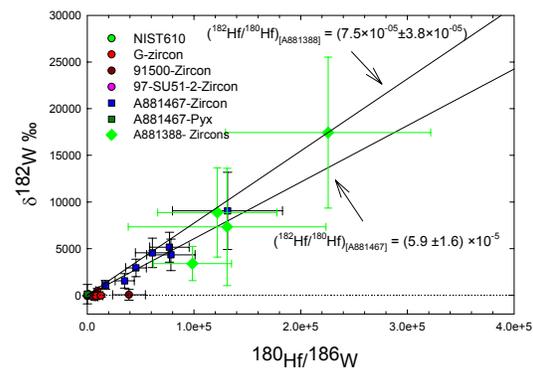
The ion microprobe uses a primary ion beam to sputter atoms from a sample. The sputtered atoms/ions are expected to be nominally representative of sample composition. However, different elements ionize to varying degrees resulting in elemental fractionation during the sputtering process. Therefore, the measured elemental ratios of [Hf] and [W] need correction to account for the ionization efficiencies of both elements relative to each other, this correction factor is commonly referred to as relative sensitivity factor (RSF). The RSF is a function of chemical composition and crystalline structure. W abundances in zircon standards are not known accurately. Hf/W relative sensitivity factor (RSF) was determined using NIST610 standard with accepted reference concentrations of Hf and W are ~ 418 and 445 ppm respectively [7]. The Hf/W RSF was estimated to be 0.21 $\pm$ 0.01. In NIST SRM 610 Hf, W abundances are similar while in zircons the typical Hf concentration

is about ~1% and even higher while W abundance  $\leq$  few ppm. Hafnium ( $\text{HfSiO}_4$ ) forms complete solid solution with zircon, and is therefore, an important structural component of the zircon crystal while W is a trace element. The estimated (Hf/W)-RSF for NIST SRM 610 is not suitable for zircon. The abundance of Yb, a trace element in zircon, is documented accurately. A prescription to use Yb as a proxy for W to estimate the correction factor determined for RSF [Hf/W] in NIST SRM610 was outlined earlier [6]. The abundance of Hf and Yb is well established for the NIST 610 [Hf 418ppm and Yb 462ppm] [7] and zircon standard 91500 [Hf ~ 5588 ppm Yb ~ 64ppm] [8,9] and zircon standard SL13 [Hf 6808ppm and Yb 12.4ppm] [8]. The measured ionic ratios of Hf/Yb isotopes and the estimated Hf/W using NIST610 (Hf/Yb)-RSF can be compared with the Hf/Yb determined from the absolute abundances determined earlier [6, 8] to estimate the correction factor that needs to be applied to (Hf/Yb)-RSF for NIST in order to make it appropriate for zircon. Using this prescription, we obtained correction factor for (Hf/Yb)-NIST RSF of 2.5 which means that  $[\text{Hf}]/[\text{Yb}] = \{[\text{NIST-RSF}]/2.5\} * [\text{Hf}^+]/[\text{Yb}^+]$ . We applied a similar correction to the [Hf/W] RSF determined from NIST values to estimate elemental ratios from measured ionic ratios of [Hf/W] in zircon. With no immediate prospect of a reliable W standard for zircon, use of Yb as a proxy for W in zircons is the only way to estimate the  $[\text{Hf}/\text{W}]_{\text{zircon-RSF}}$  and hence [Hf/W] elemental ratio in zircons.

The measured Hf-W composition in terrestrial zircons, NIST610 standard, and meteorite pyroxene show normal W isotope composition. The meteorite zircons from A881467 and A881388 show excess  $\delta^{182}\text{W}$  and normal  $\delta^{183}\text{W}$  within experimental errors. The Hf-W evolution diagram is plotted in Figure 2. The  $\delta^{182}\text{W}$  and  $\delta^{183}\text{W}$  data uncorrected for mass fractionation are shown in Figures 1a and 1b respectively. In the combined data set the highest excess in  $^{182}\text{W}$  is observed in meteorite zircons  $[\text{Hf}]/[\text{W}]$  value of  $\sim 2 \times 10^5$ , the measured  $\delta^{182}\text{W}$  value is  $17441 \pm 8101$  ‰ ( $2\sigma_m$ ) and the lowest [Hf]/[W] value of  $1.3 \times 10^4$  observed in zircon Z-7 has a  $\delta^{182}\text{W} = 1112 \pm 477$  ‰ ( $2\sigma_m$ ). The inferred  $^{182}\text{Hf}$  abundance at the time of crystallization of Asuka 881467 zircons is  $^{182}\text{Hf}/^{180}\text{Hf} = (5.9 \pm 1.6) \times 10^{-5}$  ( $2\sigma_m$ ) and the preliminary data from A881388 is  $(7.5 \times 10^{-5} \pm 3.8 \times 10^{-5})$  ( $2\sigma_m$ ).

These data demonstrate excellent correlation between  $^{182}\text{Hf}$  excess and the Hf/W values of zircons. The initial  $^{182}\text{Hf}$  abundance in zircons can be used to assign relative chronologies for these zircons with

respect to the CAI initial  $^{182}\text{Hf}$  abundance. The difference between the initial  $^{182}\text{Hf}$  in zircons suggests that igneous evolution of eucrite parent body took place in several episodes resulting in several suites of zircons with decreasing  $^{182}\text{Hf}$  abundance. A881388 zircons with  $^{182}\text{Hf}$  abundance comparable to eucrite whole-rock isochron value [2] formed contemporaneously with metal-silicate differentiation on EPB. These zircons have a CAI-model Pb age of  $\sim 4563$  million years based on CAI Pb age and  $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{SSI}}$  (SSI= solar system initial). Similarly the crystallization of individual A881467 zircons took place nearly  $3.9 \pm (-3.1/+4.0)$  million years after metal-silicate differentiation on eucrite parent body. The measured  $^{182}\text{Hf}$  abundance in A881467 zircons, together with solar system formation age  $\sim 4567$  Ma (CAI Pb age) and the  $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{SSI}}$ , indicate a model age of  $4560.1 \pm (+3.8/-4.6)$  Ma for zircon crystallization. Further work on direct measurement of W abundance in zircons using laser ablation ICPMS to estimate the Hf/W RSF factors is in progress. Work on absolute ages of A881388 zircons and further work on Hf-W in zircons is in progress.



- References: [1] Palme H and Ramanesse W. (1981) *Proc. Lunar Sci. Conf.* **12** 949-964. [2]. Quitte G. Bircck J.L. and Allegre C.J. (2000) *EPSL* **184** 83-94. Kleine T., et al. (2003) *GCA* **68** 2935-2946. [3] Lugmair G. and Shukolyukov A. (1998) *GCA* **62** 2863-2886. Srinivasan G., Goswami J.N., Bhandari N. (1999) *Science* **284** 1348-1350. Nyquist L.E., et al. (2003) *EPSL* **214** 11-25. [4] Ireland T.R. et al. (2000) *LPSC XXXI* #1540. Srinivasan G. et al. (2000) *MAPS* #5127. [5]. Srinivasan G. et al. (2004) *LPS*. 35, #1709 [6]. Ireland T.R. and Bukovanska M. (2003) *GCA* **67** 4849-4856. [7]. Pearce N.G.J., et al. (1997) *Geostand. Newsl.* **21** 115-144. [8] Wiedenbeck W. et al. (1995) *Geostand. Newsl.* **19** 1-23. [9]. Wiedenbeck M. et al. (2004) *Geostandards and Geoanalytical Research* **28** 195-201.