**U-Pb and Hf-W Chronometry of zircons from eucrite A881467.** G. Srinivasan[1], M J. Whitehouse[2], I Weber[3] and A. Yamaguchi[4]. [1]Department of Geology, University of Toronto, Toronto, ON Canada. [2]Laboratory for Isotope Geology, Swedish Museum of Natural History, SE-104 05 Stockholm, Sweden. [3]Department of Planetologie, University of Munster, Munster, Germany. [4]Antarctic Meteorite Research Center, NIPR, Tokyo 173-8515.

The decay of $^{182}$Hf to $^{182}$W with a half-life of ~ 9 million years has been used to constrain the core formation event in Earth, Mars, Moon and Vesta (the parent body of eucrites). The deficit of $^{182}$W in iron meteorites has been used to argue for the early separation of metal from silicate-rich material before the decay of $^{182}$Hf. This is possible because Hf and W show extremely strong affinities for silicate and sulphide/iron-rich material respectively. Core formation which is a product of planetary differentiation process resulted from large scale melting event separating a silicate reservoir into a mantle and metallic reservoir into the core. This event would have naturally separated the Hf and W into mantle and core respectively. If the core formation event took place before all $^{182}$Hf had completely decayed then it would result in excess $^{182}$W in the silicate reservoir and depletion in $^{182}$W in the core. Compared to primitive meteorites iron meteorites which sample the core of planetary bodies show depleted $^{182}$W abundance [1-3] while the silicate reservoir of the earth shows an enriched value [4-5]. Hf-W data has demonstrated that Earth had differentiated within the first few tens of million years of the formation of solar system, but to date these measurements have relied on bulk samples of meteorites and mineral isochron for Hf-W has remained elusive.

Zircon is an ideal mineral for determining the $^{182}$Hf abundance at the time of its formation. It usually has a high concentration of Hf (1-2%) and significantly low abundance of W. U-Pb studies coupled with laboratory based simulation studies have demonstrated that it is resistant to various processes taking place on a planetary body. Zircons have been identified in the past in eucrites and several preliminary studies have been carried out for Hf-W composition using the ion microprobe [6-8]. However, measurements appear to suggest a low $^{182}$Hf abundance.

The previous mesurements were carried out using Shrimp-RG and Shrimp at Stanford University and ANU respectively and Cameca ims 4f at PRL. The measurements were carried out using either single detector system, high mass resolution ranging from ~7000 to 11,000 (SHRIMP's) or energy filtering (4f). These factors resulted in severe loss of signal and increased measurement time.

In this abstract we report for the first time Hf-W measurements using the multi-collector Cameca ims1270 large geometry ion microprobe at the Swedish Museum of Natural History. Furthermore, the same zircons grains were measured for their U-Pb ages to calibrate the $^{182}$Hf abundance on the scale of an absolute chronometer (U-Pb system). The detector assembly consists of five movable detectors, three on low mass side and two on the high mass side of the axis. The Hf-W composition and U-Pb ages were measured in 5 zircons from the non-cumulate eucrite A881467.

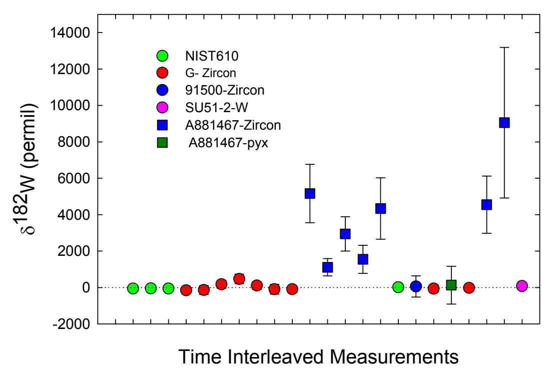
A881467 is unbrecciated non cumulate eucrite and has a crystalline rock texture. The thin sections display a granular texture of pigeonite, augite and plagioclase. The compositional range of plagioclase is very narrow from ~ $An_{87}$ to $An_{90}$. The reported Mg# of ~38 is in the field of noncumulate eucrites [10]. This eucrite has a bulk REE abundance of about ~9-12 × CI [10]. The 6 zircon grains identified in one PTS are not well shaped crystals and range in size from ~ 5-20 microns. They are usually triangular in shape and appear to resemble broken fragments. They are closely associated with ilmenite and chromite. The origin of this trace phase in this eucrite is not known and its genetic connection to ilmenite or chromite is not clear at this stage. Three zircon grains were analysed for U-Pb composition using standard techniques followed in this laboratory [11] and they have $^{207}$Pb/$^{206}$Pb ages of 4553.3±11.0, 4545.9±10.4 and 4556.2±14.4 million years.

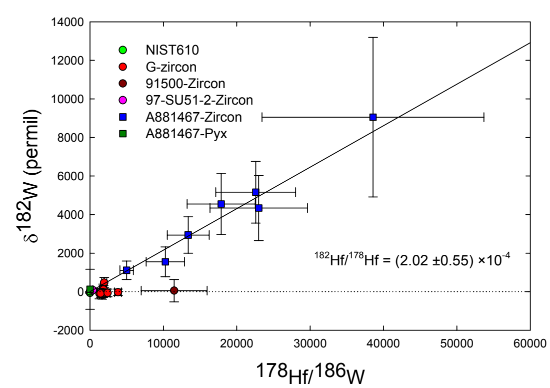
The Hf-W measurements were carried out using the multi-detector assembly at a nominal mass resolution of ~ 7500. The W isotopes were measured as metal. Although the signal strength of WO is higher compared to the atomic species, the presence of additional interference from di-oxides of REEs compromises the measurements for WO. Additionaly, $^{181}$Ta$^{16}$OH interferes at mass 198 which is the peak for $^{182}$W$^{16}$O. For example, in terrestrial zircon (G-zircon) when W was measured as an oxide, the excess $^{182}$W was in the range of 1800‰ due to signal contribution from oxides of REEs and/or TaOH. The peaks measured simultaneously included $^{178}$Hf [L2], $^{182}$W [L1], $^{183}$W [C], $^{186}$W [H1] and $^{184}$W$^{16}$O [H2]. Detector [L2] which was used as a centering detector for the measurement was shifted to the lower mass side by 5milli-amu so that effectively the cups measuring the W signals were centered on higher mass of the W peak flats. The increased *effective* mass resolution and reduced signal contribution from oxides of REE (e.g., $^{166}$Er$^{16}$O at mass 182) to W signals. The improvement in signal integrity was achieved without increasing the *actual* mass resolution or resorting to energy filtering, both of which attenuate signal resulting in lower measurement precision. The counting time for each cycle was 30 seconds and a given measurement typically consisted of 4 to 6 blocks of 4 cycles each. The typical primary current was in the range of ~ 5 nA. The Hf/W relative sensitivity factor (RSF) was determined using NIST610 standard with nominal concentration for all trace elements at ~ 500 ppm. The Hf/W RSF was estimated to be ~ 4.0.

Several terrestrial zircons with variable Hf/W values ranging from ~ 390 to 11460 have normal $^{182}$W/$^{186}$W and $^{183}$W/$^{186}$W isotopic composition. The 5 meteorite zircons analysed (including repeat measurements on two zircons) under identical conditions show excess $\delta^{182}$W and normal $\delta^{183}$W within experimental errors. A single analysis of meteoritic pyroxene with low Hf/W ratio has normal W isotopic composition. The data are shown in figures below.

In the upper panel the time interleaved measurements of terrestrial zircons and meteorite zircons are shown and lower panel the Hf-W evolution diagram is plotted. The data shown in the plots were not corrected for mass fractionation but represent raw data. The low counting statistics make fractionation correction unreliable at this stage. The highest excess in $^{182}$W is observed in zircon Z2 with Hf/W value of ~38500, the measured $\delta^{182}$W value is 15129±9050 ‰ ($2\sigma_m$). The inferred $^{182}$Hf/$^{178}$Hf at the time of crystallization of Asuka 881467 zircons is $(2.02\pm0.55)\times10^{-4}$. The convention for reporting the initial $^{182}$Hf abundance is to normalize it with respect to $^{180}$Hf. In this scheme of reporting the initial $^{182}$Hf/$^{180}$Hf at the time of formation of this meteorite is $(1.4\pm0.55)\times10^{-4}$. The initial $^{182}$Hf/$^{180}$Hf estimated on the basis of whole-rock measurement of eucrite samples is $(7.96\pm0.34)\times10^{-5}$ [12] which has been reconfirmed recently [5].

The $^{207}$Pb/$^{206}$Pb ages of zircons suggest that they are at least 10 to 20 million years younger compared to the age of the solar system. Therefore the minimum estimate for the initial $^{182}$Hf/$^{180}$Hf at the time of start of solar system formation is ~ $3.0\times10^{-4}$. This value is similar to old value estimated for early solar system [3] but a factor of 3 higher than the current accepted value of ~ $1.0\times10^{-4}$ [4-7] for $^{182}$Hf abundance.




This study represents the first successful attempt to determine the mineral isochron for Hf-W system in eucrite A881467. It is also the first report to successfully report the U-Pb ages and $^{182}$Hf abundance from a single mineral and therefore is an important step in calibrating short-lived chronometer with a long-lived chronometer. The difficulties in making W isotopic measurements using the ion microprobe were overcome by making use of the multi-collector large geometry ion microprobe. W isotopic compositions of several terrestrial zircons with a range of Hf/W values are normal within experimental errors. The Hf-W measurements of 5 meteorite zircons (including repeat measurements on two zircons) show elevated Hf/W values compared to meteorite pyroxene, and excess in $^{182}$W compared to normal abundance in meteorite pyroxene and terrestrial zircons. The inferred ($^{182}$Hf/$^{180}$Hf) value from this meteorite data is higher than the currently accepted value for early solar system. The reason for elevated $^{182}$Hf abundance inferred from zircon data is not obvious. An overestimate in relative sensitivity factor and/or uncorrected mass fractionation of W isotopes appears unlikely to result in such a high discrepancy, although both these issues warrant further investigation. The possibility of interference from REE-species appears rather low because preliminary investigation of REE abundance shows similar levels of HREE to terrestrial zircons, while elevation in LREE relative to terrestrial zircon should not generate unresolvable interferences. The normal values reported for time interleaved terrestrial zircons rules out any simple instrument artifact as an explanation. The possibility of an unkown nuclear effect for elevated $^{182}$W has not been investigated. An alternative scenario in which zircon grains could have picked up "fossil" $^{182}$W appears remote if zircons grains are products of primary crystallization in a large scale melting event which produced eucrite(s). However, zircons in terrestrial environment have been observed to be secondary in origin, precipitated from a major Zr bearing phases like ilmenite [13] during a metamorphic event. The issue of genetic connection of meteorite zircons to ilemenite and chromite and its possible effect on W isotopic composition remains to be investigated. The possibility of Hf loss without necessarily losing W, and thereby artificially producing elevated $^{182}$Hf abundance during any later metamorphic event appears very unlikely. At present there is no simple explanation which can satisfactorily explain the $^{182}$Hf abundance in these zircons which is higher than what is expected on the basis of their $^{207}$Pb/$^{206}$Pb ages. Further work is in progress.

Reference: [1] Lee D.-C. and Halliday A.N. (1996) *Nature* **378** 771. [2] Harper C.L. and Jacobsen S.B. *Geochim. Cosmochim. Acta* **60** 1131. [3] Lee D.-C. and Halliday A.N. *Science* **274** 1876. [4] Kleine et al. *Nature* **418** 952. [5] Yin et al. *Nature* **418** 949. [6] Schonberg et al. *Geochim. Cosmochim. Acta* **66** 3151. [7] Ireland T.R. *LPS* **XXII** 606. [8] Ireland T.R. et al. *LPSC* **XXXI** #1540. [9] Srinivasan G. et al. *MAPS* #5127. [10] Setoyangi et al. *LPSC* **XXXIV** #1593. [11] Whitehouse M.J. et al. *Geochim Cosmochim Acta* **61** 4429. [12] Quitte G. et al. *EPSL* **184** 83. [13] Bingen B. et al. *J Petrology* **42** 355.