^{182}Hf-^{182}W ISOTOPE SYSTEMATICS OF EUCRITES.

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Introduction: Eucrites are the oldest known basalts of the Solar System. They crystallised around 4,550 Ma ago. The study of these meteorites enables to better understand the very early magmatic processes in the solar system and especially on a small planetary body as it is often put forward that eucrites come from Vesta 4, a body with a radius of about 270 km.

The half-life of the Hf-W system ($T_{1/2}$ = 9Ma) is well suited to study early events in the solar system. Moreover this chronometer also has the advantage of involving two elements of strongly different chemical properties: Hf is a lithophile element whereas W is moderately siderophile. This means that measurable amounts of tungsten are still present in the silicate portions of planets. Both elements fractionate during core formation or any metal segregation process and the tungsten present in the silicate portion behaves similarly to the highly incompatible lithophile element Th (and U) during igneous processes [1] and formation of eucritic basalts. In addition to this, the two elements are highly refractory which should make them less sensitive to secondary processes like shock or metamorphism.

The goal of this study was to improve the analytical sensitivity to be able to analyze silicates without using too high amounts of precious meteoritic material. We performed tungsten isotopic analyses for 8 non-Antarctic eucrites (Bereba, Bouvante, Jonzac, Juvinas, Millbillillie, Pasamonte, Serra de Mage, Stannern) to better constrain the timescale of early magmatic processes on the eucrite parent body (EPB) and to establish the accurate analysis of small amounts of ^{182}W on actual samples. Two of the studied meteorites are particular : Millbillillie consists of several different lithologies [2] and Serra de Mage is a cumulate eucrite in contrast with the other eucrites measured here.

Analytical Procedure: About 100 to 150 mg of powdered sample were introduced in a clean PFA Teflon pressure bomb and dissolved with an HF - HCl - HNO_3 mixture. After dissolution an aliquot of about 10% of the supernatant was isolated for Hf-W concentration determinations. A two-stage anion-exchange procedure using the complexing properties of fluoride ions with regard to W was developed to extract the tungsten from the matrix and to purify it. The blank of the whole procedure is about 100pg.

In previous tungsten studies by negative thermal ionisation mass spectrometry (NTIMS) (e.g [3], [4]) standards and samples were generally loaded on Re filaments. As this can be harmful to Re-Os isotopic measurements on the same instrument an alternative technique using Ir filaments has been developed to circumvent this difficulty. Tungsten was ionised as WO_3^- and measured in static multicollector mode using a Finnigan MAT262 mass spectrometer. Minor WO_4^- beams are observed but always at a level at least two orders of magnitude smaller than WO_3^-. WO_3F^- is also present at significant levels at the low edge of the running temperature but rapidly decays at the optimal running temperature for WO_3^-. One of the major problems of very high precision NTIMS measurements of metal oxides is to correct out the contribution of oxygen isotopes on the different masses. The instrumental mass fractionation of oxygen and tungsten may drift independently and result in errors larger than those which would be expected from beam intensities. Oxygen was corrected in the same way as in [4].

Hf and W concentrations have been determined by isotope dilution using an ICP-MS. After addition of a ^{179}Hf-^{184}W spike to the above mentioned aliquot, an one-stage anion exchange procedure was used to separate Hf and W from the matrix elements. The isotopic measurements were carried out on a quadrupole elemental ICP-MS and ratios have been corrected for fractionation using an exponential mass discrimination law. Errors bars on concentration measurements vary between 0.4 and 7.5%.

Results: The present data are preliminary results. Tungsten isotopic data are quoted in ε-units (relative deviation in parts per 10^4 with respect to a terrestrial standard). Our terrestrial laboratory standard has an average value slightly different from the value obtained by Lee and Halliday using MC-ICP-MS [5]. The exact cause for the difference has not been identified yet but there seems to be a general difference between NTIMS (this work and [4]) and MC-ICP-MS measurements which should be clarified in the future. This is not important here for the interpretation as only relative deviations are considered and as long as the measurements are reproducible within the given error bars. All eucrites except Serra de Mage exhibit large radiogenic excesses from +2.5 ε to +39.1ε (Figure 1). The magnitude of the isotopic variations is in good agreement with previous tungsten studies of eucrites using MC-ICP-MS [6]. The Hf/W concentration ratios cover a wide range of values between 0.1 and 41.0.

In the isochron diagram the samples define a straight best-fit line corresponding to a slope of $(8.11 \pm 0.28).10^{-5}$ and an intercept with vertical axis of 0.86464 ± 4 (-0.4 ε). Most of the error does not originate in the W isotopic measurements but in the Hf concentration measurements at very low levels of concentration. The adjustment of the experimental points with the best-fit line is good except for Millbillillie.

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Discussion: Millbillillie is a mixture of different materials (granulitic breccias, impact melts, glassy veins) [2] with different ^{244}Pu-Xe ages and is composed of a coarse-grained portion and a fine-grained one. The brecciation event and the heterogeneous composition of the meteorite may be at the origin of the shift from the isochron. The case of this meteorite is quite special, therefore Millbillillie has not been considered in the calculation of the best-fit line.

The tungsten isotopic variations are related to the decay of ^{182}Hf. This basically results from two arguments: the isotopic effect correlates with Hf/W ratio and the other isotopes of W are in terrestrial proportions within the analytical resolution of the measurement. ^{186}Os decay (half-life = 2.10^{15} a) and neutron burnout during space exposure would only have minor effects [4]. Assuming a homogeneous ^{182}Hf/^{180}Hf throughout the solar system, the isotopic variations reflect fractionation between Hf and W during the lifetime of ^{182}Hf. The slope of the total-rock isochron gives the ^{182}Hf/^{180}Hf ratio at the time of the last Hf/W fractionation in the source region of the eucrites, thus dating either the melting of the mantle or the fractional crystallization of the magmatic liquids.

Considering 0.077 Ma^{-1} as the decay constant of ^{182}Hf and a ^{182}Hf/^{180}Hf ratio equal to $1.9.10^{-4}$ at the time of chondrites formation [7] an age difference of 11.1 Ma between eucrites and chondrites can be calculated, eucrites being younger. Taking into account a 5.1 Ma difference in age between Forest Vale phosphates and Allende CAIs [8], eucrites appear to have formed about 16.2 Ma after formation time of Allende CAIs. Nevertheless this must be considered as a maximum time difference because the 5.1 Ma value relies on Pb-Pb measurements on phosphates which indicate the age of metamorphism of Forest Vale. The actual formation age of Forest Vale may be older and the Hf –W system which involves more refractory elements may not record the metamorphism or show only partial reequilibration. This issue is far from being settled and requires further detailed investigation on a set of chondrites.

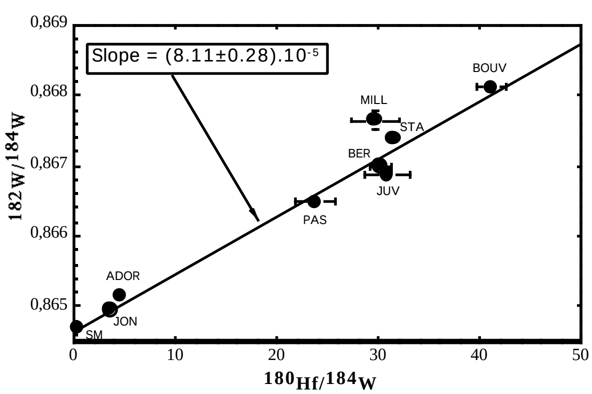

Figure 1 **: Bulk rock Hf-W isochron for 8 eucrites and ADOR.**

ADOR : Angra dos Reis
BER : Béréba
BOUV : Bouvante
JON : Jonzac
JUV : Juvinas
MILL : Millbillillie
PAS : Pasamonte
SM : Serra de Mage
STA : Stannern

Nevertheless the age obtained is concordant with the 11±4 Ma time difference between EPB formation and condensation age of CAIs, as inferred by Rb/Sr data [9], considering that the time interval between EPB accretion and mantle differentiation is short. This latest hypothesis is satisfied by the Mn-Cr data.

Halliday et al. found model ages for eucrites between 8 and 10 Ma after the start of the solar system [10]. The time interval between CAIs and eucrites determined by the present isochron is quite larger than this previous result but as mentioned earlier the 16.2 Ma value is an upper limit. On the other hand this result agrees with ^{60}Fe-^{60}Ni data (10±2 Ma between eucrites and CAIs) [11] but is more difficult to reconcile with ^{53}Mn-^{53}Cr data [12]. However chromium data from other authors [13] agree within errors with Hf-W results.

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