# $^{182}Hf$-$^{182}W$: NEW COSMOCHRONOMETRIC CONSTRAINTS ON TERRESTRIAL ACCRETION, CORE FORMATION, THE ASTROPHYSICAL SITE OF THE *r*-PROCESS, AND THE ORIGIN OF THE SOLAR SYSTEM

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Measurements of the isotopic composition of W (*Cf.*, table) separated from (Hf-free) metal of the Toluca type IAB iron meteorite show a well-resolved ~3ε (parts in ten thousand) deficit at mass 182 (fig. 1). The existence of this deficit is indicative of the presence of live $^{182}Hf$ ($T_{1/2}$ = 9My) in the early solar system at the time of the (probably impact-generated) metal segregation within the meteorite's parent body. As the source reservoirs of differentiated objects in the solar system are large, the assumption of a homogenous initial $^{182}Hf/Hf$ ratio for these reservoirs appears well-justified. Thus the initial $^{182}Hf/Hf$ and $^{182}W/^{184}W$ ratios of meteorites and planetary reservoirs can be employed to obtain chronologies for very early igneous differentiation events in the solar system [1]. Among the prospective 'planetary' applications of these systematics to early solar system processes are the following: (i) dating the formation of the cores of the Earth, Moon, Mars, and in the parent bodies of the howardites, eucrites, diogenites, angrites, aubrites, brachinites(?), pallasites and 'magmatic' iron meteorite classes; (ii) determining crystallization ages from $^{182}Hf/Hf$ ratios; and (iii) determining parental reservoir evolution histories from initial $^{182}W/^{184}W$ ratios. The $^{182}Hf$-$^{182}W$ systematics are well suited to studies of crystallization and core formation and accretion chronologies, due to the large parent/daughter ratio fractionations occurring during silicate-metal segregation and also because of the sensitivity of the siderophilic partitioning to the oxidation state of the differentiating environment.

The $^{182}Hf/Hf$ *ab initio* ratio of the bulk solar system (BSS) can also be used to constrain the cosmochronology of 'late' nucleosynthetic inputs into the protosolar reservoir. As the lifetime of $^{182}Hf$ is ~1/2 that of $^{129}I$, and as theoretically estimated nucleosynthetic production ratios, P($^{182}Hf$) / P(stable-Hf), differ considerably in the slow and rapid neutron-capture processes, the results obtained from these new systematics will likely play a critical role in constraining astrophysical models of the origin of the solar system.

Here we report the first evidence that $^{182}Hf$ was live in the early solar system and outline some implications of our data for dating terrestrial core formation, *r*-process nucleocosmochronology, and the origin of the solar system.

An ~30μg sample of W was separated from a sample of Toluca metal in HCl solution by liquid-liquid extraction with α-benzo-oxime in chloroform, followed by anion-exchange mini-column chromatography in HCl-HF. Isotopic analyses were made by means of negative thermal ionization (NTIMS) of $WO_3^-$ on a Finnigan MAT 261 mass spectrometer with a single Faraday cup collector. Toluca W was loaded in dilute $HNO_3$ and ionized as a molecular trioxide using a double Re filament geometry with $La(NO_3)_3$ emitter on the ionization filament. Experiments with other elements, (*e.g.*, P and Os), and with an $^{18}O$ enriched emitter, suggest that the oxygen in the ions comes predominantly from the $La(NO_3)_3$ emitter or residual oxygen in the ion source. Normal W was loaded as an aqueous solution of $NaWO_4$. (The use of Re filaments generated a significant $^{185}Re^{16}O_2{}^{17}O^-$ interference, disallowing use of the mass 234 peak in the discrimination measurement). Both standards and Toluca aliquots were run with 500 ng loadings, which typically produced a stable mass 230 signal intensity of 2 x $10^{-11}$ amps (2 volts) for several hours, corresponding to an ionization efficiency of 0.5-1%. Mass discrimination corrections were applied block by block on runs of at least 10 blocks of 10 ratios each, as determined from the 183/184 ratio obtained after correction for $^{182,183}W^{16}O_2{}^{17}O^-$ and $^{182}W^{16}O_2{}^{18}O^-$ interferences. A normalization reference value of $^{183}W/^{184}W$ = 0.4662537 was used. Oxide correction factors were calculated from: $^{16}O$ = 99.762; $^{17}O$ = 0.038%; $^{18}O$ = 0.200%, and the measured W composition obtained after the oxide correction. (We thus assume a constant O composition, and mass-dependent variation in the W composition, throughout the run.) The magnitude of the oxide correction applied to obtain the 'raw' 182/184 ratio is +56.3ε. That for the 183/184 ratio is +35.8ε. Error in the 183/184 ratio determination propagates with a x2 error amplification into the discrimination correction applied to the measured 182/184 ratio. Interference scans in the mass range 224-245 were made several times during each run at a sensitivity of 1ε of the $^{182}W^{16}O_3^-$ intensity. Additional scans were made over a wide range of temperatures. Evolving ratio deviations were searched for during extended runs of Toluca samples. No interference peaks or time-dependent effects were observed except those attributable to $ReO_3^-$. The $^{185}Re^{16}O_2{}^{17}O^-$ interference on $^{186}W^{16}O_3^-$ was usually less than 1.5%. Comparison of the mean Regensburg oxide-corrected W normal composition with the mean of 4 high-intensity, high-precision $W^+$ measurements obtained from bare W filament runs on the JSC 261 multi-collector, (normalized to 186/183), shows a small apparent shift of ~+1ε in the Regensburg 182/184 ratio, relative to the renormalized JSC metal beam data. We interpret this discrepancy as likely due to error in the oxide correction. This will affect all oxide data equivalently, unless O compositions differ systematically between normal and Toluca runs. The shift is modified to ~-1ε by renormalizing the oxide data to the heavier O isotopic composition measured by [2] in $NdO^+$ runs: $^{16}O$ = 99.7510; $^{17}O$ = 0.0386%; $^{18}O$ = 0.2104% . (Intermediate O compositions have been measured in JSC $NdO^+$ runs and also in Regensburg $PO_2^-$ runs [3].) A 1.4x greater difference between the mean isotopic abundances of O in the Toluca and terrestrial normal $WO_3^-$ ions would be required to produce the observed ($-2.8 \pm 1.0$, $2\sigma_m$)ε mass 182 anomaly. We find this to be unrealistically large and conclude that the Toluca deficit is real and points to the presence of live $^{182}Hf$ in BSS, (which decayed after the metal phase of the meteorite formed). According to this interpretation, terrestrial W is *radiogenic* relative to Toluca.

The basic uncertainty in interpreting our data concerns the chronology of terrestrial accretion and core formation (*cf.*, fig. 2). The Hf/W ratio of 'primitive' mantle (core formation residual reservoir: 'CFRR') is ~12x that in Orgeuil (1.16 = CHUR = BSS). This fractionation was very probably the result of W partitioning into the Earth's core [4]. Consider two 'early' and 'late' endpoint models for core formation in the Earth. If terrestrial W has the same isotopic composition as CHUR (model 1: 'late' core formation), and if Toluca W ('TOL') was segregated from a chondritic reservoir (very probable), then the BSS *ab initio* (4565 My) $^{182}Hf/Hf$ ratio was: ~($1.3 \pm 0.5$) x $10^{-4}$. (The anomaly is TOL-CHUR = A.) If the Earth's core formed early, at the same time as Toluca (~4556 My: model 2), then ~92% of the TOL-CFRR difference (B) is due to radiogenic evolution of terrestrial W relative to CHUR. In this case we obtain an *ab initio* $^{182}$Hf/Hf ratio of: ~(1.1 ±0.5) x $10^{-5}$. The uncertainty can be resolved by measuring the isotopic composition of W in a meteorite possessing a 'primitive' Hf/W ratio (*e.g.*, Allende). Results for W separated from a 12 gram sample of the Smithsonian Allende standard reference powder will be presented.

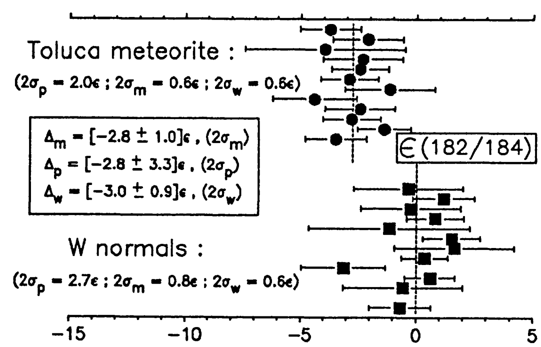
$^{182}$Hf is produced in *r* -process events and in high neutron density (pulsed) *s* -processing environments in AGB stars [5]. Estimated production ratios are $^{182}$Hf/stable-$^{r}$Hf ~0.15 and $^{182}$Hf/stable-$^{s}$Hf ~0.02 (R. Gallino, pers. comm.), respectively. Decompositions of the BSS stable Hf isotopes into *s* - and *r* -process fractions [6, 10] are shown in figure 3. $N_r/N_s$ for stable BSS Hf is ~1. Hence we obtain an *ab initio* BSS $^{182}$Hf/stable-$^{r}$Hf ratio: 2C(~1.1 ± 0.5) x $10^{-4}$, (where C represents the core-formation time uncertainty: 0.09<C<1), for comparison with $^{129}$I/$^{127}$I ~1.5 x $10^{-4}$ [7,6], which can be interpreted as an *r* -only ratio ($N_r/N$ ~0.94 for $^{127}$I [6, 10]). If P($^{129r}$I)/P($^{127r}$I) ~1.5 [8], $^{182}$Hf/stable-$^{r}$Hf ~2 x $10^{-5}$ supports a late *r* -process input into the protosolar reservoir, consistent with an OB association model for the astrophysical site of the origin of the solar system [9], and a type II supernova model for the site of the *r* -process. Moreover, as a *total* late-spike *r* -process input ($N_{*r}/N_r = 10^{-4}$) of *all* early solar system $^{129}$I and $^{182}$Hf (no decay interval) cannot produce $^{182}$Hf/Hf >~$10^{-5}$, relative to our production ratios and decomposition parameters, our data tentatively support *both* early terrestrial core formation (+ rapid accretion), and the OB association model.

***Table:***

| JSC METAL BEAM W FILAMENT NORMALS ($\pm 2\sigma_{mean}$) | | | | |
|---|---|---|---|---|
| Sample | 180/183 | 182/183 | 184/183 | N =186/183 |
| #1 | 0.00825±3 | 1.84704±9 | 2.14555±5 | 2.00000 |
| #2 | 0.00822±2 | 1.84690±5 | 2.14555±4 | 2.00000 |
| #3 | 0.00825±1 | 1.84691±4 | 2.14554±3 | 2.00000 |
| #4 | 0.00825±2 | 1.84704±5 | 2.14562±3 | 2.00000 |
| Mean: | 0.00824 | 1.84697 | 2.14557 | 2.00000 |
| RN to: | 180/184 | 182/184 | N =183/184 | 186/184 |
| Mean: | 0.00385 | 0.861484 | 0.4662537 | 0.93145 |
| REGENSBURG OXIDE DATA: NORMALS AND TOLUCA | | | | |
| Sample | 180/184 | 182/184 | N =183/184 | (186/184) |
| NORMALS (12) Uncertainties are ± 2σ: | | | | |
| #1 | .003879±10 | 0.86152±18 | 0.4662537 | 0.92742±40 |
| #2 | .003870±12 | 0.86153±42 | 0.4662537 | 0.93115±84 |
| #3 | .003895±6 | 0.86163±12 | 0.4662537 | 0.93093±12 |
| #4 | .003878±22 | 0.86131±28 | 0.4662537 | 0.93138±40 |
| #5 | .003881±12 | 0.86161±10 | 0.4662537 | 0.93097±14 |
| #6 | .003880±16 | 0.86172±42 | 0.4662537 | 0.93107±80 |
| #7 | .003880±28 | 0.86171±16 | 0.4662537 | 0.93087±86 |
| #8 | .003886±66 | 0.86148±58 | 0.4662537 | 0.93088±82 |
| #9 | .003885±26 | 0.86165±16 | 0.4662537 | 0.93108±32 |
| #10 | .003884±36 | 0.86156±34 | 0.4662537 | 0.93118±54 |
| #11 | .003876±30 | 0.86168±18 | 0.4662537 | 0.93099±34 |
| #12 | .003880±30 | 0.86155±38 | 0.4662537 | 0.93099±86 |
| Mean: | .003881±12 | 0.86158±7 | 0.4662537 | 0.9308±20 |
| TOLUCA (12) Uncertainties are ± 2σ: | | | | |
| #1 | .003900±20 | 0.86128±18 | 0.4662537 | 0.93116±38 |
| #2 | .003884±8 | 0.86146±14 | 0.4662537 | 0.93092±18 |
| #3 | .003878±20 | 0.86134±16 | 0.4662537 | 0.93099±36 |
| #4 | .003874±14 | 0.86137±22 | 0.4662537 | 0.93117±22 |
| #5 | .003874±8 | 0.86120±28 | 0.4662537 | 0.93119±54 |
| #6 | .003886±32 | 0.86148±30 | 0.4662537 | 0.93084±40 |
| #7 | .003885±24 | 0.86133±16 | 0.4662537 | 0.93106±26 |
| #8 | .003883±16 | 0.86137±16 | 0.4662537 | 0.93102±30 |
| #9 | .003876±34 | 0.86138±26 | 0.4662537 | 0.93099±38 |
| #10 | .003885±24 | 0.86124±58 | 0.4662537 | 0.93102±30 |
| #11 | .003879±20 | 0.86140±22 | 0.4662537 | 0.93090±52 |
| #12 | .003888±18 | 0.86126±18 | 0.4662537 | 0.93087±34 |
| Mean: | .003883±7 | 0.86134±5 | 0.4662537 | 0.93100±22 |

Refs: [1] E. B. Norman and D. N. Schramm, (1983). *Nature*, 304: 515; C. L. Harper *et al.*, (1990). *GSA Abs. w. Progs.*, v. 22, #7: A218; --- (1991 abstract). *Terra Nova* (in press); [2] G. J. Wasserburg *et al.*, (1981). *GCA*, 45: 2311; [3] K. G. Heumann *et al.*, (1989). In: *Proc. 37th Am. Soc. Mass Spec. Conf. Mass Spec. Allied Topics*, p. 414; [4] H. E. Newsom, (1990). In: H. E. Newsom and J. H. Jones (Eds.) *Origin of the Earth* (Oxford), p. 273; [5] F. Käppeler *et al.*, (1990). *Ap. J.*, 354: 630; [6] F. Käppeler *et al.*, (1989). *Rep. Prog. Phys.*, 52: 945; [7] R. S. Lewis and E. Anders, (1975). *Proc. Nat. Acad. Sci. USA*, 72 #1, p. 268; [8] W. A. Fowler, (1972). In: F. Reines (Ed.) *Cosmology, Fusion and Other Matters*, p. 67; [9] J.-P. Arcoragi, (1989). In: E. Vangioni-Flam et al., (Eds.) *Astrophysical Ages and Dating Methods* (Paris), p. 457, and references therein; [10] F. Käppeler *et al.*, (1991). *Ap. J.*, 366: 605.

*Figure 1.* EPSILON ($^{182}$W/$^{184}$W)



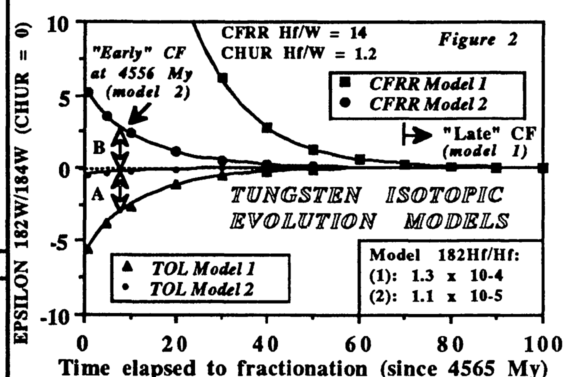




*Figure 3*