

## THE ABUNDANCE OF $^{182}\text{Hf}$ IN THE EARLY SOLAR SYSTEM;

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The abundance of  $^{182}\text{Hf}$  is a key indicator to the timing of r-process contributions to the solar system. Based on the inferred abundance of  $^{244}\text{Pu}$  ( $t_{1/2} = 82$  Ma), the last event to contribute r-process material occurred on the order of 100 Ma before the formation of solid bodies in the solar system [1, 2, 3]. The determination of this interval is highly dependent on the production of  $^{244}\text{Pu}$  in r-process nucleosynthesis and also depends on the element to which the abundance of  $^{244}\text{Pu}$  is referenced since there are no stable isotopes of Pu.  $^{182}\text{Hf}$  is also produced solely in r-process nucleosynthesis, but it has a much shorter half-life (9 Ma) and its abundance can be referenced to other stable Hf isotopes. This radionuclide might therefore give a better estimate to the interval,  $\Delta$ , between nucleosynthesis and formation of solid bodies in the solar system [4].

The daughter of  $^{182}\text{Hf}$  is  $^{182}\text{W}$ . The measurement of W isotopic compositions is very difficult because tungsten is a highly refractory metal that does not lend itself to analysis by conventional thermal ionization mass spectrometry. In addition, the solar system abundances of Hf and W are very low and relatively large samples of material are required. These problems have been circumvented to a large degree by analyzing two zircon crystals found in the Vaca Muerta mesosiderite and Simmern H5 chondrite [5, 6]. Zircon has high concentrations of Hf (around 1 to 1.5 wt %) and so is an ideal candidate in a search for excess  $^{182}\text{W}$ .  $\text{W}^{4+}$  has a similar ionic radius as  $\text{Hf}^{4+}$  (0.70 vs 0.78 Å) but significant W concentrations in zircon have never been reported.

W-Hf isotopic ratios in the zircons were measured by ion microprobe mass spectrometry. Two terrestrial zircons were analyzed as standards along with the meteoritic zircons. A minimum mass resolution of around 3000  $M/\Delta M$  was maintained with an energy offset of 100 V to further discriminate against complex molecular interferences. The positive identification of possible interferences is not possible but the main contributions in this region of the mass spectrum are from REE oxides and hydroxides, and Hf and W hydrides. In particular  $^{180}\text{HfH}_2$  was probably a large contributor to mass 182. No corrections have been applied to the data for these isobaric interferences and the analyses therefore represent upper limits to the abundance of  $^{182}\text{Hf}$  in the meteoritic zircons. The  $^{180}\text{Hf}/^{184}\text{W}$  ratio is taken as the measured ionic ratio since no standard zircon with measurable concentrations of W is available. This should be correct to first order since Hf, Zr, and W have similar ionization potentials and the energy filtering also minimizes matrix effects on ion production.

The Hf/W ratio for the four analyzed zircons ranges up to 90,000. Such high ratios were observed for the two terrestrial zircons as well as the Vaca Muerta zircon. These latter three zircons gave identical  $^{182}\text{W}/^{184}\text{W}$  ratios within error. The  $^{182}\text{W}/^{184}\text{W}$  ratios are marginally above the terrestrial values which is almost certainly due to unresolved isobaric interferences. Therefore there is no evidence for *in situ* decay of  $^{182}\text{Hf}$  and the upper limit for the abundance of  $^{182}\text{Hf}$  in the Vaca Muerta zircon is around  $5 \times 10^{-5} \times ^{180}\text{Hf}$ . In the Simmern zircon, a substantial W signal was observed which was found to be due to surface contamination. For this zircon, the much lower Hf/W ratio results in a higher upper limit for  $^{182}\text{Hf}$  at a level of  $5 \times 10^{-4} \times ^{180}\text{Hf}$ .

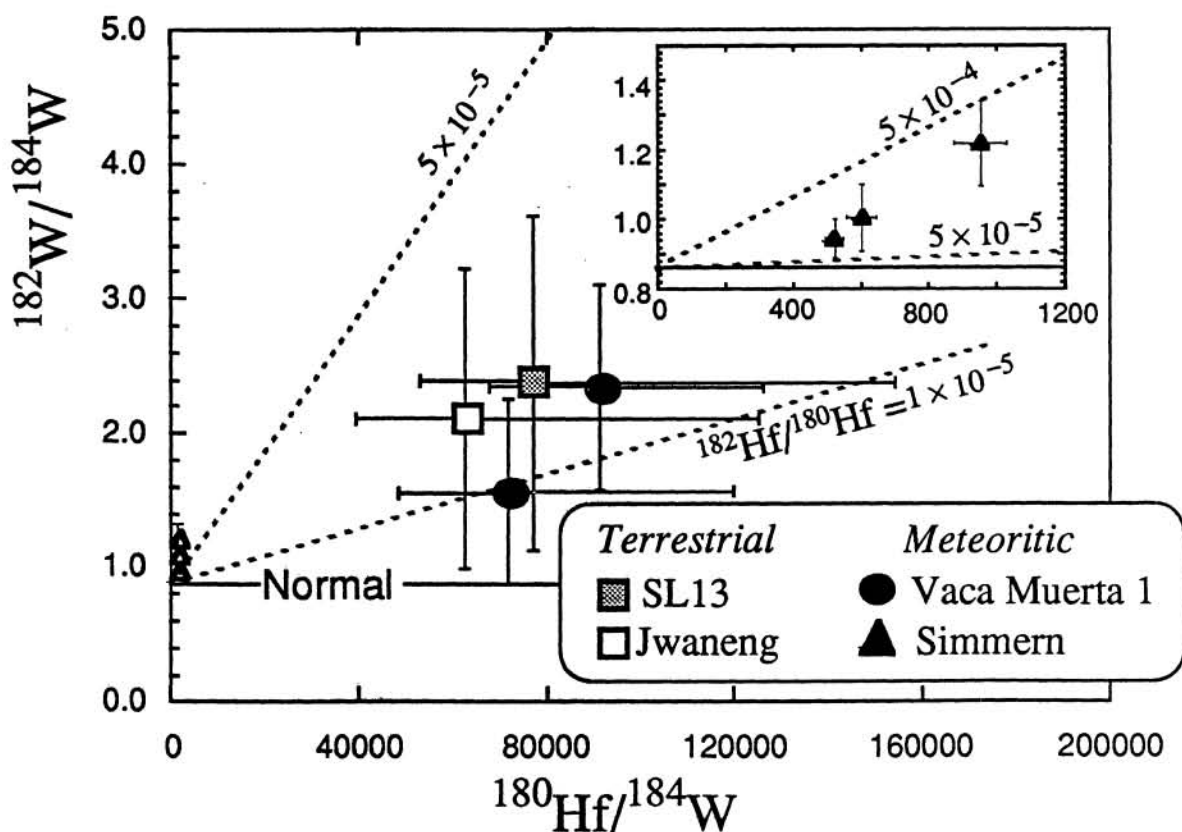
Norman and Schramm [4] predicted the abundances of  $^{182}\text{W}$  relative to  $^{186}\text{W}$  as a function of  $\Delta$ . In their formulation, the upper limit of  $5 \times 10^{-5} \times ^{180}\text{Hf}$  for the Vaca Muerta zircon corresponds to a lower limit for  $\Delta$  of approximately 120 Ma. This is consistent with the interval estimated from the  $^{244}\text{Pu}$  abundance and the absence of live  $^{247}\text{Cm}$  ( $t_{1/2} = 16$  Ma) in the early solar system [7].

Table 1. Hf-W isotopic systematics of zircons

Sample		$^{182}\text{W}/^{184}\text{W}$	$^{180}\text{Hf}/^{184}\text{W}$
<b>Terrestrial Zircons</b>			
Jwaneng		$2.12 \pm 1.12$	$63000^{+63000}_{-20000}$
SL13		$2.38 \pm 1.25$	$77000^{+77000}_{-25000}$
<b>Meteoritic Zircons</b>			
VM-1	1	$1.57 \pm 0.69$	$71000^{+48000}_{-21000}$
	2	$2.36 \pm 0.76$	$91000^{+35000}_{-19000}$
Simmern	1	$0.95 \pm 0.05$	$520^{+28}_{-26}$
	2	$1.22 \pm 0.12$	$951^{+78}_{-66}$
	3	$1.01 \pm 0.10$	$598^{+44}_{-38}$

All errors are  $1\sigma$ .Terrestrial  $^{182}\text{W}/^{184}\text{W} = 0.8587 \pm 0.0013$  [8].

**Figure 1.** Plotted are uncorrected W isotopic compositions of zircons from the Vaca Muerta mesosiderite, the Simmern H5 chondrite, and terrestrial zircons from Jwaneng and Sri Lanka. The Vaca Muerta zircon has high Hf/W similar to the terrestrial zircons and also shows similar  $^{182}\text{W}/^{184}\text{W}$  ratios. The elevated ratios of all these zircons are probably due to the presence of  $^{180}\text{HfH}_2$ . The Simmern zircon shows lower Hf/W ratios. For these analyses, surface contamination of W was noted with an exponential decay of the W signal with sputtering on the zircon as well as surrounding phases. In addition, W hydrides are probably present. The maximum  $^{182}\text{Hf}/^{180}\text{Hf}$  for the Simmern zircon is around  $5 \times 10^{-4}$  whereas the maximum ratio for the Vaca Muerta zircon is about  $5 \times 10^{-5}$ . These values represent absolute upper limits because of the presence of unresolvable isobaric interferences. A  $^{182}\text{Hf}/^{180}\text{Hf}$  ratio of less than  $5 \times 10^{-5}$  corresponds to a free-decay interval of no less than 120 Ma for a production ratio of  $^{182}\text{Hf}/^{180}\text{Hf}$  of 0.5 [4].



**References:** [1] Goles and Anders (1961) *J. Geophys. Res.* **66**, 889. [2] Rowe and Kuroda (1965) *J. Geophys. Res.* **70**, 709. [3] Alexander et al. (1971) *Science* **172**, 837. [4] Norman and Schramm (1983) *Nature* **304**, 515. [5] Wlotzka et al. (1990) *Meteoritics* **25**, in press. [6] Ireland et al. (1990) *Meteoritics* **25**, in press. [7] Chen and Wasserburg (1981) *Earth Planet. Sci. Lett.* **52**, 1. [8] White and Cameron (1948) *Phys. Rev.* **74**, 991.