THE ABUNDANCE OF $^{182}$Hf IN THE EARLY SOLAR SYSTEM;
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The abundance of $^{182}$Hf is a key indicator to the timing of r-process contributions to the
solar system. Based on the inferred abundance of $^{244}$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 $^{244}$Pu in r-process nucleosynthesis and also depends on the element to which
the abundance of $^{244}$Pu is referenced since there are no stable isotopes of Pu. $^{182}$Hf is also
produced solely in r-process nucleosynthesis, but it has a much shorter short 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 $^{182}$Hf is $^{182}$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
$^{182}$W. W$^{4+}$ has a similar ionic radius as Hf$^{3+}$ (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/ΔM 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 $^{180}$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 $^{182}$Hf in the meteoritic zircons. The $^{180}$Hf/$^{184}$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 $^{182}$W/$^{184}$W ratios within error. The $^{182}$W/$^{184}$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 $^{182}$Hf and the upper limit for
the abundance of $^{182}$Hf in the Vaca Muerta zircon is around 5×10$^{-5}$$^{180}$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
$^{182}$Hf at a level of 5×10$^{-4}$×$^{180}$Hf.

Norman and Schramm [4] predicted the abundances of $^{182}$W relative to $^{186}$W as a
function of $\Delta$. In their formulation, the upper limit of 5×10$^{-5}$×$^{180}$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 $^{244}$Pu abundance and the absence of live $^{247}$Cm ($t_{1/2} = 16$ Ma) in the
early solar system [7].
Table 1. Hf-W isotopic systematics of zircons

<table>
<thead>
<tr>
<th>Sample</th>
<th>(^{182}\text{W}/^{184}\text{W} \pm \text{error}</th>
<th>(^{180}\text{Hf}/^{184}\text{W} \pm \text{error}</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Terrestrial Zircons</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jwaneng</td>
<td>2.12 ± 1.12</td>
<td>63000 ± 63000</td>
</tr>
<tr>
<td>SL13</td>
<td>2.38 ± 1.25</td>
<td>77000 ± 77000</td>
</tr>
<tr>
<td><strong>Meteoritic Zircons</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VM-1</td>
<td>1.57 ± 0.69</td>
<td>71000 ± 71000</td>
</tr>
<tr>
<td>2</td>
<td>2.36 ± 0.76</td>
<td>91000 ± 91000</td>
</tr>
<tr>
<td>Simmern</td>
<td>0.95 ± 0.05</td>
<td>520 ± 520</td>
</tr>
<tr>
<td>2</td>
<td>1.22 ± 0.12</td>
<td>951 ± 951</td>
</tr>
<tr>
<td>3</td>
<td>1.01 ± 0.10</td>
<td>598 ± 598</td>
</tr>
</tbody>
</table>

All errors are 1σ.
Terrestrial \(^{182}\text{W}/^{184}\text{W} = 0.8587 ± 0.0013 \) [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 unresolved 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].