

# Search for Live $^{182}\text{Hf}$ in Deep-Sea Sediments

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## Abstract

The presence of live  $^{182}\text{Hf}$  ( $t_{1/2} \sim 9$  Myrs) in the early solar system is well established but the understanding of its abundance is still challenging. Live  $^{182}\text{Hf}$  is expected to be present in the interstellar medium (ISM) as a result of recent nucleosynthesis activity. We are attempting a search for live  $^{182}\text{Hf}$  possibly deposited on Earth. The search focuses on deep-ocean sediments and a method for chemical extraction of the Zr-Hf fraction from sediments has been developed. The detection of  $^{182}\text{Hf}$  is performed at the Vienna Environmental Research Accelerator (VERA). Measurements of Hf and W isotopic abundances for the Zr-Hf fraction extracted from deep-sea sediment samples were performed. Present limits for the  $^{182}\text{Hf}$  abundance derived from the measured isotopic abundances are discussed.

*Key words:* accelerator mass spectrometry, extinct radioactivities,  $^{182}\text{Hf}$ , ISM

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## 1 Introduction

The presence of live  $^{182}\text{Hf}$  ( $t_{1/2} (9 \pm 2)$  Myrs [1]) in the early-solar system was first shown [2] through W isotopic anomalies in the iron meteorite Toluca and later confirmed [3, 4, 5]. The most recent values for the  $^{182}\text{Hf}/^{180}\text{Hf}$  initial abundance have been determined as  $1.0 \times 10^{-4}$  [6, 7, 8]; however, this ratio is still considered not well established and seems to be a lower limit [9, 10].  $^{182}\text{Hf}$

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is believed to be produced by  $r$ -process nucleosynthesis; its early-solar system abundance seems to be in line with steady-state production but contrasts with the suppression of other  $r$ -process nuclides (*e. g.*  $^{129}\text{I}$  [11]). A significant amount of  $^{182}\text{Hf}$  could also be produced through the fast  $s$ -process in massive stars [12, 13].

In any production scenario, live  $^{182}\text{Hf}$  is expected to be present in the interstellar medium (ISM) as a result of recent nucleosynthesis.  $\gamma$ -ray detection of  $^{182}\text{Hf}$  (similarly to  $^{26}\text{Al}$  [14]) is unfeasible due to its overall low activity. However, deposition of ISM grains by accretion onto Earth could make direct detection of live  $^{182}\text{Hf}$  possible in slow-accumulating reservoirs such as deep-sea sediments. Importantly,  $^{182}\text{Hf}$  is one of the few extinct radionuclides without significant natural or artificial production on Earth. Production from spallation in the atmosphere is prevented by the lack of heavy target nuclei. In the lithosphere, neutron-induced reactions are absent since they start from unstable nuclides and production by  $\mu$ -induced spallation on stable W isotopes should be extremely small due to the low W abundance. In addition,  $^{182}\text{Hf}$  is above the fission peaks and has not been produced in nuclear tests. Recently, an indication for a nearby supernova has been found through detection of  $^{60}\text{Fe}$  ( $t_{1/2} = 1.5$  Myrs) in ferro-manganese crusts [15]. There are two independent measurements of the longer-lived  $^{244}\text{Pu}$  ( $t_{1/2} = 81$  Myr) [16, 17] but more measurements are needed [18]. We report here on a first attempt to detect live  $^{182}\text{Hf}$  in the Hf-Zr separated fraction of deep-sea sediment by accelerator mass spectrometry (AMS).

## 2 Chemical preparation and AMS measurements

A sediment core (TRIPOD 7P,  $17^{\circ}30'\text{N}$   $113^{\circ}00'\text{W}$ , water depth 3763 m, sediment depth 3–228 cm) was selected at Scripps Oceanographic Institute [19]. The sediment (red clay) 5 cm-diameter core was divided along its length in four quarters and one quarter, divided in sections of 3–8 cm long, was made available to us. Table 1 lists the average concentrations of some relevant elements in the sediment core. A method for extraction of the Zr-Hf and actinides fractions was developed at Hebrew University. Three of the sections (sediment depths 3–11 cm, 12–19 cm and 19–37 cm) were processed in the present work. The final residue is dissolved in a 60% HF solution and then evaporated to dryness to obtain a  $\text{ZrF}_4\text{-HfF}_4$  sample. Alternatively for small samples, Ba is added as nitrate in the final solution to precipitate the  $\text{Ba}[\text{HfF}_6]$  complex.

A first measurement of the Hf-Zr fractions was performed at the Vienna Environmental Research Accelerator (VERA) in Vienna, Austria, a dedicated AMS facility based on a 3 MV tandem accelerator recently upgraded for heavy ion measurement [20]. The feasibility of measuring  $^{182}\text{Hf}/^{180}\text{Hf}$  isotopic ratios

Table 1  
ICPMS analysis of the TRIPOD 7p sediment core.

element:	Zr	Hf	Ta	W	Th	U	Ce	Sm
concentration (ppm dry weight):	390	8.0	1.6	11	15	2.6	110	21

down to  $10^{-11}$  was shown using activated Hf from used control rods of a nuclear research reactor [21]. The method relies on two main properties : (*i*) high mass resolution to separate neighboring isotopes; (*ii*) efficient suppression ( $\sim 1 : 6000$ ) of the  $^{182}\text{W}$  stable isobar achieved by injection of  $\text{HfF}_5^-$  ions (see [21] for details). At the high-energy side,  $\text{Hf}^{3+}$  ions are analyzed at an energy of  $\sim 7.8$  MeV. For identification, a Bragg-type ionization chamber is used. Using a very thin 50 nm silicon nitride membrane (from Silson, UK) as entrance window results in an energy resolution of 6% FWHM, sufficient to suppress background ions with the same mass to charge ratio, which have at least 33% lower energies. Because of the low Hf/Zr abundance in the separated sample,  $^{180}\text{Hf}$  ions could not be measured as charge current but were counted in a pulsed mode using the multi-beam switcher as chopper to reduce the average count rate.

Table 2  
Results of isotope ratio measurements in calibration samples.

Sample	$\frac{^{182}\text{Hf}+^{182}\text{W}}{^{180}\text{Hf}}$		$\frac{^{182}\text{Hf}+^{182}\text{W}}{^{183}\text{W}}$	$\frac{^{182}\text{Hf}+^{182}\text{W}}{^{184}\text{W}}$	$\frac{^{183}\text{W}}{^{184}\text{W}}$
	nominal ( $\times 10^{-10}$ )	measured ( $\times 10^{-10}$ )			
Dilu2 <sup>a</sup>	$4.7 \pm 0.7$	$4.5 \pm 1.7$	19.0	11.0	0.55
Dilu3 <sup>a</sup>	$1.8 \pm 0.4$	$1.9 \pm 0.3$	4.59	2.42	0.55
HfF4 <sup>a</sup>	$0.17 \pm 0.01$	$0.35 \pm 0.01$	2.20	1.10	0.50

<sup>a</sup>Samples prepared from activated Hf and diluted to different isotope ratios. HfF4 is commercial  $\text{HfF}_4$  (Alfa Aesar). The nominal  $(^{182}\text{Hf}+^{182}\text{W})/^{180}\text{Hf}$  ratios were established in a previous work [21].

The fully automated measuring sequence between the isotopes allows to measure precise isotopic ratios, even if the output of the source is changing. The results for the calibration samples and sediment samples are listed in table 2 and 3 respectively. In the latter, measured W isotopic ratios are in agreement with natural values within a precision of  $\sim 5\%$ . No indication of live  $^{182}\text{Hf}$  is observed at the present W levels in the samples and the corresponding limits are discussed below.

### 3 Present limit for $^{182}\text{Hf}$ deposition from ISM and discussion

Following the approach of Paul et al. [17] for  $^{244}\text{Pu}$  a present limit for  $^{182}\text{Hf}$  deposition can be derived. Assuming the sediment is homogeneous in  $^{182}\text{Hf}$

Table 3

Results of isotope ratio measurements in samples from deep-sea sediment

Sample	Layer (cm)	Dry weight (g)	$\frac{^{182}\text{Hf}+^{182}\text{W}}{^{180}\text{Hf}}$ ( $\times 10^{-5}$ )	$\frac{^{182}\text{Hf}+^{182}\text{W}}{^{183}\text{W}}$	$\frac{^{182}\text{Hf}+^{182}\text{W}}{^{184}\text{W}}$	$\frac{^{183}\text{W}}{^{184}\text{W}}$
Bulk3	surface	25	$6.3 \pm 1.4$	1.89	0.90	0.48
TRIP7P3	3 – 11	9.2	$3.2 \pm 0.7$	1.88	0.96	0.51
TRIP7P12	12 – 19	10.0	$10 \pm 3$	1.84	0.85	0.46
TRIP7P19	19 – 37	25.5	$41 \pm 6$	1.96	0.92	0.47
mean of all sediments:				1.90	0.91	0.48
nominal value:				1.839	0.864	0.467
deviation from nom. value:				2.3%	5.0%	2.7%

and using the lowest measured ratio  $\frac{^{182}\text{Hf}+^{182}\text{W}}{^{180}\text{Hf}} = 3.2 \times 10^{-5}$ , we can correct for the  $^{182}\text{W}$  contribution and obtain a limit of  $^{182}\text{Hf}/^{180}\text{Hf} < 1 \times 10^{-6}$  or  $< 1 \times 10^{10}$   $^{182}\text{Hf}$  atoms (g sed) $^{-1}$ , taking into account the Hf content of the sediment (8 ppm). The sections used from the core from 3 to 37 cm, cover  $\sim 3.4 \times 10^5$  years if a typical accumulation rate of 1 mm/kyr is assumed; the dry weight of these sections is 44.7 g; the actual cross section of the core is  $5 \text{ cm}^2$ . From this, we calculate a limit for the average flux of  $^{182}\text{Hf}$  into the sediment of  $\Phi_{^{182}\text{Hf}} < 2 \times 10^5$   $^{182}\text{Hf}$  atoms  $\text{cm}^{-2} \text{ yr}^{-1}$ . This value is compared below with the expected flux from steady-state ISM grain accretion.

The mass flux of ISM accretion onto Earth is still uncertain. However, based on measurements onboard the Ulysses and Galileo spacecrafts [22] and the Advanced Meteor Orbit Radar (AMOR) facility in New Zealand [23], a mass flux  $\Phi_{\text{Earth}}^{\text{ISM}} > 4 \times 10^{-12}$  g – ISM  $\text{cm}^{-2} \text{ yr}^{-1}$  was estimated [17]. Further assuming that the ISM has the same Hf abundance as the solar system (104 ppb, [24]), this results in an ISM flux of Hf onto Earth of  $\Phi_{\text{Hf}} = 1500$  Hf atoms  $\text{cm}^{-2} \text{ yr}^{-1}$ . Taking the early-solar system value for  $^{182}\text{Hf}$  [6, 7, 8] as  $^{182}\text{Hf}/^{180}\text{Hf} = 1 \times 10^{-4}$ , we get for the expected flux of  $^{182}\text{Hf}$  onto Earth  $\Phi_{^{182}\text{Hf}}^{\text{ISM}} = \Phi_{\text{Hf}} \cdot \frac{^{182}\text{Hf}}{^{180}\text{Hf}} \cdot 0.351 = 0.05$   $^{182}\text{Hf}$  atoms  $\text{cm}^{-2} \text{ yr}^{-1}$ , assuming that in-falling ISM distribute globally and all of the material is deposited in the sediment.

The above estimates stress that a large improvement in sensitivity is still required. Further chemistry is necessary to enrich Hf in the sample material and to reduce the W content. A chemical separation of Hf and Zr, which would increase the Hf concentration in the separated sample is unfortunately extremely difficult because of their nearly identical ionic radii. Although  $\text{HfF}_5^-$  injection does suppress W by a large factor, residual W must be separated further at the detection stage. An experiment, performed very recently at the Koffler 14UD Pelletron tandem accelerator (Rehovot, Israel), confirmed the

level of W suppression with  $\text{HfF}_5^-$  injection but could not improve the overall separation. A first test at the ATLAS accelerator at the Argonne National Laboratory showed that Hf–W separation in a gas-filled magnet is possible at energies  $>1$  GeV. However, W contamination from the positive-ion ECR source was still prohibitive. An improved setup would be a combination of a tandem accelerator, starting with negative-ion injection, followed by post acceleration to higher energies for separation of  $^{182}\text{Hf}$  from  $^{182}\text{W}$ .

We thank D. Lal and W. Smith (Scripps Institute of Oceanography) for their help and for making available to us part of the TRIPOD 7P sediment core. This work was supported in part by Israel Science Foundation grant Nr. 43/01-1.

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