

# Improving the detection limit for $^{182}\text{Hf}$

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Available online 30 January 2007

## Abstract

A nearby supernova would deposit radionuclides on earth. The long-lived radionuclide  $^{182}\text{Hf}$  ( $t_{1/2} = 8.9$  Ma) is one of a number of candidates for an isotopic signature of such an event. Together with  $^{60}\text{Fe}$ , observation of  $^{182}\text{Hf}$  would be direct evidence for a supernova site of the r-process. The most suitable site for searching for such a signature would be a deep-sea sediment of slow deposition rate. Measurement of  $^{182}\text{Hf}$  at the anticipated level requires very effective suppression of the interfering stable isobar  $^{182}\text{W}$ . Chemical separation and the injection of  $\text{HfF}_5^-$  allow for suppression by several orders of magnitude, but more is needed for detection of  $^{182}\text{Hf}$  as a supernova isotope signature. We are currently developing AMS methods for measuring  $^{182}\text{Hf}/^{180}\text{Hf}$  isotope ratios at the required level using a 15 MV tandem accelerator. Both projectile X-ray emission and the use of a solid passive absorber with a subsequent measurement of the residual energy are being explored. The former suffers from low efficiency, but the latter looks promising.

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PACS: 07.75.+h; 26.30.+k; 29.30.Aj; 29.40.Cs

Keywords: AMS;  $^{182}\text{Hf}$ ; Supernova; Energy-loss

## 1. Introduction

Supernovae near the solar system have a number of effects on earth. Among them is the direct deposition of radionuclides from supernova ejecta and swept-up interstellar matter (ISM) [1]. The solar system is situated in a bubble of hot, low-density ISM, believed to be result of relatively recent supernovae [2]. The detection of a signature of  $^{60}\text{Fe}$  ( $t_{1/2} = 1.5$  Ma) attributed to a supernova-deposition event about 3 Ma ago [3,4], has encouraged the search for signatures of other radionuclides (for example [5–9]). Most interesting are the r-process nuclides  $^{182}\text{Hf}$  ( $t_{1/2} = 8.9$  Ma [10]) and  $^{244}\text{Pu}$  ( $t_{1/2} = 80.8$  Ma), which do not suffer from significant terrestrial background production such as uranium fission or spallation of heavy nuclei in the atmosphere.  $^{182}\text{Hf}$  has higher r-process production than  $^{244}\text{Pu}$ , but  $^{244}\text{Pu}$  may be significantly enhanced by

contribution from the swept-up ISM, as accumulation can be expected due to the long half-life. A signature of  $^{182}\text{Hf}$  would confirm the nature of the already measured signature of  $^{60}\text{Fe}$  and provide direct evidence for a supernova site of the r-process.

In this paper, the development of methods for the detection of  $^{182}\text{Hf}$  at the sensitivity required for observation of a supernova signal are described and discussed.

## 2. Expected signature

The number of  $^{182}\text{Hf}$  atoms deposited on the earth as a consequence of a nearby supernova is determined by two factors. One is the production in the supernova of  $^{182}\text{Hf}$  by the r-process. The other is the fraction of this production transported to the earth. An estimate of the production can be obtained by using r-process residuals [11] of the solar system initial abundances and the estimated average r-process output per supernova [12] of  $1 \times 10^{-4}$  solar masses. The r-process residual for mass 182 can be normalized to all other r-process residuals. Multiplied with the

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average r-process output we obtain an average  $^{182}\text{Hf}$  output per supernova of  $\sim 9 \times 10^{-8}$  solar masses. The transport to the earth depends on the distance of the supernova. For a supernova at a distance of 40 pc [4] we expect an average surface density of  $\sim 7 \times 10^5$  atoms/cm $^2$ . A more sophisticated estimate based on a supernova model and observational data [13] finds surface densities of the same magnitude.

The measured quantity is the  $^{182}\text{Hf}/^{180}\text{Hf}$  isotope ratio and this will depend on the properties of the sediment core to be employed and the selected time resolution. In a deep-sea sediment with a dry density of 3 g/cm $^3$ , a slow deposition rate of 1 mm/ka [14] and a Hf content of 10 ppm, a ratio as high as  $\sim 5 \times 10^{-13}$  would be expected in a 300 ka time window around the period of maximum deposition. Such sediments (pelagic clays) are found at depths below 4000 m where any carbonate is dissolved. For a supernova event  $\sim 3$  Ma ago, which coincides with the  $^{60}\text{Fe}$  signature reported by Knie et al. [3,4], the decay of  $^{182}\text{Hf}$  does not significantly reduce the isotope's concentration.

### 3. Isobar separation at tandem-accelerator energies

The first two stages of isobar suppression in  $^{182}\text{Hf}$  AMS are chemical separation followed by further suppression of tungsten in the ion source. Hf and W show distinctly different chemical properties, allowing for good chemical separation (references in [15]). More difficult is the separation from zirconium, because Zr and Hf are very similar chemically and indeed, commercial sources of Hf typically contain at least  $\sim 1\%$  Zr. Zirconium is of concern because  $^{91}\text{Zr}^{n+}$  ions have the same  $m/q$  as  $^{182}\text{Hf}^{2n+}$  and hence will, in principle, pass through all of the ion optical elements if an even charge state of  $^{182}\text{Hf}$  is selected. In practice, however, the difference in fractional mass defects of  $^{91}\text{Zr}$  and  $^{182}\text{Hf}$  results in separation of the two ions by the high-energy analysing magnet. In a test using analytical grade hafnium tetrafluoride ( $\text{HfF}_4$ -Sigma-Aldrich) and with the ion optics optimised for  $^{182}\text{Hf}^{12+}$ , no  $^{91}\text{Zr}^{6+}$  ions were observed in the detector.

Further suppression of tungsten is achieved in the ion source by using  $\text{HfF}_4$  as the source material and selecting the  $\text{HfF}_5^-$  ion for injection. It has been demonstrated [16] that  $^{182}\text{W}$  can be suppressed by up to four orders of magnitude relative to  $^{182}\text{Hf}$  and this excellent suppression has been confirmed here.

The typical  $^{182}\text{W}/^{180}\text{Hf}$  background ratio which can be expected from these two stages is  $1 \times 10^{-10}$  (as indicated by tungsten background levels in [16]). In view of the estimated isotope ratio, another three orders of magnitude in suppression of tungsten have to be achieved at the detection stage.

The maximum useful energy that can be attained for such heavy ions using the 14UD tandem accelerator at the Australian National University is  $\sim 200$  MeV, i.e.  $\sim 1$  MeV/nucleon. This requires a terminal voltage of 14.5 MV and selection of the 13+ charge state for which

the stripping yield is  $\sim 7\%$ . At these energies, techniques such as a gas-filled magnet or multiple energy-loss measurements in an ionization chamber, which are effective for isobar separation of lighter ions at higher energy/nucleon, are not applicable. Consequently, we have investigated the following two alternative methods of isobar separation which might be applicable for the slower heavy ions of interest here:

1. Projectile X-ray AMS (PXAMS) and
2. Differences in energy loss of Hf and W in a solid absorber as determined by measurement of the residual energy (hereinafter called the  $\Delta E$ -method).

The PXAMS results are presented in a companion paper. Briefly, the conclusions are that this technique is limited by a low efficiency of only 1.2% for detection of L X-rays, compounded by a suppression factor of only  $\sim 50$ .

For the  $\Delta E$ -method, on the other hand, the efficiency can in principle be 100% if the residual energy detector is placed immediately after the absorber foil. A solid foil is preferred to a gas cell because the ratio between energy loss and straggling has been found to be more favourable in a solid as opposed to a gas [17]. Note that Bohr straggling is not applicable at energies below the Bragg peak [18]. In the present work, thick mylar foils totalling 12.70 or 18.05  $\mu\text{m}$  were employed as absorbers. The residual energies of the ions after passing through these absorbers were measured by an ionization chamber with a 0.7  $\mu\text{m}$  thick mylar entrance window positioned 5 cm behind the absorbers. The resolution of this detector was 1.1% for 150 MeV Hf ions.

Fig. 1 shows the separation of  $^{182}\text{Hf}$  from  $^{182}\text{W}$  at a beam energy of 180 MeV and an absorber foil thickness

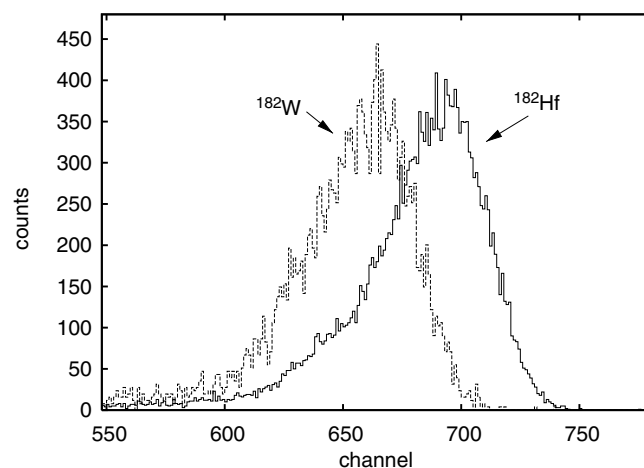


Fig. 1. Residual energy spectra showing the separation of  $^{182}\text{Hf}$  and  $^{182}\text{W}$  in an ionization chamber after passing 13.4  $\mu\text{m}$  of mylar. The  $^{182}\text{W}$  peak has been normalized to have same area as the  $^{182}\text{Hf}$ -peak. The Hf peak is from a cathode containing  $^{182}\text{Hf}$  in high amounts ( $^{182}\text{Hf}/^{180}\text{Hf} = 10^{-7}$ ). The W peak is from traces of tungsten in a cathode of commercial  $\text{HfF}_4$ . The separation of the peaks is almost twice the HWHM of the high-energy side of the peaks. Peak widths are a composite of energy-loss straggling, mylar foil surface roughness and detector resolution.

of 12.7  $\mu\text{m}$ . The residual energy of the  $^{182}\text{Hf}$  ions after traversing the foil is 28 MeV. Although it has not yet been measured, the detector resolution for ions of this energy is anticipated to be  $\sim 2.5\%$  on the basis of an observed resolution of 3% for 24 MeV plutonium ions. The  $^{182}\text{Hf}$  ions were obtained from a sample with a  $^{182}\text{Hf}/^{180}\text{Hf}$  ratio of  $\sim 5 \times 10^{-7}$  for which the count rate of  $^{182}\text{Hf}$  was a factor of  $\sim 30$  higher than  $^{182}\text{W}$ . The  $^{182}\text{W}$  ions were obtained from a sample of commercial  $\text{HfF}_4$  that contained suitably low levels of tungsten to achieve a modest count rate. Clearly the peaks are asymmetric with a pronounced tail towards lower energy. Fortunately, the discrimination between  $^{182}\text{Hf}$  and  $^{182}\text{W}$  is determined by the sharper high-energy side of the peak for which the half-width at half-maximum is (HWHM) is  $\sim 3\%$  of the deposited energy. A cut in residual energy that accepts 30% of the  $^{182}\text{Hf}$  events would reject all but 4% of the  $^{182}\text{W}$  counts. Even this 4% contribution could be estimated from the known shape of the  $^{182}\text{W}$  spectrum.

The FWHM of the strongly asymmetric peaks is 2.2 MeV. This is in reasonable agreement with simulation results (FWHM of 1.8 MeV) of SRIM 2003 [19] based on energy-loss straggling alone. If the typical surface roughness of 38 nm rms (as specified by the manufacturer [20]) of Mylar foils is also taken into account, the observed total peak widths are well accounted for. Hence, we conclude that the contribution of the intrinsic resolution (the detector resolution from charge collection and electronics alone) of the detector is negligible. This is consistent with the anticipated resolution of the detector noted above. Higher resolution detection systems such as time of flight or magnetic spectrometers may not, therefore, be necessary to employ the method.

The measurements above utilised the 12+ charge-state. For this charge state, the maximum beam energy corresponds to a terminal voltage of 14.2 MV and is limited by the analysing magnet rather than by the maximum terminal voltage of the 14UD accelerator. Higher beam energies would clearly be advantageous and in principle could be obtained by using a higher charge state than 12+, albeit with reduced stripper yields. The next two higher charge states are, however, problematic. Both 13 and 14 are divisors of 182 and hence ions with the same  $m/q$  as the  $^{182}\text{Hf}$  ions can produce unwanted backgrounds. For example, when  $^{182}\text{Hf}^{13+}$  is selected, the low-energy tail from  $^{196}\text{Pt}^{14+}$  ions constitutes a serious interference. Platinum is known for high sputter efficiency and contamination is often difficult to avoid. In addition,  $^{238}\text{U}^{17+}$  ions are observed and contribute background under the  $^{182}\text{Hf}$  peak. If  $^{182}\text{Hf}^{14+}$  ions are selected, then  $^{195}\text{Pt}^{15+}$  ions are the principal source of background.

Choice of the 15+ charge state would lead to higher energies while avoiding the  $m/q$  interferences but overall efficiency would be a factor of 20 less than for the 12+ charge state as a result of the lower stripping yield.

Using an appropriate cut in the spectrum, the detection limit can be enhanced by two orders of magnitude, using

Table 1  
Silicon nitride thickness versus isobar separation

Thickness ( $\mu\text{m}$ )	HWHM (MeV)	$\Delta E$ (MeV)	$\Delta E/\text{HWHM}$	Residual $E$ (MeV)
4	0.84	$1.53 \pm 0.02$	1.82	91
5	0.91	$1.61 \pm 0.11$	1.77	73
6	0.87	$1.70 \pm 0.13$	1.95	57
7	0.76	$1.48 \pm 0.03$	1.95	44
8	1.12	$1.73 \pm 0.03$	1.54	29

Peak positions were determined by fitting Gram-Charlier functions. The uncertainty in  $\Delta E$  largely depends on the (low) statistics for the tungsten peaks. The best result has been achieved for 6–7  $\mu\text{m}$  silicon nitride, however the surprising result for 8  $\mu\text{m}$  thickness has not yet been explained or confirmed in a repeat measurement.

this method with the foil and ion energy combination mentioned above. While this is still not sufficient to measure  $^{182}\text{Hf}$  from supernova-deposition, it is more promising than other methods.

A significant improvement can be expected from the replacement of the mylar foils by a stack of 1  $\mu\text{m}$  silicon nitride membranes. These are known to have much lower surface roughness and hence would be expected to have a narrower straggling distribution. In addition, they would allow the absorber thickness to be optimised. Recently, we implemented such a stack of silicon nitride membranes. A first test of this stack showed that these membranes are more suitable to this application than mylar foils. Only peak separation versus HWHM was determined in this test. For mylar foils the best ratio of separation versus HWHM was 1.52. For silicon nitride thicknesses between 4 and 8  $\mu\text{m}$  this ratio was found to range from 1.54 to 1.95, with the optimum at total thicknesses of 6–7  $\mu\text{m}$ . Results are summarized in Table 1.

#### 4. Measurement of test samples

Using the  $\Delta E$  method, a series of test samples containing low levels of  $^{182}\text{Hf}$  have been measured. These measurements used the original (13.4  $\mu\text{m}$ ) mylar foil setup. Peak shapes of  $^{182}\text{Hf}$  and  $^{182}\text{W}$  were determined from the spectra shown in Fig. 1. These peak shapes were then used to extract the  $^{182}\text{Hf}$  contribution from residual energy spectrum, as shown for the lowest-level sample in Fig. 2. These materials have been measured previously at the Vienna Environmental Research Accelerator (VERA), using background subtraction of  $^{182}\text{W}$  by measuring the higher mass tungsten isotopes [16]. As shown in Table 2 we confirmed the VERA results with our method. The  $^{182}\text{W}$  levels were higher ( $^{182}\text{W}/^{180}\text{Hf} \sim 10^{-9}$ ) than in the measurement at VERA ( $^{182}\text{W}/^{180}\text{Hf} \sim 10^{-10}$ ), but decreased as the measurement proceeded. For “Dilu3”, the sample with the lowest  $^{182}\text{Hf}/^{180}\text{Hf}$  ratio, the  $^{182}\text{W}$  rate was up to 15 times the  $^{182}\text{Hf}$  rate. Due to poor ion source output during this run, the number of counts is small. Typical ion source outputs of 10–20 nA were considerably lower than the usual 100–300 nA observed in earlier runs.

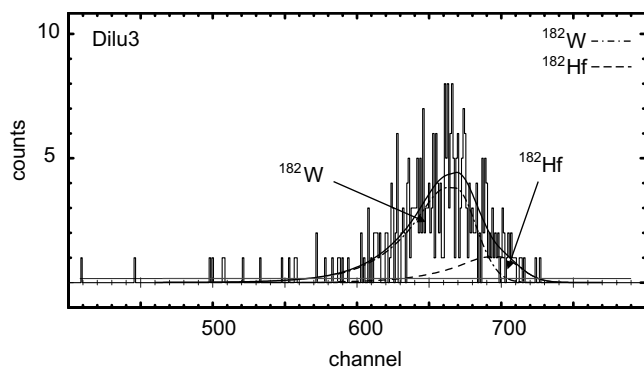


Fig. 2. Residual energy spectrum from the measurement of Dilu3, the lowest level test sample. Peak shapes and positions were established from the  $^{182}\text{Hf}$  and  $^{182}\text{W}$  spectra shown in fig. 1 and used to fit the observed line shape in order to extract the  $^{182}\text{Hf}$  contribution. This spectrum represents an acquisition time of 900 s. The number of counts is small because the beam current from the samples was low. The source output of  $\text{HfF}_5^-$  for this sample was  $\sim 7$  nA and the  $^{180}\text{Hf}$  current at the Faraday cup before the detector was only  $\sim 0.07$  pA.

Table 2

Measurement of test samples previously measured at the Vienna Environmental Research Accelerator (VERA)

Material	$^{182}\text{Hf}/^{180}\text{Hf}$ (VERA)	$^{182}\text{Hf}/^{180}\text{Hf}$ (ANU)
Dilu1	$(5.5 \pm 0.4) \cdot 10^{-7}$	$(5.1 \pm 0.5) \cdot 10^{-7}$
Dilu2	$(4.2 \pm 0.4) \cdot 10^{-10}$	$(4.2 \pm 0.5) \cdot 10^{-10}$
Dilu3	$(11 \pm 2) \cdot 10^{-11}$	$(8.8 \pm 1.7) \cdot 10^{-11}$

The results for Dilu2 and Dilu3 represent a total acquisition time per sample of 1800 s. We used a different method, but our results (ANU) agree well within the uncertainties. This is the first successful measurement of  $^{182}\text{Hf}/^{180}\text{Hf}$  involving some degree of isobar separation in the detection system.

## 5. Conclusions and outlook

In principle a detectable signature of supernova-deposited  $^{182}\text{Hf}$  can be expected in suitable sediment cores. We have shown that measurement of  $^{182}\text{Hf}$  at close to the anticipated  $^{182}\text{Hf}/\text{Hf}$  ratio is within the capability of our accelerator. In order to accomplish this, it is necessary to suppress the interfering isobar  $^{182}\text{W}$  by many orders of magnitude, which can be achieved by the combination of good chemical separation, discrimination in the ion source by choice of the  $\text{HfF}_5^-$  negative ion and separation of energetic  $^{182}\text{Hf}$  and  $^{182}\text{W}$  ions by measurement of their differences in energy loss in an absorber foil. Both better discrimination and higher efficiency are observed for this energy-loss method than for the projectile X-ray (PXAMS) described in the accompanying paper. The current gain in

detection limit is not yet sufficient for the detection of a supernova signal, but several technical improvements are now being implemented and hence a measurement of  $^{182}\text{Hf}/^{180}\text{Hf}$  at the  $10^{-13}$  level may soon be possible.

## Acknowledgements

The authors are indebted to C. Vockenhuber, P. Steier and W. Kutschera for providing the  $^{182}\text{Hf}$  test samples.

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