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Reassessment of ^{182}Hf AMS measurements at VERA

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ABSTRACT

The radioisotope ^{182}Hf ($t_{1/2}$ = 8.9 Ma) is of great interest for astrophysical applications as a chronometer for the early solar system or as possible live supernova remnant on earth. However, AMS measurements of ^{182}Hf are seriously influenced by the presence of the stable isobar ^{182}W, which cannot be separated at typical AMS energies. Previous studies revealed a possible suppression of ^{182}W against ^{182}Hf by extracting the negatively charged pentafluoride HfF_5^- from the ion source, leading to a detection limit for ^{182}Hf/^{180}Hf in the order of 10^{-11}. However, this suppression behavior is in contrast to theoretical calculations of the electron affinity and recent measurements using SIMS instruments, where the achieved suppression cannot be reproduced. The aim of our study is to determine the effects of ion source background as well as further investigate the suppression of tungsten against hafnium by extracting negatively charged fluoride ions from different sample materials. The previously reported suppression factor of about 6000 could be increased to 36000 by careful tuning of the ion source using HfF_4 as sample material. The trend of the theoretical electron affinities could be reproduced using atomic tungsten and hafnium instead of HfF_4 as sample material. This supports the assumption that the major contribution of the tungsten background is not sputtered from the target matrix but comes from somewhere else in the ion source. Measurements from the second ion source show a higher background of tungsten and a lower suppression factor, i.e. careful design of the ion source is crucial. Moving the sputter beam over the target surface extending over the wheel holding the targets revealed the highest tungsten background was detected outside the sputter target position. Further investigations are necessary to locate the origin of the tungsten background in the ion source. Possible sources are the material used for the ion source construction or contaminations in the cesium used for sputtering.

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1. Introduction

Previous ^{182}Hf accelerator mass spectrometry (AMS) measurements performed at the 3 MV tandem accelerator facility VERA (Vienna Environmental Research Accelerator) in Vienna, Austria, revealed a measurement limit of the ^{182}Hf/^{180}Hf isotopic ratio in the order of 10^{-11} [1,2]. The main interference in such measurements is the stable isobar ^{182}W, which cannot be separated from the ion of interest with particle energies achievable with a 3 MV tandem accelerator. However, previous measurements have shown that ^{182}W can be already reduced by a factor of 6000 with respect to ^{182}Hf in the cesium sputter ion source by using HfF_4 as target material and extracting HfF_5^- [1]. It has been shown that with increasing number of fluorine atoms the yield of HfF_x^- increases whereas the yield of WF_x^- decreases. This behavior is in contrast to theoretical calculations of the electron affinities of the WF_x^- ions [3]. Recent secondary ion mass spectrometry (SIMS) measurements [4] as well as measurements at the negative ion beam spectrometer GUNILLA (Göteborg University Negative Ion Laser Laboratory) [5–7] support the theoretical prediction. A recently published survey about the yield of fluoride anions also does not support the achievable suppression [8].

Recently, a new injection beamline with a second MC-SNICS (multi cathode source of negative ions by cesium sputtering) ion source (in the following called S2) was installed at VERA [9]. From the time of installation of the new ion source special care was taken in choosing the sample material used in this source. The aim was to minimize the background of unwanted contaminations in

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the source. For example, former attempts to determine ratios of stable platinum isotopes for trace element analysis using the previously only available source at VERA (in the following called S1) showed high backgrounds of platinum in natural ratios which still remained even after thorough cleaning of the source. Using S2, these measurements are now possible and the background of natural platinum is greatly reduced. Similar improvements are expected for other isotopes where stable isobar contamination was previously installed into the original source S1 in macroscopic amounts. During previous test measurements tungsten powder was used as target material in the source S1 and therefore a higher ^{182}W background level is expected if the background is mainly related to ion source contamination.

The goals of our study were to compare the suppression of ^{182}W against ^{182}Hf for the two ion sources at VERA and to determine the suppression factors for the various fluorides using both molecular HfF4 mixed with silver powder or atomic tungsten and hafnium powder mixed with PbF_2 as target material.

2. Comparison of the ion sources S1 and S2

To compare the suppression of tungsten against hafnium, measurement series using calibration samples and blank materials were performed from the two available ion sources S1 and S2.

Sample material present in form of HfF_4 powder mixed with silver powder was used as cathode material. Commercial available HfF_4 (Alfa Aesar hafnium(IV) fluoride, 99.9%) was used as blank material. As calibration samples previously prepared material [1] produced by dilution of activated hafnium from used control rods of a nuclear research reactor were used. The original material with an isotopic ratio ^{182}Hf/^{180}Hf of $(3.9 \pm 0.2) \times 10^{-6}$ was diluted 1:10000 and spiked to an isotopic ratio of 5.6×10^{-10} (material Hf_Dilu4_1) and 1:100000 to an isotopic ratio of 5.9×10^{-11} (material Hf_Dilu4_2). More details about the chemical preparation of the samples can be found in [1].

From the HfF_4 target material HfF_5^- ions were extracted from the cesium sputter ion source. After mass separation the ions were injected into the tandem accelerator where molecule break-up and stripping to positively charged ions occurred. The charge state 4+ was selected with the analyzing magnet. Stable isotope currents were measured directly after the analyzing magnet in a Faraday cup. After energy over charge state selection in an electrostatic analyzer, the rare isotope ions were detected with a time-of-flight (TOF) setup consisting of two timing detectors and a Bragg-type ionization chamber for residual energy determination [10]. In the timing detectors the particles passed diamond-like carbon (DLC) foils where they produce secondary electrons which were collected by a microchannel plate detector. The acquisition of the TOF signal together with the residual energy for each particle allowed a clear identification of the particle species.

As it is impossible to discriminate ^{182}W from ^{182}Hf in the detector, the events in the mass 182 bin have to be corrected for the tungsten contribution to get the number of ^{182}Hf events. In addition to mass 182, the stable tungsten isotopes ^{183}W, ^{184}W and ^{186}W were measured sequentially. The injector was tuned to the respective W^- and the high energy analyzer was set to the corresponding W^{4+}. Using this information the number of ^{182}W events in the mass 182 bin was calculated. Already at the tuning stage the tungsten background from the source S2 was found to be significantly higher than that of S1 by more than an order of magnitude. The W^{4+} count rate from W^- was above an acceptable limit. The count rate was reduced by injecting WF^- instead of W^- for the measurements from ion source S2 to get the necessary information for the tungsten background correction.

The results of the ^{182}Hf AMS measurements comparing the performance of ion source S1 and S2 are shown in Table 1. The measurement using source S1 is in agreement with the already established measurement limits for VERA [1,2]. However, for source S2 the high tungsten background significantly reduces the achievable precision and induces a higher blank level. This renders the source S2 basically useless for ^{182}Hf measurements until the cause of the tungsten background is identified. A careful examination of the materials used for constructing the ion source is necessary.

3. Suppression factor determination

For the determination of the suppression of WF_x against HfF_x, tungsten and hafnium powder mixed with lead (II) fluoride and silver powder as well as HfF_4 mixed with silver powder was used as cathode material. Because of the possible ion source contamination, and considering that we did not know that the "clean" source S2 has actually a higher tungsten background than S1, these tests were performed solely from source S1. In case of the tungsten molecules the isotope ^{183}W was selected, ^{180}Hf was chosen for the hafnium molecules. Depending on the ion source yield, either the ion current was measured in the offset Faraday cup after the analyzing magnet or the count rate in the detector. The resulting suppression using HfF_4 as target material is shown in Table 2. The ^{182}W suppression is defined as the relative formation probability of the various negative Hf ions divided by the relative formation probability of the various negative W ions. The tungsten suppression in the case of the pentafluorides is even a factor of six higher compared to [1]. A possible explanation is that for the results in [1] the ion source was optimized for high output which slightly increased the cesium beam spot size and therefore raised the tungsten background coming from the surrounding of the target material (see also below for the discussion on the possible contamination of the sample wheel or the target holder).

In the case of the atomic tungsten and hafnium target material the yield of the negatively charged fluorides extracted from the source behaves differently (Table 3). In the case of HfF_4 as target material, the tungsten count rate decreased with increasing number of fluorine atoms whereas in the latter case the WF_4^- and WF_5^- have a higher yield compared to the molecules with lower number of fluorine atoms. These results are in agreement with the measurements in [4] and the trend follows the theoretical prediction of the electron affinity of WF_x^-.

Our conclusion from these results is that tungsten in the HfF_4 material is not present in the form of WF_4 but as atomic impurity either in the target material or in the surrounding of the ion source. It seems that HfF_4 is sputtered as a molecule and the probability for

Table 1
^{182}Hf AMS measurements comparing the performance of the two different ion sources at VERA. The isotopic ratios measured using the ion source S1 are in agreement with the calculated ratios based on the dilution series reproducing the previous measurement limit in the order of 10^{-11}. However, using the ion source S2 the significantly higher tungsten background introduces a larger uncertainty in the ^{182}W correction leading to a lower precision and a higher blank value.

Material	Nominal ^{182}Hf/^{180}Hf	^{182}Hf/^{180}Hf (ion source S1)	^{182}Hf/^{180}Hf (ion source S2)
Hf_Dilu4_1	5.6×10^{-10}	$(5.9 \pm 0.3) \times 10^{-10}$	$(5.3 \pm 0.6) \times 10^{-10}$
Hf_Dilu4_2	5.9×10^{-11}	$(6.8 \pm 2.3) \times 10^{-11}$	$(8.3 \pm 5.3) \times 10^{-11}$
HfF4 (blank)	0	$(0.5 \pm 0.5) \times 10^{-11}$	$(2.0 \pm 2.5) \times 10^{-11}$

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Table 2
Yield of the hafnium and tungsten atomic and fluoride anions collected as $^{180}Hf^{4+}$ current after the analyzing magnet and $^{183}W^{4+}$ count rate in the detector. In the case of HfF_6^- the current was too low and the count rate in the detector is given. The target material was HfF_4 mixed with silver powder with a ratio of 1:1.

Ion species	Typical $^{180}Hf^{4+}$ current [nA]	Ion species	Typical $^{183}W^{4+}$ count rate [1/s]	^{182}W suppression
Hf^-	0.001	W^-	2500	0.00024
HfF^-	0.092	WF^-	2000	0.027
HfF_2^-	1.26	WF_2^-	150	5
HfF_3^-	7.8	WF_3^-	6	770
HfF_4^-	0.037	WF_4^-	1	22
HfF_5^-	11	WF_5^-	0.18	36000
HfF_6^-	1000 cts/s	WF_6^-	0.01	0.12

Table 3
Yield of the hafnium and tungsten atomic and fluoride anions collected as $^{180}Hf^{4+}$ or $^{183}W^{4+}$ ions after the analyzing magnet. In the case of Hf^- the current was too low and the count rate in the detector is given. The sample material was a mixture of Hf + W + PbF_2 powders with a ratio of 1:1:4.

Ion species	Typical $^{180}Hf^{4+}$ current [nA]	Ion species	Typical $^{183}W^{4+}$ current [nA]	^{182}W suppression
Hf^-	10^5 cts/s	W^-	0.025	0.008
HfF^-	0.02	WF^-	0.9	0.2
HfF_2^-	0.049	WF_2^-	0.22	0.2
HfF_3^-	0.64	WF_3^-	0.095	6.7
HfF_4^-	0.017	WF_4^-	1.1	0.015
HfF_5^-	190	WF_5^-	4.9	39
HfF_6^-	0.036	WF_6^-	0.055	0.7

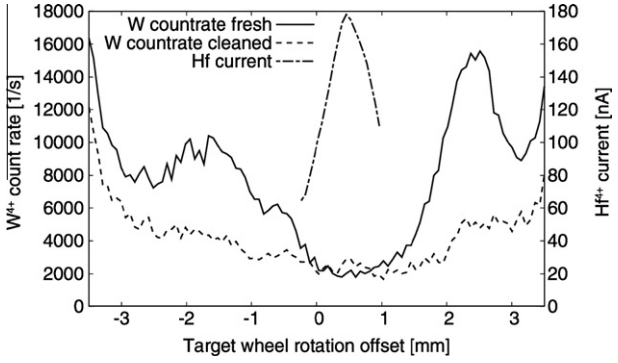

Fig. 1. Scans over the target wheel by turning the wheel. The center of the target is at position 0.521 mm. The diameter of the sample holder is about 3 mm. The left axis gives the W^{4+} counts collected in the detector injected as W^- into the tandem. On the right axis the Hf^{4+} current injected as HfF_5^- is given. The solid line shows the scan over an HfF_4 + Ag target. The dashed line shows the same target after "cleaning" it by scanning back and forth a few times. The tungsten yield from the target remains the same but the contamination surrounding the target is reduced significantly. The dash-dotted line shows the Hf^{4+} current coming from the sample material in the target holder.

the formation of HfF_5^- is enhanced compared to the probability of forming WF_5^-, where the molecule has to be composed from the sputtered tungsten atom and a sufficient number of fluorine atoms from the emission site. The formation yield of WF_5^- is therefore hindered with respect to the formation of HfF_5^- from HfF_4.

To shed light on the possible origin of the tungsten contamination, scans of the cesium beam over the target and the surrounding sample wheel surface were performed. During these scans the tungsten count rate in the detector and the hafnium current were acquired. Typical scans are shown in Fig. 1. The maximum hafnium current is observed at the center of the target (at position 0.521 mm in Fig. 1). In contrast, the tungsten count rate shows two maxima about 2 mm away from the target center. This position lies just outside of the aluminum target holder (3 mm diameter) containing the sample material. To further pin down the tungsten contamination we tested the target holder and the sample wheel material for possible tungsten impurities. Preliminary studies with SIMS give an upper limit for tungsten atomic concentration in the aluminum target holder of 2×10^{-8}. However, the results are not yet conclusive and further investigations are necessary.

4. Conclusion and outlook

For AMS measurements of ^{182}Hf at 3 MV terminal voltage a precise knowledge of the origin of the stable isobar contribution of ^{182}W is crucial, as a separation is presently only possible in the ion source. The previously published suppression factor for $^{182}W/^{182}Hf$ of 6000 [1] could be increased to 36000 by careful tuning of the ion source. On the other hand, our results have shown that the suppression of ^{182}W against ^{182}Hf cannot be related to the different electron affinities of the respective fluorides, but is consistent with a tungsten contamination coming from outside of the target matrix. Scans over the target and wheel surface have proven that the main tungsten background is not coming from the sample material itself but from surrounding background. Further investigations are necessary to locate the origin of this background and subsequently lower the detection limit of ^{182}Hf at VERA.

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