A New Half-life Measurement of ^{182}Hf - Sharpening a Tool for the Chronology of the Early Solar System

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The decay of ^{182}Hf, now extinct, into stable ^{182}W has developed into an important chronometer for the early solar system, especially for studying the formation of the Earth and the Moon. However, the only ^{182}Hf half-life measurements available were performed 40 years ago and resulted in an imprecise half-life of $(9 \pm 2) \times 10^6$ y. We redetermined the half-life by measuring the specific activity of ^{182}Hf based on two independent methods, resulting in a value of $t_{1/2}(^{182}\text{Hf}) = (8.90 \pm 0.09) \times 10^6$ y, in good agreement with the previous value, but with a 20 times smaller uncertainty. The greatly improved precision of this half-life now permits very precise intercalibration of the ^{182}Hf–^{182}W decay system with other chronometers.

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Subsequent to the formation of the solar system some 4.6 billion years ago, radionuclides with half-lives in the million-year range present at an early stage became extinct. However, these radionuclides still provide timing information through isotopic anomalies in the final stable decay product [1].

In cosmo- and geo-chronology the absolute timescale is established by long-lived radioactive isotopes. The formation of Ca-Al rich inclusions in meteorites (the oldest known solid materials of our solar system) for example has been dated at $(4567.2 \pm 0.6) \times 10^6$ y using U-Pb systematics [2]. On the other hand "fast-running" clocks based on short-lived radionuclides can provide only relative ages, but often with higher resolution, depending mainly on the half-life and its precision. The steady improvement of mass spectrometric methods utilizing these chronometers calls for improved decay constants, both for long-lived chronometers [3] and the now extinct chronometers such as ^{182}Hf–^{182}W.

With a half-life of about 9 million years ^{182}Hf decays finally into stable ^{182}W (Fig. 1), which is the basis of a powerful chronometer for dating the formation of objects of the inner solar system, first proposed by Norman and Schramm [4]. Both parent and daughter elements (Hf and W) are highly refractory and were thus not affected by high-temperature processes in the early solar system. On the other hand, Hf is lithophile whereas W is moderately siderophile, which leads to a strong fractionation of these two elements during partial melting and planet core formation. Lee and Halliday [5] and Harper and Jacobsen [6] were the first to apply this chronometer to derive constrains for the timing of accretion and terrestrial core formation. Models for the formation of the Moon by a giant impact of a Mars-sized body during a late stage of the Earth's accretion can be supported by Hf–W data [7–10]. This chronometer has also been used to study iron meterorites [e. g. 11] and eucrites [12].

However, among all the important chronometers the ^{182}Hf–^{182}W system has the largest uncertainty in the half-life, a fact which is often not taken into account in models of evolution of inner solar system objects. This does not affect chronologies established by this chronometer, but limits inter-comparison with other isotopic chronometers (e. g. U–Pb).

^{182}Hf was discovered in 1961 in Hf irradiated by an intense flux of thermal neutrons, with first estimates of the half-life of 8.5×10^6 y [14] and $(8 \pm 5) \times 10^6$ y [15]. In the same year Wing *et al.* [16] published the most detailed half-life measurement so far. Their half-life value of $(9 \pm 2) \times 10^6$ y has been used for the last 40 years and has never been remeasured.

In addition to its use as a geochronometer, ^{182}Hf plays an important role for the understanding of nucleosynthesis of heavy elements in stellar environments. ^{182}Hf is primarily an *r*-process nuclide (Fig. 1). However, the high initial solar system abundance of ^{182}Hf (^{182}Hf/^{180}Hf $\sim 1 \times 10^{-4}$ [10, 17, 18], or 1.6×10^{-4} [12], as compared to other *r*-process nuclei (e. g. ^{129}I, $t_{1/2} = 1.7 \times 10^7$ y) challenges simple nucleosynthesis models. In order to overcome the contradiction generated by explaining the abundances of ^{182}Hf and ^{129}I by a uniform production model, Qian *et al.* [19] proposed two different *r*-process sites at

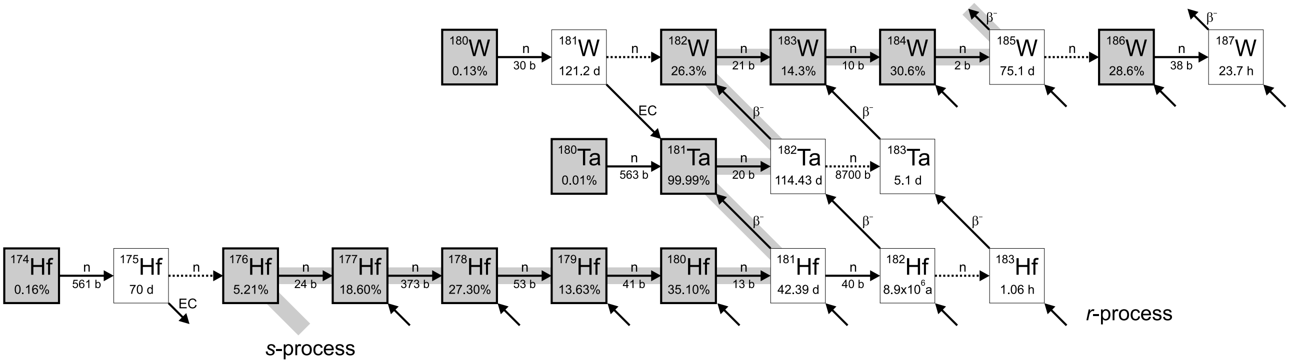

FIG. 1: Nuclear chart of the isotopes of hafnium, tantalum and tungsten. The naturally occurring stable isotopes and their relative abundances are shown in shaded squares, whereas the radioactive isotopes and their half-lives are displayed in open squares. Production paths for neutron irradiation are shown as arrows, with labels denoting neutron capture cross sections and decay modes for the radioactive isotopes. The main *s*-process follows the shaded path. The *r*-process is indicated by short arrows. The data are taken from [13].

different rates. In another model by Meyer and Clayton [20] the high abundance of ^{182}Hf is due to a production by a 'fast' *s*-process in helium and carbon burning shells of massive stars, with only the outer layers then being injected into the early solar nebula [21]. In this context, ^{182}Hf may complement other radionuclides produced by recent nucleosynthesis events (e. g. ^{60}Fe, $t_{1/2}= 1.5 \times 10^6$ y, identified in deep-sea Fe-Mn crusts [22]), which may help the understanding of heavy element nucleosynthesis [23]. An accurate knowledge of the half-life of the nuclei involved in these models is crucial for an interpretation based on measured data.

In the present work the half-life of ^{182}Hf was remeasured by absolute determinations of the activity and the amount of atoms of the radionuclide. We used Hf materials which has been produced by intense neutron irradiation by Helmer and Reich more than 30 years ago, initially for the study of the high-spin isomer of $^{178\mathrm{m}2}$Hf [24] and then has also been used for the study of the decay of ^{182}Hf to ^{182}Ta ($t_{1/2}$=114 d) [25]. According to these studies the most abundant γ-ray line (270.4 keV) following the β^- decay has an absolute intensity of (80±5)%. This value has been recently improved to $P_{270} = (79.0 \pm 0.6)\%$ by measuring the 270.4 keV line relative to the 222.1 keV line of the decay of ^{182}Ta, which is in perfect equilibrium after more than 30 years [26]. For the half-life measurement two different source materials were used, here called Helmer 1 with 260 Bq of ^{182}Hf and Helmer 2 with 300 Bq ^{182}Hf. In order not to mask potential systematic bias, the two materials were measured independently. Helmer 1 was used for combining neutron activation and isotopic ratio measurements with activity measurements, and Helmer 2 for combining isotope dilution with activity measurements.

The chemical composition of the Helmer 1 material was unknown, and it contained a large fraction of residual filter material. To avoid extensive chemical preparation, neutron activation analysis was adopted to meet the requirements for a precise half-life measurement: By irradiating the material with neutrons, ^{181}Hf ($t_{1/2}$= 42.39 d) is produced by neutron capture on ^{180}Hf. By measuring the activity of the induced ^{181}Hf (with a γ-count rate r_{181}, see equation 3) the quantity of ^{180}Hf in the sample can be determined. The induced ^{181}Hf activity in the ^{182}Hf sample material is compared to an induced ^{181}Hf activity (r_{181_St}) of a high purity standard material with a known amount of ^{180}Hf atoms (n_{180_St}). Together with an isotopic ratio of $R(^{182}\mathrm{Hf}/^{180}\mathrm{Hf})$ measured by mass spectrometry and the activity of ^{182}Hf, A_{182} (determined in the same measurement as ^{181}Hf, see equation 2), the half-life can be determined without having to resort to gravimetric methods:

$$\lambda_{182} = \frac{A_{182}}{r_{181}} \frac{r_{181\_\mathrm{St}}}{n_{180\_\mathrm{St}}} R \left(\frac{^{180}\mathrm{Hf}}{^{182}\mathrm{Hf}} \right). \tag{1}$$

The isotopic composition of the ^{182}Hf-samples was measured at the Department of Earth Sciences, ETH Zentrum, Zürich/Switzerland, using Nu 1700, a new high-resolution multiple-collector inductively coupled mass spectrometer (MC-ICPMS) built by Nu Instruments Ltd. A small aliquot of Helmer 1 material was dissolved and purified by an anion column procedure adopted from [27] in order to minimize W isobaric interference on mass 182. The latter step was necessary because under the intense neutron flux required for ^{182}Hf production, ^{182}W and ^{183}W can build up from the decay products of ^{181}Hf [28]. This could cause the isotopic composition of W to diverge from natural composition and thus compromise correction for ^{182}W contribution. Six sample runs (40 simultaneous readings at masses 172-174-175-176-177-178-179-180-182-184 at 10 seconds integration time each) were performed at low mass resolution ($\sim$ 700, 10% valley convention), since previous checks in high-resolution mode indicated absence of isobaric interference at mass 182 other than ^{182}W. These runs (approx. 100 ppb Hf in 0.01M HF–0.01M HNO_3 solution) were bracketed by identical runs of a standard solution prepared from high-purity Hf (Ames Laboratory, Iowa State University), in order to correct for instrumental mass bias by linear interpolation versus time. Corrections were performed for isobaric interference from W, Lu and ArXe on the Hf masses, whereas ^{181}Ta contributions were negligible. The average correction for W on mass 182 using $^{182}\mathrm{W}/^{184}\mathrm{W} = 0.8647$ amounted to 0.09%. $R(^{182}\mathrm{Hf}/^{180}\mathrm{Hf})$ was determined as $(3.1367 \pm 0.0015) \times 10^{-3}$. The uncertainty is dominated by an estimated systematic error component of 0.04% related to potential bias in mass fractionation correction, with the reproducibility of the 6 runs (0.017%, 1σ) contributing only a minor increment. A preliminary experiment carried out on a solution aliquot of Helmer 1, which had not been purified by ion-exchange and thus had ~ 16 times more W, gave $R(^{182}\mathrm{Hf}/^{180}\mathrm{Hf}) = 3.1358$, identical within error limits to the above value. This indicates that the accuracy of the result is not affected by uncertainties in W isotopic composition.

The neutron activation was performed at the TRIGA MkII reactor at the Atominstitut der Österreichischen Universitäten in Vienna/Austria, at a moderate neutron flux of 10^8 cm^{-2} s^{-1} for one to five hours to obtain approximately equal count rates for ^{182}Hf and ^{181}Hf. The samples were placed beside the core of the reactor. A homogeneous neutron flux for all samples (standard materials and ^{182}Hf containing samples) was guaranteed by irradiating all samples together in a rotating sample holder.

The activity of the samples was measured by the most abundant γ-rays in the respective decay (270 keV for ^{182}Hf and 482 keV for ^{181}Hf). A coaxial high-purity germanium (HPGe) detector (Canberra GC4518) with 50% relative photo-peak efficiency and a resolution of 1.8 keV for 1.33 MeV of ^{60}Co was used. For an independent check measurements were also performed at a 30% HPGe detector and different detector electronics.

The activity of ^{182}Hf, A_{182}, is calculated from the background-corrected peak area of the 270 keV line, N_{270}, the measuring time, Δt, the correction factor for the self-attenuation of the 270 keV γ-rays in the sample material, K_{270}, the efficiency for 270 keV γ-rays, ϵ_{270}, and P_{270}:

$$A_{182} = \frac{N_{270}}{\Delta t} \frac{K_{270}}{P_{270}\epsilon_{270}}. \tag{2}$$

The γ-efficiency of the detectors was determined using mixed radionuclide γ-ray reference standard solutions from Amersham, Buckinghamshire/UK, containing nine radionuclides with γ-rays in the energy range from 88 keV to 1836 keV. We used solutions QCY46, and later fresh QCY44, which has higher activity especially for the important 279.2 keV line of ^{203}Hg ($t_{1/2}$= 46.62 d). The results of all calibration samples agree within the measuring uncertainty. The combined uncertainty of the efficiency for the three calibration samples from QCY44 is around ±1%.

The count rate of the induced ^{181}Hf (r_{181} and r_{181_St}) was calculated from the background corrected area of the full energy peak of the 482 keV γ-ray line, N_{482}. Corrections were applied for the decay between the end of the irradiation and the start of the measurement, ΔT, the decay during the γ-activity measurement, Δt, the self-attenuation of the 482 keV γ-rays in the sample material, K_{482}, and for the attenuation of the neutrons in the sample material during the irradiation, K_n:

$$r_{181} = N_{482}\lambda_{181} \frac{e^{\lambda_{181}\Delta T}}{1 - e^{-\lambda_{181}\Delta t}} K_{482} K_\mathrm{n}. \tag{3}$$

All samples were filled into the same type of 0.5 ml polyethylene tubes to avoid bias from neutron irradiation and γ-activity measurements. The difference between the samples of different mass (which implies different volume and therefore different irradiation and measurement geometry) were corrected with a factor for the attenuation of the neutrons in the sample material during the irradiation and for the self-attenuation of the respective γ-rays in the sample material [29]. A boron content of (0.0128 ± 0.0003) g/g, which critically influences the neutron attenuation corrections, was determined for Helmer 1 by comparing the induced ^{181}Hf activity of two neutron activations before and after chemical purification.

Altogether four neutron irradiation runs were performed, one test irradiation and three irradiations on Helmer 1 materials, the last of them performed on a purified sample. The activity was measured in several independent measurement series with partly different geometry. Correlated uncertainties were taken into account when combining uncertainties. The half-life value obtained for Helmer 1 is $(9.034 \pm 0.251) \times 10^6$ y. The main contribution to the uncertainty is the correction for the neutron attenuation during the irradiation (±2.4%).

A completely different approach was chosen for the measurements on sample Helmer 2. The number of ^{182}Hf-atoms, n_{182}, was determined very precisely by isotope dilution, whereas the activity of ^{182}Hf was measured in two different measurement series, using a HPGe detector with 15 % relative photo-peak efficiency and the 50% HPGe detector described above. The decay constant is calculated from

$$\lambda_{182} = \frac{N_{270}}{\Delta t} \frac{1}{\epsilon_{270} P_{270} n_{182}}. \tag{4}$$

77 mg of the solid sample Helmer 2 were dissolved in 2 ml of hot concentrated (25M) HF, diluted by addition of H_2O and centrifuged in order to obtain a clear solution devoid of particles (e. g., filter debris). The material was then passed through an ion-exchange column for removal of W as described for Helmer 1. The Hf fraction was redissolved in 63 ml 1M HF/0.5M HCl. From this

TABLE I: The half-life of ^{182}Hf from the two measurements.

Material	Method	Half-life ($\times 10^6$ y)	Uncorrelated error ($\times 10^6$ y)	Total error ($\times 10^6$ y)
Helmer 1	neutron activation + activity measurement	9.034	±0.241	±0.251
Helmer 2	isotope dilution + activity measurement	8.896	±0.057	±0.089
	weighted mean	8.904	±0.056	±0.088

primary sample solution, four gravimetrically controlled aliquots of different Hf content were taken for the activity measurement, three equal aliquots for isotope dilution (ID), and an aliquot for isotopic composition (IC) measurements. The IC aliquot was again purified by ion-exchange in order to further deplete the sample in residual W, and the isotopic composition was measured as described above. The solution volumes of the three ID aliquots were expanded to ~ 80 ml by addition of 1M HF/0.5M HCl, and a gravimetrically controlled aliquot of each primary aliquot was then spiked with a tracer solution 94.76% enriched in ^{178}Hf, in a proportion to optimize the ^{179}Hf/^{178}Hf ratio of the spike-sample mixtures for error propagation. Six to eight runs each were performed on the three sample-tracer mixtures, using ^{179}Hf/^{178}Hf and ^{180}Hf/^{179}Hf determined by the IC experiments to quantify Hf contents and simultaneously correct for instrumental mass bias. The four aliquots for the activity measurement were quantitatively transferred into PFA vials, evaporated and redissolved in 3 ml of 1M HF/0.5M HCl mixed solution in order to establish identical geometries for activity measurements. We estimate an overall error of 0.1% for the contents of ^{182}Hf, mainly related to uncertainties in weighing solution aliquots. Due to the low density of Hf in the solution (4 to 15 mg Hf in 3 ml) the correction for attenuation of 270 keV γ-rays is less than $< 0.1\%$ and thus here negligible.

In addition, three γ-calibration samples of different intensity were prepared from the QCY44 standard solution for γ-efficiency calibration in the same type of PFA vials and filled up with carrier solution to 3 ml to establish identical geometries for all experiments. All measured efficiencies from the three calibration samples agree very well, resulting in a combined uncertainty of $< \pm 1\%$.

For the two activity measurement setups the half-life is calculated independently and than combined, again considering correlated uncertainties, to a half-life of $(8.896 \pm 0.089) \times 10^6$ y. The uncertainty is dominated by the statistical uncertainty of the activity and efficiency measurements (±0.64%) and P_{270}, which is ±0.8%, whereas the uncertainty of n_{182} of ±0.1% is negligible.

The results of the two independent measurements agree rather well, and are very close to the previously reported value associated with a quoted large uncertainty of ±22% [16]. Our final, refined half-life value, calculated as the weighted mean for samples Helmer 1 and 2, is $t_{1/2}$=$(8.90 \pm 0.09) \times 10^6$ y (Tab. I).

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