New half-life measurement of ^{182}Hf: Improved chronometer for the early solar system

C. Vockenhuber,[1,*] F. Oberli,[2] M. Bichler,[3] I. Ahmad,[4] G. Quitté,[2] M. Meier,[2] A. N. Halliday,[2] D.-C. Lee,[5] W. Kutschera,[1] P. Steier,[1] R. J. Gehrke,[6] and R. G. Helmer[6]

[1] *Vienna Environmental Research Accelerator (VERA), Institut für Isotopenforschung und Kernphysik, Universität Wien, Währinger Strasse 17, A-1090 Wien, Austria*
[2] *Department of Earth Sciences, ETH-Zentrum, Sonneggstrasse 5, CH-8092 Zürich, Switzerland*
[3] *Atominstitut der Österreichischen Universitäten, Stadionallee 2, A-1020 Wien, Austria*
[4] *Physics Division, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439, USA*
[5] *Institute of Earth Sciences, Academia Sinica, Nankang, Taipei 115, Taiwan, ROC*
[6] *Idaho National Engineering and Environmental Laboratory, 2525 Fremont Ave., Idaho Falls, ID 83415, USA*
(Dated: August 16, 2004)

The decay of ^{182}Hf, now extinct, into stable ^{182}W has developed into an important chronometer for studying early solar system processes such as the accretion and differentiation of planetesimals and the formation of the Earth and the Moon. 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 isotopic system with other chronometers.

PACS numbers: 21.10.Tg, 27.70.+q, 91.35.Nm, 96.35.Cp

Radionuclides with half-lives in the million years range that were initially present 4.6 billion years ago, became extinct soon after the solar system formed. However, they still provide timing information through isotopic anomalies in their final stable decay products [1].

In cosmo- and geochronology absolute timescales are 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 among other parameters 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 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 nebula. 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 constraints 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 eucrites [11], martian [12] and iron [13] meterorites.

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 in particular limits inter-comparison with other isotopic chronometers (e.g. U–Pb) [15]. First estimates of the half-life of 8.5×10^6 y [16] and $(8 \pm 5) \times 10^6$ y [17] were made directly in connection with its discovery in 1961. The half-life value of $(9 \pm 2) \times 10^6$ y published in the same year by Wing *et al.* [18] has been used for the last 40 years and has never been remeasured.

In addition to its use as a chronometer, ^{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 ratio $^{182}\text{Hf}/^{180}\text{Hf} \sim 1 \times 10^{-4}$ [10, 19, 20], or 1.6×10^{-4} [11], as compared to other r-process nuclei (e.g. ^{129}I, $t_{1/2}$= 1.7×10^7 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.* [21] proposed the existence of two distinct r-process sites characterized by different rates. According to another model by Meyer and Clayton [22] ^{182}Hf is mainly produced by a 'fast' s-process in helium and carbon burning shells of massive stars [23]. An accurate knowledge of the half-life of the nuclei involved in these models is crucial for an interpretation based on measured data.

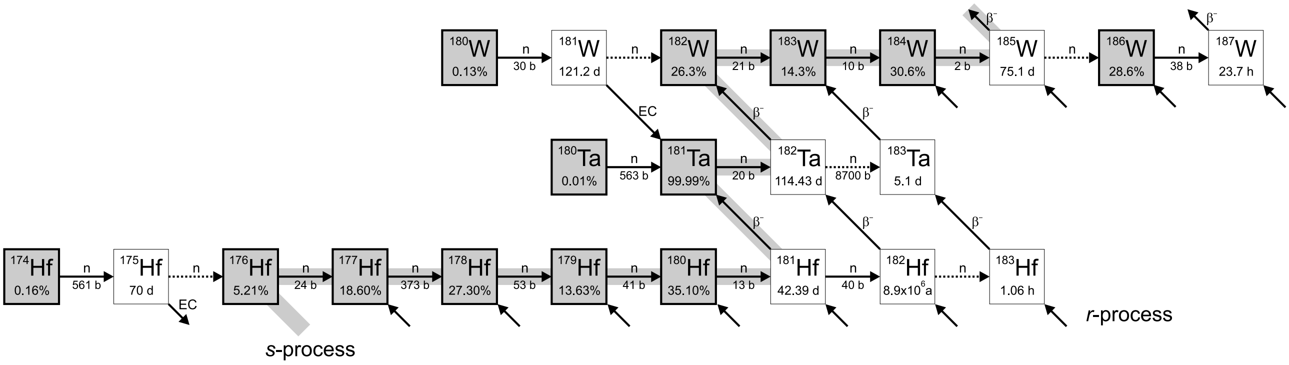

FIG. 1: Nuclear chart of the isotopes of Hf, Ta and W. Stable isotopes and their relative abundances are shown in shaded squares, whereas the radioactive isotopes and their half-lives are displayed in open squares. Production paths for neutron irradiation are shown as arrows, with labels denoting neutron capture cross sections and decay modes for the radioactive isotopes (data are taken from [14]). The main *s*-process follows the shaded path. The *r*-process is indicated by short arrows.

In the present work the half-life of ^{182}Hf was remeasured by joint determination of the activity and the number of atoms of the radionuclide. We used Hf materials which were irradiated with an intense neutron flux 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 later 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 0.80 ± 0.05. In the framework of this half-life measurement this value has been improved to $P_{270} = 0.790 \pm 0.006$ [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. Neutron irradiation of the sample leads to production of ^{181}Hf ($t_{1/2}$ = 42.39 d) by neutron capture on ^{180}Hf. From the measured activity of the induced ^{181}Hf (γ-count rate r_{181}) the quantity of ^{180}Hf in the sample can be determined by comparison with the induced ^{181}Hf activity (r_{181_St}) of a high purity standard material with a known amount of ^{180}Hf atoms (n_{180_St}). In combination with the 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), the half-life is calculated from:

$$t_{1/2} = \ln 2 \frac{r_{181}}{A_{182}} \frac{n_{180\_\mathrm{St}}}{r_{181\_\mathrm{St}}} R\left(\frac{^{182}\mathrm{Hf}}{^{180}\mathrm{Hf}}\right). \qquad (1)$$

The Hf isotopic composition of the Helmer samples is strongly anomalous (Tab. I). It was measured at the Department of Earth Sciences, ETH Zentrum, Zurich/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 material Helmer 1 was dissolved and purified by an anion column procedure adopted from [28] 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 [29]. 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. Mass 182 was corrected for isobaric interference from ^{182}W, whereas contributions to mass 180 from ^{180}W and ^{180}Ta 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 quoted uncertainty is dominated by an estimated systematic error component of 0.04% related to potential bias in mass fractionation correction, the reproducibility of the 6 runs (0.017%, 1σ) contributing only a minor increment.

The neutron activation was performed at the TRIGA Mark II reactor at the Atominstitut der Österreichischen Universitäten in Vienna/Austria, at a moderate neutron

TABLE I: Hf isotopic composition of Helmer 1 and 2 materials, measured at the Department of Earth Sciences, ETH Zentrum, Zurich/Switzerland using Nu 1700 MC-ICPMS. The natural composition is shown for comparison (data are taken from [14]).

Material	Atomic abundance (%)						
	^{174}Hf	^{176}Hf	^{177}Hf	^{178}Hf	^{179}Hf	^{180}Hf	^{182}Hf
Helmer 1	≈ 0.0058	4.791	0.605	29.06	25.77	39.64	0.124
Helmer 2	≈ 0.00014	4.377	0.149	17.15	31.30	46.91	0.112
natural	0.16	5.21	18.60	27.30	13.63	35.10	

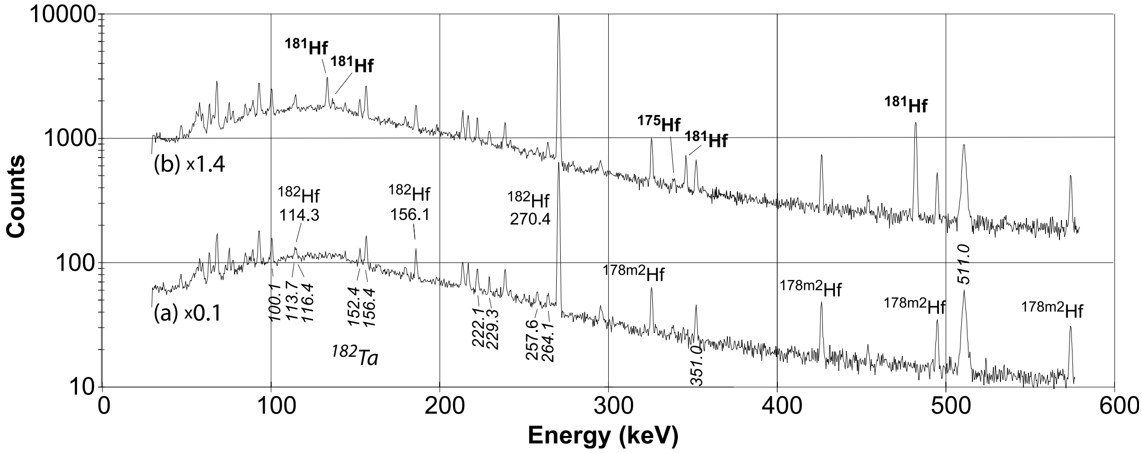

FIG. 2: γ-ray spectrum of a 20 mg sample of material Helmer 1 measured before (a) and after (b) neutron irradiation. Relevant γ-ray lines present in the original sample (^{182}Hf, ^{178m2}Hf, ^{182}Ta) and induced by the irradiation (^{181}Hf, ^{175}Hf) are indicated.

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. A homogeneous neutron flux for all samples (^{182}Hf and standard samples) was achieved by filling all samples into the same type of 0.5 ml polyethylene tubes and irradiation all together in a rotating sample holder.

The activity of the samples was measured by the most abundant γ-rays (270 keV for ^{182}Hf and 482 keV for ^{181}Hf, Fig. 2) using a high-purity germanium (HPGe) detector with 50% relative photopeak efficiency. For an independent check measurements were also performed with a 30% HPGe detector. The γ-efficiency of the detectors was determined using samples prepared from mixed radionuclide γ-ray reference standard solutions from Amersham, Buckinghamshire/UK, first QCY46 (resulting in an uncertainty of ±4.8%) and later fresh QCY44, which had higher activity especially for the important 279.2 keV line of ^{203}Hg ($t_{1/2}$ = 46.62 d) and thus provided an uncertainty of around ±1%. Corrections for the activity were applied for differences in sample geometry resulting from variation of sample mass, which influences 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. Details about the activity calculation are given in [27].

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 (see Tab. I in [27]). The half-life value obtained on Helmer 1 is $(9.034 \pm 0.251) \times 10^6$ y (Tab. II). 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, A_{182} was measured in two different measurement series, using a HPGe detector with 15 % relative photopeak efficiency and the 50% HPGe detector described above. The half-life is calculated from

$$t_{1/2} = \ln 2 \frac{n_{182}}{A_{182}}. \quad (2)$$

77 mg of the solid sample were dissolved in 2 ml of hot concentrated (25M) HF, diluted with 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 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

TABLE II: The half-life of ^{182}Hf from the two measurements. All uncertainties are 1σ uncertainties.

Material	Method	Half-life ($\times 10^6$ y)	Uncorrelated uncertainty ($\times 10^6$ y)	Total uncertainty ($\times 10^6$ 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

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 were performed on each of 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 ^{182}Hf concentrations calculated from the three ID experiments cover a narrow range of $(3.1193 - 3.1206) \times 10^{-9}$ moles/g. The four aliquots for the activity measurement were quantitatively transferred into PFA teflon 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 uncertainty of 0.1% for the contents of ^{182}Hf, mainly related to uncertainties in weighing solution aliquots. Due to the low concentration of Hf in the solution (4 to 15 mg Hf in 3 ml) the correction for attenuation of 270 keV γ-rays is $< 0.1\%$ and thus here negligible.

From the QCY44 solution three γ-calibration samples of different intensity were prepared in the same type of PFA vials and filled with carrier solution to 3 ml to match the geometry of the samples. The measured efficiencies from the three calibration samples are in excellent agreement, resulting in a combined uncertainty of $< \pm 1\%$.

Two measurement series on Helmer 2 (see Tab. II in [27]) resulted in a half-life of $(8.896 \pm 0.089) \times 10^6$ y (Tab. II). The uncertainty is dominated by the statistical uncertainty of the activity and efficiency measurements ($\pm 0.64\%$) and P_{270}, which is $\pm 0.8\%$, whereas the uncertainty of n_{182} of $\pm 0.1\%$ 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 $\pm 22\%$ [18]. Our final half-life value, calculated as the weighted mean of both sample materials, is $t_{1/2}(^{182}\text{Hf}) = (8.90 \pm 0.09) \times 10^6$ y (Tab. II). We believe that the improved half-life now provides a precise and accurate clock for the early solar system history.

This work was supported in part by the U.S. Department of Energy, Office of Nuclear Physics, under contract No. W-31-109-ENG-38.

* Electronic address: christof.vockenhuber@univie.ac.at

[1] T. Lee *et al.*, Astrophys. J. **211**, L107 (1977).
[2] Y. Amelin *et al.*, Science **297**, 1678 (2002).
[3] F. Begemann *et al.*, Geochim. Cosmochim. Acta **65**, 111 (2001).
[4] E.B. Norman and D.N. Schramm, Nature **304**, 515 (1983).
[5] D.-C. Lee and A. N. Halliday, Nature **378**, 771 (1995).
[6] C. L. Harper and S. B. Jacobsen, Geochim. Cosmochim. Acta **60**, 1131 (1996).
[7] D.-C. Lee *et al.*, Science **278**, 1098 (1997).
[8] A. N. Halliday, Earth Planet. Sci. Lett. **176**, 17 (2000).
[9] D.-C. Lee *et al.*, Earth Planet. Sci. Lett. **198**, 267 (2002).
[10] T. Kleine *et al.*, Nature **418**, 952 (2002).
[11] G. Quitté and J. L. Birck, Earth Planet. Sci. Lett. **219**, 201 (2004).
[12] D.-C. Lee and A. N. Halliday, Nature **388**, 854 (1996).
[13] M. F. Horan *et al.*, Geochim. Cosmochim. Acta **62**, 545 (1998).
[14] R. B. Firestone and V. S. Shirley, *Table of Isotopes* (Wiley Interscience, 1996).
[15] A. N. Halliday, *In: Treatise on Geochemistry* **Vol. 1**, (Elsevier, 2003).
[16] W. H. Hutchin and M. Lindner, J. Inorg. Nucl. Chem. **16**, 369 (1961).
[17] R. A. Naumann and M. C. Michel, J. Inorg. Nucl. Chem. **17**, 189 (1961).
[18] J. Wing *et al.*, Phys. Rev. **123**, 1354 (1961).
[19] Q. Yin *et al.*, Nature **418**, 494 (2002).
[20] R. Schoenberg *et al.*, Geochim. Cosmochim. Acta **66**, 3151 (2002).
[21] Y.-Z. Qian, Progr. Part. Nucl. Phys. **50**, 153 (2003).
[22] B. S. Meyer and D. D. Clayton, Space Sci. Rev. **92**, 133 (2000).
[23] B. S. Meyer *et al.*, LPSC **XXXIV**, A2074 (2003).
[24] R. G. Helmer and C. W. Reich, Nucl. Phys. **A211**, 1 (1973).
[25] R. G. Helmer *et al.*, Nucl. Phys. **A168**, 449 (1971).
[26] I. Ahmad *et al.*, Submitted to Phys. Rev. C (2004).
[27] *See EPAPS document no. ? for supplementary information. A direct link to this document may be found in the online article's html reference section. The document may also be reached via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. see the EPAPS homepage for more information.*
[28] G. Quitté *et al.*, Geostandards Newsletter **26**, 149 (2002).
[29] C. Vockenhuber *et al.*, Nucl. Insr. Meth. B **223-224**, 823 (2004).