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Initial $^{182}\text{Hf}/^{180}\text{Hf}$ in meteoritic zirconsT. R. IRELAND^{1,2,*} and M. BUKOVANSKÁ³¹Research School of Earth Sciences, The Australian National University, Canberra ACT 0200, Australia²Department of Geological and Environmental Sciences, Stanford University, Stanford, CA 94305-2115, USA³National Museum, Prague, Czech Republic

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Abstract—Zircons from the Simmern H5 chondrite and Pomozdino eucrite have been analyzed for their Hf-W isotope systematics. Zircons have high intrinsic Hf contents and coupled with low W, make them ideal Hf-W chronometers. However, measurements of $(^{182}\text{Hf}/^{180}\text{Hf})_0$ are far from straightforward with low signals of radiogenic ^{182}W and difficulties in calibrating Hf/W ratios. Zircons were analyzed from the Simmern chondrite, and the Pomozdino eucrite. The Simmern zircon has an ultrarefractory-enriched trace element pattern, a feature commonly associated with refractory inclusions. Analyses of Simmern zircon show variable Hf/W that is likely due to surface contamination. Simmern chondrite zircon yields a $(^{182}\text{Hf}/^{180}\text{Hf})_0$ of $7.2 (\pm 4.5) \times 10^{-5}$. Pomozdino eucrite zircon analyses show very high Hf/W values indicating $(^{182}\text{Hf}/^{180}\text{Hf})_0$ of $1.7 (\pm 1.1) \times 10^{-5}$. The Simmern value is in good agreement with the initial value of the solar system indicated from Hf-W systematics of chondrites. The Pomozdino value is lower than expected if eucrites formed within several million years of refractory inclusions as suggested from Al-Mg systematics of eucrites. *Copyright © 2003 Elsevier Ltd*

1. INTRODUCTION

The ^{182}Hf - ^{182}W decay scheme has a number of attributes that make it a highly useful chronometer for early solar system processes. Both Hf and W are refractory and thus are not susceptible to perturbations caused by high-temperature processing in the early solar system. The ^{182}Hf half-life of 9 million years is close to the possible lifetime of the solar nebula allowing good analytical age resolution to be obtained. Hf and W have quite different geochemical affinities, Hf is lithophile while W is predominantly siderophile, and hence Hf-W systematics can be used for constraining the timing of planetary core formation. This latter aspect has attracted great interest in cosmochemistry. The first W isotope measurements of iron meteorites indicated a deficit in ^{182}W and this was inferred to be related to fractionation of low Hf/W metal away from high Hf/W silicate before ^{182}Hf decayed (Harper et al., 1991). However, it was the work of Lee and Halliday (1995, 1996) that demonstrated the utility of Hf-W isotopic systematics for early solar system chronometry.

Lee and Halliday (1995) first used Hf-W chronometry to infer that core formation could not have occurred until approximately 60 Ma after accretion of Earth. This paradigm was based on W-isotope measurements that indicated the compositions of chondritic and terrestrial tungsten were the same. This could only occur if tungsten was not separated from ^{182}Hf , i.e., core-mantle separation, before decay of essentially all ^{182}Hf (approximately 5–6 half lives in this case). Lee and Halliday (1995) also inferred an initial $^{182}\text{Hf}/^{180}\text{Hf}$ of 2×10^{-4} based on W isotopic measurements, including the compositions of iron

meteorites, and the modeling of bulk Hf and W abundances for Earth and chondrites. It was subsequently supported by an internal isochron of the Forest Vale chondrite (Lee and Halliday, 2000). Recently, new measurements indicate that the chondritic W isotopic composition is some 2 ϵ u lower than terrestrial (Kleine et al., 2002; Schoenberg et al., 2002; Yin et al., 2002). These workers also infer shorter times for core formation after accretion, and a lower initial $^{182}\text{Hf}/^{180}\text{Hf}$ for the solar system of around 1.0 to 1.2×10^{-4} .

We have attempted to determine the initial $^{182}\text{Hf}/^{180}\text{Hf}$ from an alternative approach using Hf-W isotope measurements of meteoritic zircons (Ireland, 1991; Ireland et al., 2000). Zircon offers a high Hf concentration (ca. 1–2 wt%) and low W levels and so high Hf/W ratios can be obtained. Zircon is a resilient mineral in geological processes and is resistant to disturbance of isotopic systems, most notably U-Pb. Zircons have been found as uncommon trace phases in meteorites, particularly eucrites, and although they are typically quite small ($\leq 10 \mu\text{m}$), they are quite suitable for analysis by ion microprobe (Ireland and Wlotzka, 1992). In our first attempt to measure the ^{182}Hf abundance in meteoritic zircons (Ireland, 1991), unresolvable isobaric interferences and scattering required the use of energy filtering to suppress unwanted signals. Energy filtering also greatly suppresses the signal as a whole and so no conclusive determination of the ^{182}Hf abundance could be made. The initial work of Ireland (1991) suggested that the maximum $^{182}\text{Hf}/^{180}\text{Hf}$ was less than 5×10^{-5} , lower than the ratio used by Lee and Halliday (1995), although consistent with the models of Harper and Jacobsen (1996).

Recently we reported a new attempt at determining the Hf-W isotopic systematics of meteoritic zircons. This work was based on the added resolution capabilities of the SHRIMP RG ion microprobe that allows very high sensitivity measurements of W isotopes free of isobaric interferences.

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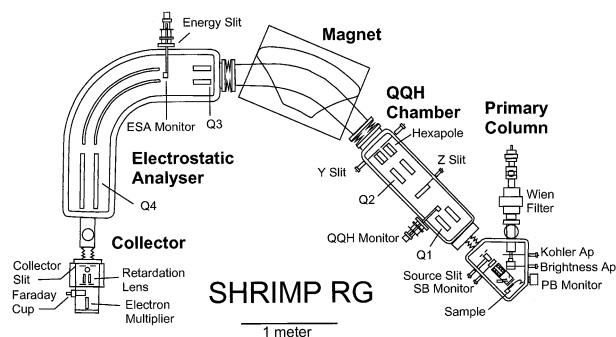


Fig. 1. Schematic diagram of the SHRIMP RG (reverse geometry). The reverse geometry indicates the reversal in order of the magnetic and electrostatic sectors with a resultant increase in mass resolution over the forward geometry SHRIMP II ion microprobes.

2. ANALYTICAL TECHNIQUES

2.2. SHRIMP RG

Hf and W isotopic measurements have been carried out on the SHRIMP RG ion microprobes of The Australian National University and Stanford University (Fig. 1). The SHRIMP RG uses the same primary column and source chamber as the SHRIMP II models but the mass analyzer is based on a design of Matsuda (1990) for minimization of third-order aberrations and is reverse geometry (magnet precedes the electrostatic analyzer). This design offers higher mass resolution (approximately four times) than the forward geometry SHRIMP II design (also used for SHRIMP I) for similar transmission. For the SHRIMP RG design, the dispersion is $3.0 \times 10^6 \mu\text{m}$ and the magnification is 0.32 (compared to $0.75 \times 10^6 \mu\text{m}$ dispersion and 0.44 magnification for SHRIMP II).

For the Hf-W and U-Pb isotopic measurements of meteoritic zircons, the SHRIMP primary beam was focused to $10 \mu\text{m}$ diameter with primary beam current of c. 2 nA. For measurements of the terrestrial standards, a $30 \mu\text{m}$ spot with primary current of c. 8 nA was used. A source slit of $200 \mu\text{m}$ with $200 \mu\text{m}$ collector slit was used to obtain mass resolution of 11000 ($M/\Delta M$, 1% valley), and $100 \mu\text{m}$ source slit and $100 \mu\text{m}$ collector slit were used to obtain mass resolution of 20,000. A divergence-limiting aperture at the entrance to the magnet was used to trim the beam to reduce aberrations at high mass resolution. The energy slit was withdrawn and secondary ions are not selected from an energy range at the energy crossover at the entrance to the electrostatic analyzer.

2.3. Hf-W Measurements

The measurement of W isotopic composition and Hf/W ratio in meteoritic zircon is problematical because of possible isobaric interferences, and the difficulties associated with calibrating the measured Hf/W ratios. Ireland (1991) used combined energy filtering and mass resolution of ca. 5000 to eliminate potential isobaric interferences. This method resulted in low sensitivity for the W isotopes. For the Hf-W measurements presented here, SHRIMP RG was operated at a mass resolution of approximately 11000. At this level, the simple REE oxide species were well resolved from the W isotopes (Fig. 2). In addition, the lack of additional interferences can be further verified by a mass spectrum at mass resolution of 22000 that shows the absence of significant species between $^{166}\text{ErO}^+$ and ^{182}W . Transmission at mass resolution of 22000 was approximately 10% of maximum transmission at 6000.

While the $^{166}\text{ErO}^+$ peak is well resolved, tailing of this peak could still produce significant contributions to the $^{182}\text{W}^+$ peak at the high Hf⁺/W⁺ ratios inherent in zircon. A systematic contribution such as this could mimic enhancement of ^{182}W as expected from ^{182}Hf decay. Analytically, we have addressed this issue in three ways. First, we have carried out mass scans with long counting times to establish the tailing contribution to ^{182}W . Second, we measured a background contribution

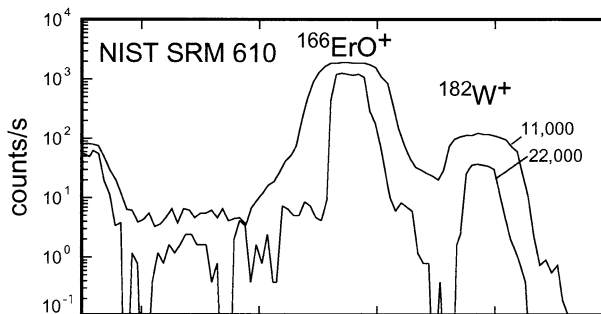


Fig. 2. Mass spectra of mass 182 from NIST SRM 610. The glass contains approximately $445 \mu\text{g/g}$ W. The predominant interference at mass 182 is $^{166}\text{ErO}^+$ (requires c. 9000 R for separation). Analysis of $^{182}\text{W}^+$ was carried out at ca. 11000 R to avoid any tailing from ErO^+ . A further scan at 22000 R indicates no additional isobaric interferences.

to ^{182}W during the analyses. Third, we measured the W isotopic composition of terrestrial zircons to verify the absence of ErO^+ tailing contributions.

A detailed scan of mass 182 (Fig. 3) shows a superimposed tailing estimate for $^{166}\text{ErO}^+$ based on the peak shape measured for $^{180}\text{Hf}^{16}\text{O}^+$. Both mass scans are taken with 10-s counting times at each magnetic-field step. The mass-182 spectrum is shown with a baseline of 0.01 c/s; a single count registers at 0.1 c/s. The mass-196 scan is scaled to the mass-180 peak and shifted so that the peaks overlap. In this way, the contribution from scattering can be estimated at the lower intensity ErO^+ peak. For the Mud Tank zircon shown in Fig. 3, the scattered contribution is approximately 0.004 c/s, which equates to an abundance sensitivity of 7×10^{-5} at the 23.3 mamu mass offset.

During analysis, a background position at 10 mamu above the $^{182}\text{W}^+$ peak position was monitored and this contribution was removed from all W^+ peaks. The ratio $^{166}\text{Er}/^{168}\text{Er}$ is very close to unity as is the $^{182}\text{W}/^{184}\text{W}$ and so the background correction for both counting system and tailing contributions is appropriate. In addition, the closeness of values of the $^{166}\text{Er}/^{168}\text{Er}$ and $^{182}\text{W}/^{184}\text{W}$ ratios means any residual not accounted for in terms of $^{166}\text{ErO}^+$ and $^{168}\text{ErO}^+$ tailing will not produce an anomalous $^{182}\text{W}/^{184}\text{W}$.

The accuracy of the $^{182}\text{W}/^{184}\text{W}$ is verified in the measurements of

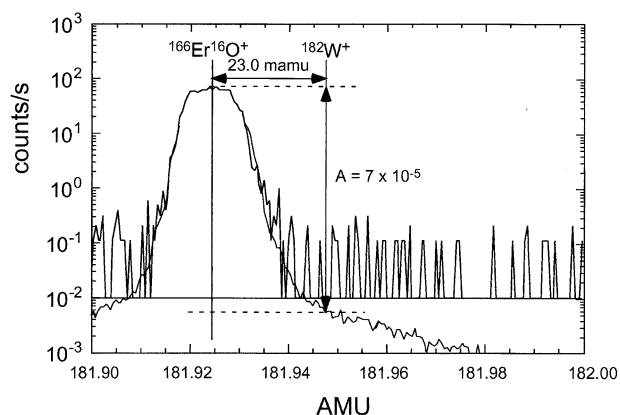


Fig. 3. High-resolution scan of mass 182 from a zircon from the Mud Tank carbonatite. The $^{166}\text{ErO}^+$ falls to 7×10^{-5} of the $^{166}\text{ErO}^+$ intensity for the mass position of $^{182}\text{W}^+$ (mass offset of 0.023 mamu). The shape of the tail is estimated by aligning the high intensity $^{180}\text{HfO}^+$ peak with the $^{166}\text{ErO}^+$ peak. The resulting tail contribution (4×10^{-3} c/s) is close to the measurement background. Any residual tailing interference will not produce a significant increase in $^{182}\text{W}/^{184}\text{W}$ attributable to $^{182}\text{Hf}^+$ because of the similarity of the value for $^{166}\text{Er}/^{168}\text{Er}$.

Table 1. Runtable for zircon Hf-W analysis.

Peak	Trim Mass ^a	Offset ^b	Time ^c	Delay ^d	Q2 bits ^e	AutoC ^f	Time ^g	
1	180Hf	179.98224	0.00000	5.0	3.0	1742	YES	1.0
2	182W	181.98698	0.02300	10.0	1.0	1740	YES	1.0
3	183W	182.99519	0.00000	10.0	1.0	1739	NO	
4	184W	183.99946	0.00000	10.0	1.0	1739	NO	
5	186W	186.00832	0.00000	10.0	1.0	1738	NO	
6	188O _s	187.99100	0.00000	5.0	1.0	1735	NO	
7	HfO	195.99570	0.00000	2.0	1.0	1730	YES	1.0
8	WO	199.98576	0.00000	2.0	1.0	1720	NO	

^a Trim Mass is based on actual field request to center peak.

^b Peak centering is carried out at specified trim mass (^{166}ErO) before adding offset.

^c Acquisition time.

^d Settling time.

^e Automatic adjustment of focus to allow for mass dependent focal shift.

^f Autocentering ON or OFF.

^g Total acquisition time for scan of mass to be centered.

terrestrial zircons with varying Hf concentrations. In all terrestrial zircons analyzed, the W concentration is close to detection limits, and so the inferred Hf/W ratio is limited only by the number of counts collected from the W peaks. Hf-W isotopic compositions were measured with the mass stations listed in Table 1. All W isotope species were measured to monitor possible interference contributions. Both Hf and W oxide species are produced at a higher level than the atomic species in NIST glass and zircon ($\text{MO}^+/\text{M}^+ \approx 3$), but the presence of $^{180}\text{Hf}^{18}\text{O}^+$, most particularly in zircon) excludes the possibility of measuring $^{182}\text{W}^{16}\text{O}^+$ (mass resolution of 104000 required) to determine W isotopic compositions. Mass 188 (^{188}Os) was measured for correction for ^{184}Os in the NIST SRM 610 glass; the correction is <2%. The mass-188 peak is dominated by $^{94}\text{Zr}_2^+$ in zircon analysis and as such, the data cannot be used.

The low abundance W-isotope peaks could not be centered during analysis; their mass positions were maintained relative to the adjacent $^{166}\text{ErO}^+$ peak. That is, $^{166}\text{ErO}^+$ was centered and a mass offset of 0.0233 amu applied to measure $^{182}\text{W}^+$. The $^{183}\text{W}^+$, $^{184}\text{W}^+$, and $^{186}\text{W}^+$ peaks then trailed the mass deviations recorded from centering the $^{166}\text{ErO}^+$ peak. Most analytical runs showed variations of less than 0.002 amu during the run (10 cycles through Table 1). To verify this routine, analyses of NIST SRM 610 glass were carried out (Table 2). Five analyses show reproducibility within analytical errors. Data from the mean of the 5 analyses are shown in Fig. 4 with ratios referenced to the W isotopic ratios of Yin et al. (2002). Mass fractionation based on the $^{182}\text{W}/^{186}\text{W}$ ratio is approximately $-11\%/amu$. No correction is applied to the W isotope ratios measured from zircon; the effect is small compared to the errors of the analyses.

The ion microprobe analyses involve extremely small amounts of material. An analysis of NIST SRM 610 constitutes ca. 1 ng of material, 460 $\mu\text{g}/\text{g}$ of which is W, equating to 0.46 pg. Of this ^{182}W comprises 33.6%, or 0.15 pg. At the elevated Hf/W ratios of the meteoritic zircons, the amount of ^{182}W is even lower. For instance, the

Pomozdino $^{180}\text{Hf}/^{184}\text{W}$ value of 30000, with 1 wt % Hf, this would constitute a concentration of 0.33 $\mu\text{g}/\text{g}$, and therefore 0.33 fg of total ^{182}W in an analysis. Sensitivity for ^{184}W in the NIST SRM 610 is 160 cps/140 ppm $^{184}\text{W}/4.7$ nA or 0.24 cps/ppm/nA. For comparison under these conditions, Pb sensitivity is approximately 2 cps/ppm/nA.

The determination of $(^{182}\text{Hf}/^{180}\text{Hf})_0$ requires a calibration between the Hf/W ratio in zircon and the measured $^{180}\text{HfO}^+ / ^{184}\text{W}^+$. While the WO^+ species cannot be used for W isotopic measurements, the higher abundance of $^{184}\text{WO}^+$ (and HfO^+) is useful in better constraining the Hf/W ratio in zircon where the W levels are very low. The measured $^{180}\text{Hf}^{16}\text{O}^+ / ^{184}\text{W}^{16}\text{O}^+$ must be calibrated through relative sensitivity factors to yield the true $^{180}\text{Hf}/^{184}\text{W}$ in the sample.

For SIMS calibration, standards of similar mineralogical (structural) and chemical composition should be used to avoid matrix effects. The calibration of Hf/W is problematical because we have found no terrestrial zircon with sufficient W for this purpose. Even zircons from W-rich granites contained W at less than ca. ng/g levels. The lack of W in zircon is somewhat surprising given the similarity in ionic size between Zr^{4+} , Hf^{4+} and W^{4+} . It is likely therefore, that W is largely present as W^{6+} in the terrestrial environment and will not enter the zircon structure. However, even under reducing conditions, the meteoritic zircons have very low W levels. As such, we do not have satisfactory standards for a direct normalization of the Hf/W relative sensitivity factor in zircon and a more indirect method must be adopted.

Table 2. W isotopic analyses of NIST SRM 610.^a

	$\delta^{182}\text{W}/^{183}\text{W}$	$\delta^{184}\text{W}/^{183}\text{W}$	$\delta^{186}\text{W}/^{183}\text{W}$
1	15 ± 16	-5 ± 11	-5 ± 12
2	7 ± 13	-2 ± 19	-20 ± 13
3	25 ± 11	-4 ± 13	-14 ± 12
4	-12 ± 16	-39 ± 11	-54 ± 19
5	16 ± 18	-44 ± 18	-31 ± 11
Mean	12 ± 13	-18 ± 12	-32 ± 12

^a W isotopic measurements taken with zircon runttable. Errors of individual analyses 1 σ ; Errors of mean 2 σ . Deviations expressed relative to terrestrial W isotopic composition of Yin et al. (2002)

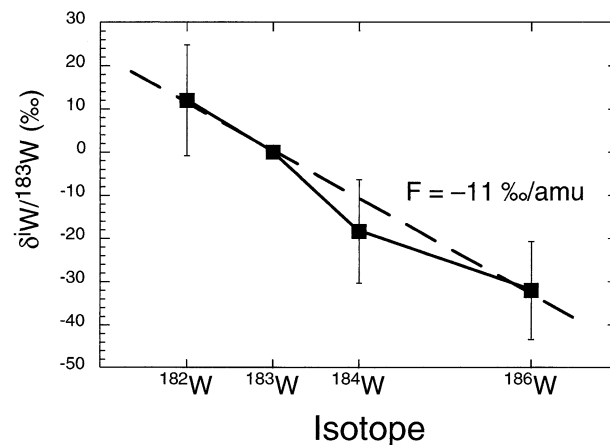


Fig. 4. W isotope ratios measured from NIST SRM 610 using the analytical protocol for zircon measurement. The W isotopic composition is fractionated, enriching the light isotopes by ca. 11‰/amu, but no other residual effects are apparent. Error bars are 2 σ .

The Hf/W elemental ratio can be normalized initially to the relative sensitivity factor (RSF) determined from NIST SRM 610 glass. The Pearce et al. (1997) preferred values of 418 $\mu\text{g/g}$ Hf and 445 $\mu\text{g/g}$ W were used ($^{180}\text{Hf}/^{184}\text{W} = 0.818$). During the course of the meteoritic zircon measurements, repeat analyses of NIST SRM 610 yield ($^{180}\text{HfO}^+ / ^{184}\text{WO}^+$) of 3.71 ± 0.07 (σ), equating to an $\text{RSF}_{(\text{Hf-W, glass})}$ of 0.220 ± 0.004 , that is, HfO^+ is more efficiently produced from the NIST glass than WO^+ .

The RSF measured from NIST glass represents the combination of chemical (Hf-W) as well as structural (glass) matrix effects. The chemical matrix effect is a response to the composition of the target and the presence or absence of different elements can have an effect on ionization yields. Iron in particular is known to have significant effects on ion yields in the same mineral matrix (e.g., Catlos et al., 2000). The structural matrix effect is a response to the mineralogical bonding in the target. For instance, the three polymorphs of TiO_2 , rutile, brookite, and anatase yield different instrumental mass fractionations for the Ti isotopes (Ireland, 1986). Thus, it must be established if zircon has a different $\text{RSF}_{\text{Hf-W}}$ than the NIST glass.

It has been found that the relative sensitivity factors for trace elements are rather insensitive to the matrix, that is, the absolute sensitivity changes, but the relative yields between trace elements remains constant (Zinner and Crozaz, 1986). This is particularly evident when a major element is used to normalize trace element concentrations (e.g., relative to Ca or Si). The pattern of RSF is very similar between matrices, but the ratio of the overall pattern to the major element is variable. In the case of REE abundance measurements, this would produce the correct REE pattern, but a systematic bias in the absolute concentrations could be present. For SHRIMP measurements of garnet and pyroxene inclusions in diamonds however, the similarity in ionization yields from glass and mineral standards was sufficiently similar to allow a common calibration (Ireland et al., 1994).

While this characteristic has been demonstrated for high-energy secondary ions (Energy Filtering Technique of Zinner and Crozaz, 1986), it also appears to hold for low energy ions, and most notably for zircon measurements on SHRIMP. While the Pb^+/U^+ ratio is calibrated against UO^+/U^+ to achieve optimal precisions of ca. 1%, the ratios of ThO^+/U^+ and $\text{Zr}_2\text{O}^+/\text{U}^+$ are used to calibrate concentrations in the SL13 standard. It has been found that these ratios are quite consistent and are generally within 10% of a long term average, which is at the same level of homogeneity as the U, Th, and Pb concentrations in the SL13 zircon. On this basis, it appears that low-energy ions on SHRIMP can behave in a similar fashion to high-energy ions with systematic behavior dominated by concentration in the target for trace elements.

On this basis, we would expect that W should behave as a trace element and the RSF for W measured from NIST glass is appropriate for a specific normalization procedure in zircon. However, the measurement of Hf is problematical because it is a major constituent of zircon and the RSF for major elements may not behave coherently with trace elements (q.v. Ca and Si normalizations for trace elements noted above). As such, an assessment must be made as to whether an elemental ratio including Hf from zircon will behave consistently with the measured ionic ratio from NIST SRM 610.

We have examined the matrix effect for Hf in zircon by measuring $^{180}\text{HfO}^+ / ^{172}\text{YbO}^+$ ratios in a series of zircons whose Hf and Yb contents have been determined independently, relative to that measured in NIST glass. The Pearce et al. (1997) preferred value for [Yb] is 462 $\mu\text{g/g}$ ($^{180}\text{Hf}/^{172}\text{Yb} = 1.31$). The fundamental assumption here is that Yb behaves as a trace element and it will behave coherently with other trace elements in zircon. The zircons used include 91500 (Wiedenbeck et al., 1995) and ANU standards SL1 and SL13 for which independent Hf and Yb concentration data are available (Hoskin, 1998). SL1 has quite variable Hf and Yb concentrations making it unsuitable for this calibration, 91500 appears the best constrained (Hf 5588 ppm, Yb 64 ppm); while SL13 has low Yb (Hf 6808 ppm, Yb 12.4 ppm). Both 91500 and SL13 give consistent results with a RSF relative to NIST of 1.30 ± 0.03 , that is Hf^+ is ionized 30% more efficiently in zircon than in NIST SRM 610.

The uncertainty on the Hf/W calibration is dominated by the variability in the standard zircons. Zircon 91500 has a cited Hf concentration of 5588 ppm $\pm 5\%$ (Wiedenbeck et al., 1995), and Yb concentration variability less than 10% so the overall contribution to the

Table 3. Hf-W systematics of terrestrial zircons.^a

	$^{180}\text{Hf}/^{184}\text{W}$	$^{182}\text{W}/^{184}\text{W}$	$(^{182}\text{Hf}/^{180}\text{Hf})_0$
SL13			
1	$9.48 \pm 3.39\text{E}+05$	1.37 ± 0.91	$5.0 \pm 9.6\text{E}-07$
2	$4.23 \pm 0.83\text{E}+05$	1.52 ± 1.09	$1.5 \pm 2.6\text{E}-06$
3	$1.20 \pm 0.39\text{E}+06$	0.38 ± 0.22	$-4.2 \pm 1.8\text{E}-07$
91500			
1	$5.20 \pm 2.35\text{E}+04$	0.94 ± 0.54	$0.1 \pm 9.6\text{E}-06$
2	$1.73 \pm 2.81\text{E}+05$	0.70 ± 0.70	$-0.1 \pm 3.7\text{E}-06$
3	$2.02 \pm 1.64\text{E}+05$	1.31 ± 1.02	$1.9 \pm 4.6\text{E}-06$
Mud Tank			
1	$5.20 \pm 6.71\text{E}+05$	1.30 ± 1.25	$0.7 \pm 2.2\text{E}-06$
2	$5.42 \pm 6.98\text{E}+05$	1.11 ± 0.94	$0.4 \pm 1.6\text{E}-06$
3	$4.98 \pm 6.10\text{E}+05$	3.14 ± 3.36	$4.1 \pm 6.2\text{E}-06$

^a Errors are $\pm 1\sigma$. ($^{182}\text{Hf}/^{180}\text{Hf})_0$ determined relative to terrestrial W isotope composition.

uncertainty is likely less than 20%. The uncertainties in the data for SL13 are probably similar. For the low W levels in the meteoritic zircons, this is not a large effect on an individual basis, although it could be significant as a systematic bias on the final ($^{182}\text{Hf}/^{180}\text{Hf})_0$. Nevertheless, if a systematic bias is present it will not affect a relative measurement between different zircons, it will only affect a comparison between different techniques, and in particular the SIMS measurement of zircons and the ICP-MS/TIMS data from meteorites.

Combining the elemental $\text{RSF}(\text{Hf}/\text{W})_{\text{NIST610}}$ and the matrix $\text{RSF}(\text{Hf}/\text{Yb})_{\text{ZIRCON}}$ gives a total RSF of 0.286 ± 0.010 (σ). That is $^{180}\text{Hf}/^{184}\text{W} = 0.286 \times (^{180}\text{HfO}^+ / \text{WO}^+)$. To better constrain the effects of Hf-W calibration, it will be necessary to obtain a W-bearing zircon that can be analyzed independently (e.g., ICP-MS). At this stage, no zircon has been found with any significant W concentration. The calibration presented above therefore represents a best endeavor at this stage.

Hf-W systematics are evaluated as XY-error regressions using IsoPlot version 3.0 (Ludwig, 1999). The inclusion or exclusion of a terrestrial ratio makes little difference to the determination of slope ($^{182}\text{Hf}/^{180}\text{Hf})_0$ and so has been omitted to allow an estimation of the intercept ($^{182}\text{W}/^{184}\text{W})_0$. No correlation coefficient is used because Hf/W and W isotopic measurements are essentially two independent measurements, the former based on $^{180}\text{HfO}^+ / ^{184}\text{WO}^+$, the latter based on $^{182}\text{W}^+ / ^{184}\text{W}^+$. The results reported here differ from those reported in Ireland et al. (2000) because data assessment in that work was based on a model-dependent approach to determine the probable composition of the radiogenic end member. To provide consistency with the isochrons determined from TIMS and ICP-MS, only the IsoPlot results are reported here.

Analysis of terrestrial zircons SL13, 91500, and a zircon from the Mud Tank carbonatite yielded extremely low W isotope count rates and effective Hf/W ratios of up to 10^6 (Table 3). The W isotope composition is normal within analytical uncertainty for all zircons indicating any residual isobaric interferences are not significantly affecting the measured W isotopic ratio. The measured Hf^+/W^+ abundance ratios are higher in the terrestrial zircons than in the meteoritic zircons largely because of the higher Hf count rates that were attainable on the larger zircons. These zircons provide an estimate of the background and resolution of the technique. From IsoPlot regressions with the NIST SRM 610 analyses for terrestrial, the effective ($^{182}\text{Hf}/^{180}\text{Hf})_0$ ratios are $-0.4 (\pm 0.4) \times 10^{-6}$ for SL13, $0.3 (\pm 6.1) \times 10^{-6}$ for 91500, and $0.8 (\pm 3.3) \times 10^{-6}$ for Mud Tank zircon (errors are 2σ). These data indicate that unresolved isobaric interferences or tailing corrections do not induce aberrant isotope ratios, and that resolution in ($^{182}\text{Hf}/^{180}\text{Hf})_0$ of the order of 10^{-6} is possible under appropriate circumstances on SHRIMP RG.

2.4. U-Pb Measurement

The Pomozdino zircon was analyzed for U-Pb systematics following standard SHRIMP techniques (cf. Ireland and Wlotzka, 1992). The Pb/U and U, Th, and Pb concentrations are calibrated relative to the

ANU standard SL13. The SL13 standard was in the alternate mount in the source chamber and so the Pb/U ratio for the meteoritic zircon is only indicative of the age; different sample preparations, especially conductivity of the coating, can cause calibration bias. Ultimately, the Pb/U ratio is not useful for age determinations at this time and the Pb/U is mainly used for estimation of concordance. In an effort to constrain its formation age to a higher level than the zircons from the mesosiderite zircons analyzed by Ireland and Wlotzka (1992), the Pomozdino zircon was analyzed for 22 sets of ten ratios. However, the U-Pb calibration does not hold for this length of analysis and it is evident that the inferred Pb/U age of the Pomozdino zircon gets progressively older during the course of the analysis. This is an artifact of the analytical procedure and should not be regarded as indicating an intrinsic age change. No such systematic change can be discerned from the Pb isotopic composition and so the $^{207}\text{Pb}/^{206}\text{Pb}$ age is based on all 220 cycles.

3. RESULTS

Zircons from the Pomozdino eucrite and Simmern chondrite were chosen for analysis. The Pomozdino zircons were typical for eucrites occurring at the interstices of larger grains. Two of the Pomozdino zircons were over $10\ \mu\text{m}$ in diameter and one of these was targeted for combined U-Pb and Hf-W systematics. The Simmern chondrite has an unusual zircon-chromite assemblage occurring as a dumbbell shaped object approximately $500\ \mu\text{m}$ long. The zircon has elevated ultrarefractory elements and very low U concentrations (Ireland and Wlotzka, 1992). Zircon from this assemblage was analyzed previously for Hf-W by Ireland (1991); it was found to contain higher levels of W than the Vaca Muerta mesosiderite zircons.

One zircon grain from Pomozdino was analyzed. Initially, the analyses produced low Hf/W ratios due to both low $^{180}\text{Hf}^+$ count rate and high $^{184}\text{W}^+$ count rate (Table 4). The primary beam spot was repositioned by a few microns to maximize the $^{180}\text{Hf}^+$ count rate concomitantly leading to high $^{180}\text{Hf}/^{184}\text{W}$. In the Pomozdino zircons at the highest Hf/W ratios, $^{182}\text{W}/^{184}\text{W}$ is elevated relative to the terrestrial ratio. The IsoPlot regression yields a $(^{182}\text{Hf}/^{180}\text{Hf})_0$ of $1.7 (\pm 1.1) \times 10^{-5}$ (95% conf) with a $(^{182}\text{W}/^{184}\text{W})_0$ of 0.889 ± 0.011 (Fig. 5a). This grain was analyzed subsequently for U-Pb isotopic composition (Table 5). The grain has a concentration range from 32 to 48 ppm U with a mean of 37 ppm, Th from 5 to 27 ppm with a mean of 11 ppm and Th/U from 0.14 to 0.65 with a mean of 0.28. The Th concentration systematically fell during the course of analysis while the U remained stable. The common Pb correction was less than 0.2% for ^{206}Pb and less than 0.3% for ^{207}Pb . The U-Pb systematics are near concordant for the first few data sets and the mean $^{207}\text{Pb}/^{206}\text{Pb}$ age is $4560 \pm 5\ \text{Ma}$ ($2\sigma_m$) (Fig. 6). This age and uncertainty is consistent with primary formation during eucrite crystallization.

The Simmern chondrite zircon yields lower Hf^+/W^+ ratios relative to Pomozdino zircon, which is likely due to the presence of W surface contamination because the W^+ signal decays with time. Again, $^{182}\text{W}/^{184}\text{W}$ ratios are only slightly elevated above terrestrial values but at the lower ultimate Hf/W ratios these correspond to a higher initial $^{182}\text{Hf}/^{180}\text{Hf}$ of $7.2 (\pm 4.5) \times 10^{-5}$ (2σ) with an initial $^{182}\text{W}/^{184}\text{W}$ of 0.887 ± 0.042 (Fig. 5b).

Both Pomozdino and Simmern zircons show $(^{182}\text{W}/^{184}\text{W})_0$ values that are marginally higher than the inferred solar system initial (cf. Yin et al., 2002), but they are consistent with the fractionated W isotopic composition measured from NIST 610

Table 4. Hf-W systematics of meteoritic zircons.^a

	$^{180}\text{Hf}/^{184}\text{W}$	$^{182}\text{W}/^{184}\text{W}$	$(^{182}\text{Hf}/^{180}\text{Hf})_0$
Pomozdino			
1	$6.24\text{E}+02 \pm 9.89\text{E}+00$	0.891 ± 0.044	$5.0\text{E}-07 \pm 9.6\text{E}-07$
2	$1.47\text{E}+03 \pm 7.15\text{E}+01$	0.698 ± 0.100	$1.5\text{E}-06 \pm 2.6\text{E}-06$
3	$4.36\text{E}+02 \pm 1.27\text{E}+01$	0.864 ± 0.051	$-4.2\text{E}-07 \pm 1.8\text{E}-07$
4	$2.06\text{E}+04 \pm 1.84\text{E}+03$	2.245 ± 0.650	$3.4\text{E}-06 \pm 7.1\text{E}-05$
5	$2.05\text{E}+02 \pm 2.94\text{E}+03$	1.341 ± 0.363	$-1.3\text{E}-04 \pm 6.8\text{E}-05$
6	$2.56\text{E}+04 \pm 2.73\text{E}+03$	1.573 ± 0.359	$-5.7\text{E}-05 \pm 1.2\text{E}-04$
7	$2.67\text{E}+04 \pm 3.71\text{E}+03$	1.726 ± 0.561	$6.6\text{E}-05 \pm 3.2\text{E}-05$
8	$2.95\text{E}+04 \pm 2.84\text{E}+03$	1.286 ± 0.240	$2.2\text{E}-05 \pm 1.8\text{E}-05$
9	$3.13\text{E}+04 \pm 3.96\text{E}+03$	1.035 ± 0.281	$2.7\text{E}-05 \pm 1.4\text{E}-05$
Simmern			
1	$1.68\text{E}+02 \pm 5.71\text{E}+00$	0.927 ± 0.069	$2.3\text{E}-04 \pm 4.1\text{E}-04$
2	$3.97\text{E}+02 \pm 8.17\text{E}+00$	0.895 ± 0.026	$1.6\text{E}-05 \pm 6.5\text{E}-05$
3	$7.65\text{E}+02 \pm 3.10\text{E}+01$	0.961 ± 0.046	$9.5\text{E}-05 \pm 6.0\text{E}-05$
4	$6.61\text{E}+02 \pm 2.40\text{E}+01$	0.993 ± 0.053	$1.6\text{E}-04 \pm 8.0\text{E}-05$
5	$5.60\text{E}+02 \pm 1.81\text{E}+01$	0.932 ± 0.040	$7.8\text{E}-05 \pm 7.2\text{E}-05$
6	$1.37\text{E}+03 \pm 4.34\text{E}+01$	1.042 ± 0.141	$1.1\text{E}-04 \pm 1.0\text{E}-04$
7	$2.80\text{E}+02 \pm 7.86\text{E}+00$	0.914 ± 0.069	$9.1\text{E}-05 \pm 2.5\text{E}-04$
8	$4.57\text{E}+02 \pm 1.61\text{E}+01$	0.917 ± 0.079	$6.1\text{E}-05 \pm 1.7\text{E}-04$
9	$1.19\text{E}+03 \pm 5.85\text{E}+01$	0.860 ± 0.103	$-2.4\text{E}-05 \pm 8.6\text{E}-05$
10	$1.00\text{E}+03 \pm 5.85\text{E}+01$	1.083 ± 0.169	$1.9\text{E}-04 \pm 1.7\text{E}-04$
11	$2.25\text{E}+03 \pm 1.73\text{E}+02$	0.861 ± 0.136	$-1.2\text{E}-05 \pm 6.0\text{E}-05$
12	$9.41\text{E}+03 \pm 1.12\text{E}+03$	1.631 ± 0.446	$7.9\text{E}-05 \pm 4.7\text{E}-05$
13	$7.15\text{E}+03 \pm 5.96\text{E}+02$	1.214 ± 0.291	$4.6\text{E}-05 \pm 4.1\text{E}-05$
14	$4.42\text{E}+03 \pm 3.10\text{E}+02$	1.307 ± 0.319	$9.5\text{E}-05 \pm 7.2\text{E}-05$
15	$3.20\text{E}+03 \pm 1.73\text{E}+02$	1.201 ± 0.124	$9.8\text{E}-05 \pm 3.9\text{E}-05$
16	$4.29\text{E}+03 \pm 2.96\text{E}+02$	1.399 ± 0.335	$1.2\text{E}-04 \pm 7.8\text{E}-05$

^a Errors are $\pm 1\sigma$. $(^{182}\text{Hf}/^{180}\text{Hf})_0$ determined relative to terrestrial W isotope composition.

(Table 2). As such, no significance can be attached to these values in terms of solar system evolution.

4. DISCUSSION

The meteoritic zircons yield fossil isochrons consistent with the presence of live ^{182}Hf as expected from previous studies (op. cit.). The Simmern zircon shows a higher initial ratio than the Pomozdino zircon consistent with earlier formation assuming a uniform distribution of ^{182}Hf in the early solar system. The ratio of the apparent initial $^{182}\text{Hf}/^{180}\text{Hf}$ of the two zircon-types can be used to estimate an interval between the formation events. The initial ratio for Pomozdino ($1.7 \pm 1.1 \times 10^{-5}$) could be produced after $2.2_{-2.2}^{+3.5}$ half-lives of ^{182}Hf (20_{-20}^{+32}Myr), from the closure of the Simmern zircon ($7.2 \pm 4.5 \times 10^{-5}$).

These error bounds are large and hence time resolution is poor for these samples. In large part, this is due to the small size of the zircons as exposed at the surface to the primary ion beam, which limits the amount of material that can be analyzed. Effectively this is a limit in the signal-to-noise ratio. This limitation is demonstrated in the analyses of the terrestrial zircons that give error limits an order of magnitude better than the meteoritic zircons, largely through the larger primary beam available and hence higher $^{180}\text{Hf}^+$ count rates. The corollary is that if larger zircons can be found, there should be a substantial improvement in the time resolution from meteoritic zircons.

However, the data obtained do yield some indications relevant to Hf-W systematics of the early solar system. The Simmern-chondrite zircon has a $(^{182}\text{Hf}/^{180}\text{Hf})_0$ of $7.2 (\pm 4.5) \times 10^{-5}$ and is some 5σ below the $(^{182}\text{Hf}/^{180}\text{Hf})_0$ deduced by Lee

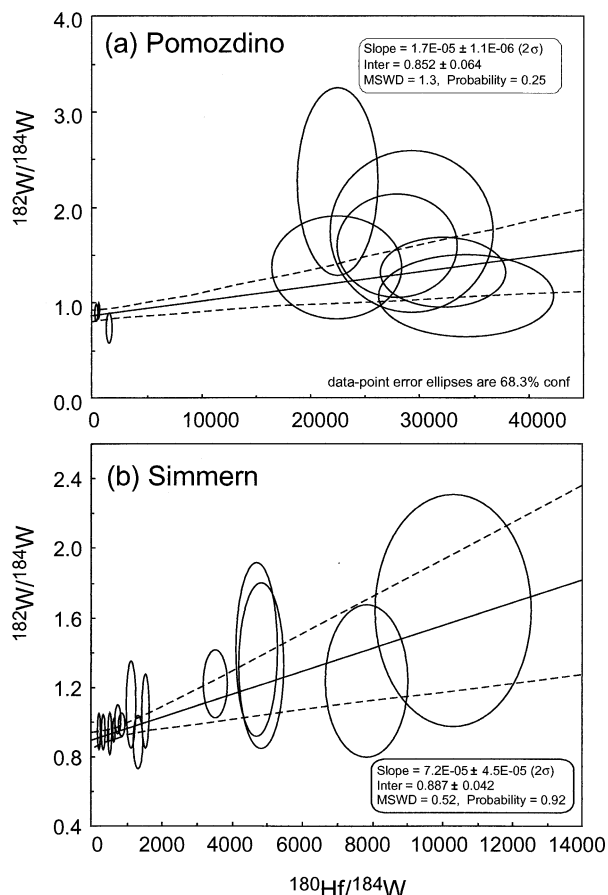


Fig. 5. Hf-W isotope measurements of meteoritic zircons. Data are assessed in the Isoplot program (Ludwig, 1999).

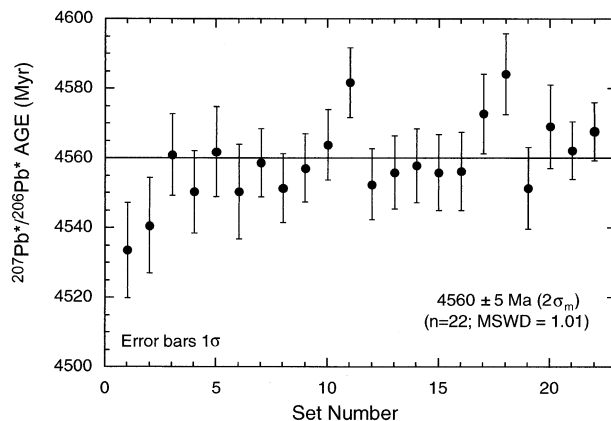


Fig. 6. ^{207}Pb - ^{206}Pb ages measured from Pomozdino eucrite. The data are consistent with a formation age of 4560 ± 5 Myr. Pb/U ages are concordant initially but systematically increase as the analyses progress and is a result of sputtering to greater depth affecting the Pb^+/U^+ rather than a change in intrinsic Pb/U.

and Halliday (2000). This value further supports the claims by Schoenberg et al. (2002), Yin et al. (2002), and Kleine et al. (2002) that the original Forest Vale isochron of Lee and Halliday (2000), indicating $(^{182}\text{Hf}/^{180}\text{Hf})_0$ of 1.9×10^{-4} , is too high.

Short-lived chronometers can only produce relative ages and the system must be tied into an absolute chronology framework. Ideally, the same samples should be used to produce the absolute chronometry as well as the short-lived chronometry. In this regard, neither chondrites nor eucrites are particularly satisfactory. Chondrites are breccias and contain a variety of materials from different provenance, particularly refractory in-

Table 5. U-Th-Pb systematics of Pomozdino zircon.^a

Set	U (ppm)	Th (ppm)	Th/U	$^{204}\text{Pb}/^{207}\text{Pb}$	$^{206}\text{Pb}^*/^{238}\text{U}$	$^{207}\text{Pb}^*/^{206}\text{Pb}^*$	f206 (%)	AGE 6/38 (Myr)	AGE 7/6 (Myr)
1	39	23	0.60	0.00004 ± 0.00004	1.13 ± 0.04	0.6107 ± 0.0057	0.03	4864 ± 127	4533 ± 13
2	41	26	0.65	0.00015 ± 0.00008	1.02 ± 0.04	0.6137 ± 0.0058	0.14	4541 ± 117	4540 ± 13
3	40	23	0.59	0.00021 ± 0.00008	1.04 ± 0.03	0.6224 ± 0.0050	0.19	4584 ± 98	4561 ± 11
4	37	18	0.48	0.00015 ± 0.00007	1.05 ± 0.03	0.6178 ± 0.0050	0.14	4619 ± 98	4550 ± 11
5	35	12	0.36	0.00017 ± 0.00010	1.07 ± 0.03	0.6227 ± 0.0055	0.16	4683 ± 103	4561 ± 12
6	34	9	0.27	0.00013 ± 0.00011	1.08 ± 0.03	0.6178 ± 0.0058	0.12	4707 ± 108	4550 ± 13
7	37	16	0.44	0.00006 ± 0.00004	1.11 ± 0.03	0.6214 ± 0.0042	0.05	4825 ± 91	4558 ± 9
8	36	14	0.38	0.00000 ± 0.00003	1.14 ± 0.03	0.6183 ± 0.0042	0.00	4904 ± 94	4551 ± 9
9	35	11	0.31	0.00001 ± 0.00004	1.16 ± 0.03	0.6207 ± 0.0042	0.00	4951 ± 95	4557 ± 9
10	34	8	0.25	0.00017 ± 0.00007	1.22 ± 0.03	0.6236 ± 0.0044	0.15	5143 ± 102	4564 ± 10
11	33	6	0.21	0.00001 ± 0.00004	1.25 ± 0.04	0.6314 ± 0.0043	0.01	5236 ± 104	4581 ± 9
12	33	6	0.19	0.00012 ± 0.00006	1.28 ± 0.04	0.6187 ± 0.0043	0.11	5324 ± 108	4552 ± 10
13	32	5	0.17	0.00014 ± 0.00006	1.32 ± 0.04	0.6202 ± 0.0045	0.13	5422 ± 113	4556 ± 10
14	33	5	0.16	0.00004 ± 0.00003	1.40 ± 0.05	0.6210 ± 0.0045	0.04	5645 ± 122	4557 ± 10
15	33	5	0.15	0.00010 ± 0.00006	1.43 ± 0.05	0.6202 ± 0.0046	0.09	5721 ± 129	4556 ± 10
16	34	5	0.14	0.00012 ± 0.00007	1.48 ± 0.05	0.6203 ± 0.0048	0.11	5859 ± 135	4556 ± 11
17	35	5	0.15	0.00013 ± 0.00007	1.51 ± 0.05	0.6274 ± 0.0049	0.12	5920 ± 140	4572 ± 11
18	35	5	0.15	0.00013 ± 0.00007	1.54 ± 0.06	0.6324 ± 0.0050	0.12	6006 ± 144	4584 ± 11
19	37	5	0.15	0.00005 ± 0.00004	1.54 ± 0.06	0.6183 ± 0.0050	0.05	6005 ± 151	4551 ± 11
20	40	5	0.14	0.00007 ± 0.00007	1.62 ± 0.07	0.6258 ± 0.0052	0.06	6201 ± 163	4569 ± 12
21	44	6	0.14	0.00004 ± 0.00003	1.68 ± 0.05	0.6229 ± 0.0036	0.04	6359 ± 110	4562 ± 8
22	48	6	0.14	0.00000 ± 0.00002	1.68 ± 0.05	0.6252 ± 0.0036	0.00	6353 ± 111	4567 ± 8

^a f206-percentage of common ^{206}Pb /measured ^{206}Pb $^{206}\text{Pb}^*$, $^{207}\text{Pb}^*$ -radiogenic Pb; AGE based on radiogenic Pb Errors 1σ. Systematic increase in U/Pb due to change in calibration during sputtering.

clusions (calcium, aluminum-rich inclusions, CAI) and chondrules, but also metal grains and matrix. Eucrites have proven difficult to date accurately primarily because of an extended thermal history that has disturbed many chronometers (e.g., Bogard et al., 1990).

The tie points used to calibrate absolute age to the abundance of a short-lived nuclide have an important bearing on early solar system cosmochemistry. Lee and Halliday (2000), and subsequently Kleine et al. (2002), used U-Pb phosphate ages of chondrites to establish an absolute age control and inferred $(^{182}\text{Hf}/^{180}\text{Hf})_0$ values for the earliest solar system. The Kleine et al. (2002) Ste Marguerite $(^{182}\text{Hf}/^{180}\text{Hf})_0$ value of $0.85 \pm 0.05 \times 10^{-4}$ at the phosphate age of 4561 Myr was recalculated to $1.09 \pm 0.09 \times 10^{-4}$ at 4566 Myr using the same procedure as Lee and Halliday (2000). For reference, the $(^{182}\text{Hf}/^{180}\text{Hf})_0$ of $1.87 \pm 0.16 \times 10^{-4}$ for Forest Vale by Lee and Halliday (2000) was recalculated to $2.75 \pm 0.24 \times 10^{-4}$ for the same U-Pb age constraints. On the other hand, Yin et al. (2002) determined that the Hf-W isotope composition of a CAI lay on the chondrite evolution curve and therefore the chondrite Hf-W age must be within a few million years of the CAI formation age, consistent with ^{26}Al and ^{53}Mn chronologies. In this case, no adjustment to the $(^{182}\text{Hf}/^{180}\text{Hf})_0$ was applied and they use the uncorrected $(^{182}\text{Hf}/^{180}\text{Hf})_0$ value of $1.00 \pm 0.08 \times 10^{-4}$ for the early solar system (at 4567 Myr). In this case, the two methods agree despite the different interpretative bases.

Schoenberg et al. (2002) did not directly tie their data to an absolute chronometry but estimated the $(^{182}\text{Hf}/^{180}\text{Hf})_0$ based on the lowest inferred ^{182}W deficit in iron meteorites. With the initial W isotopic composition of the solar system at $-4.5 \text{ \text{‰}}$, the $(^{182}\text{Hf}/^{180}\text{Hf})_0$ would be 1.5×10^{-5} , while it would be 1.2×10^{-5} at the lowest measured value of $^{182}\text{W}/^{183}\text{W}$ at $-3.6 \text{ \text{‰}}$.

As noted above, the Simmern zircon has an ultrarefractory-enriched REE pattern. Such patterns are most commonly found in refractory inclusions where volatility fractionations of these elements are widespread (Ireland and Fegley, 2000). Such a pattern may therefore indicate an original petrogenesis as part of the CAI formation event. It should also be noted that W can become less refractory in an oxidized state and therefore Hf/W fractionations could be produced by high-temperature fractionation.

In terms of absolute chronology, the CAI forming event has been dated at $4567 \pm 1 \text{ Myr}$ (Amelin et al., 2002), while the chondrule-forming event was likely within a few million years. The U-Pb systematics of the Simmern zircon do not allow any inferences on absolute chronology because U is present at very low concentrations (order 1 ppm), likely a response to the high-temperature fractionation. At this concentration level, only a broad scale chronology could be determined with error limits of several hundred million years (Ireland and Wlotzka, 1992).

The chondrite Hf-W systematics are dominated by metal-silicate fractionation. Metal-rich chondrites are found that show evidence of condensation through volatility-fractionated siderophile elements with indications of changing conditions within individual grains (Meibom et al., 2000; Campbell et al., 2001). It is therefore likely that the Hf-W systematics reflect nebular processing rather than any later events associated with the parent body, and therefore a timeline in accord with refractory inclusion formation or chondrule formation is appropriate. Fur-

thermore, a short interval to eucrite formation is suggested by the agreement in both Hf-W and Al-Mg isotope systematics for eucrites and for chondrites. For eucrites, Quitté et al. (2000) determined an initial $^{182}\text{Hf}/^{180}\text{Hf}$ of $7.96 \pm 0.34 \times 10^{-5}$, and Srinivasan et al. (1999) determined the $(^{26}\text{Al}/^{27}\text{Al})_0$ in Piplia Kalan eucrite to be $7.5 \pm 0.9 \times 10^{-7}$. In comparison, the Ste Marguerite chondrite has $(^{182}\text{Hf}/^{180}\text{Hf})_0$ of $8.5 \pm 0.5 \times 10^{-5}$ (Kleine et al., 2002) and the maximum inferred $(^{26}\text{Al}/^{27}\text{Al})_0$ based on plagioclase-bearing inclusions is $8.1 \pm 1.5 \times 10^{-7}$ (Zinner et al., 2002).

Strictly speaking, this does not itself equate eucrite formation to chondrite formation but rather eucrite formation to the formation of a population of inclusions in chondrites. There is no independent reason to tie the chondrite Hf-W systematics (metal/silicate fractionation) to the Al/Mg systematics in the plagioclase-bearing inclusion. However, the agreement between the Ste Marguerite chondrite and eucrite systematics indicates that these do indeed represent a specific time point in solar system evolution. In this case, the segregation of metal-silicate and the formation of the plagioclase inclusions must have occurred at close to the same time.

This event occurred 4.5 Myr after CAI formation (based on projection of $^{26}\text{Al}/^{27}\text{Al}$ of 8×10^{-7} to 5×10^{-5} as measured in CAI). Similarly if the $(^{182}\text{Hf}/^{180}\text{Hf})_0$ of 8×10^{-5} is projected back to this time, it would indicate a minimum $(^{182}\text{Hf}/^{180}\text{Hf})_0$ for the solar system of 1.2×10^{-4} . This value is very similar to the solar system initial values proposed by Schoenberg et al. (2002) based on the lowest ^{182}W deficits measured from iron meteorites. It is only marginally higher than the values suggested by Yin et al. (2002) and Kleine et al. (2002). However, it does suggest that CAI should have a $(^{182}\text{Hf}/^{180}\text{Hf})_0$ that is 50% higher than in chondrites. Yin et al. (2002) noted that the CAI they measured was on the same evolution line as chondrites, indicating the same $(^{182}\text{Hf}/^{180}\text{Hf})_0$. Such details warrant further attention.

The Pomozdino zircon data suggest a much lower $(^{182}\text{Hf}/^{180}\text{Hf})_0$ at the time of formation than that indicated by previous data from eucrites (Quitté et al., 2000; Yin et al., 2002). The $^{182}\text{Hf}/^{180}\text{Hf}$ time interval from the Simmern zircon is therefore also longer than would be expected, although the error overlap at the limits of the data would allow a penecontemporaneous origin. At this stage, the reason for this discrepancy is unclear. It is possible that this is due to late-stage thermal or shock perturbation in the meteorite (Bogard et al., 1990). However, the $^{207}\text{Pb}/^{206}\text{Pb}$ age of the zircon indicates that such an event could not have occurred after 4555 Myr (the 2σ limit of the $^{207}\text{Pb}/^{206}\text{Pb}$ age), which equates to approximately 1.3 half-lives of ^{182}Hf after CAI formation at 4567 Myr. This would suggest a lower limit for $^{182}\text{Hf}/^{180}\text{Hf}$ for the Pomozdino eucrite of ca. 4.0×10^{-5} (at 4555 Myr; based on $^{182}\text{Hf}/^{180}\text{Hf}$ ca. 1.0×10^{-4} at 4567 Myr), still significantly higher than the upper limit of the measured value of $1.7 \pm 1.1 \times 10^{-5}$. Furthermore, the inferred 12 Myr time difference would not be consistent with the $^{26}\text{Al}/^{27}\text{Al}$ of 7×10^{-7} measured in the Piplia Kalan eucrite (Srinivasan et al., 1999) that suggests a eucrite formation only 4.5 Myr after formation of CAI.

Alternatively, this situation is potentially similar to the case of mineral versus whole-rock isochrons encountered in Sr in complex metamorphic terranes on Earth. The mineral isochrons give the last age of closure, whereas the whole-rock isochron

yields the age of regional scale fractionation of Rb-Sr. This situation is also possible for the eucrite system. The zircon age could reflect the crystallization age of the Pomozdino eucrite whereas the whole-rock isochron reflects the metal-silicate fractionation of the parent body. However, this scenario is not consistent with the correlated behavior of ($^{26}\text{Al}/^{27}\text{Al}$)₀.

Reconciliation between the chondrite and eucrite zircon data presented here is therefore difficult to effect at this stage. There may still be outstanding issues with Hf-W calibration that will move the zircon chronology into line with the isotope dilution techniques. Further work is required on eucrite zircons, particularly of sufficiently large size to permit high precision Hf-W systematics to be determined. Unfortunately, the Simmern zircon appears unique and a larger sample of that inclusion is not possible.

5. CONCLUSIONS

Meteoritic zircons can be used to determine ($^{182}\text{Hf}/^{180}\text{Hf}$)₀ by ion microprobe mass spectrometry. Zircon from the Simmern chondrite reveals ($^{182}\text{Hf}/^{180}\text{Hf}$)₀ of $7.2 \pm 4.5 \times 10^{-5}$ (95% confidence limit) in agreement with the Ste Marguerite chondrite ($^{182}\text{Hf}/^{180}\text{Hf}$)₀ of $8.5 \pm 0.5 \times 10^{-5}$ of Kleine et al. (2002). Zircon from the Pomozdino eucrite indicates a ($^{182}\text{Hf}/^{180}\text{Hf}$)₀ of $1.7 \pm 1.1 \times 10^{-5}$. This value is lower than that determined from a whole-rock eucrite isochron (Quitté et al., 2000) and appears lower than is consistent with the $^{207}\text{Pb}/^{206}\text{Pb}$ age of the zircon (4560 ± 5 Myr), and the presence of ^{26}Al suggesting eucrite formation c. 4.5 Myr after formation of refractory inclusions. Further work is required to resolve these issues.

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