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New W-isotope evidence for rapid terrestrial accretion and very early core formation

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Abstract—The short-lived ^{182}Hf-^{182}W-isotope system is an ideal clock to trace core formation and accretion processes of planets. Planetary accretion and metal/silicate fractionation chronologies are calculated relative to the chondritic ^{182}Hf-^{182}W-isotope evolution. Here, we report new high-precision W-isotope data for the carbonaceous chondrite Allende that are much less radiogenic than previously reported and are in good agreement with published internal Hf-W chronometry of enstatite chondrites. If the W-isotope composition of terrestrial rocks, representing the bulk silicate Earth, is homogeneous and 2.24 ε_{182W} units more radiogenic than that of the bulk Earth, metal/silicate differentiation of the Earth occurred very early. The new W-isotope data constrain the mean time of terrestrial core formation to 34 million years after the start of solar system accretion. Early terrestrial core formation implies rapid terrestrial accretion, thus permitting formation of the Moon by giant impact while ^{182}Hf was still alive. This could explain why lunar W-isotopes are more radiogenic than the terrestrial value. *Copyright © 2002 Elsevier Science Ltd*

1. INTRODUCTION

Knowledge of the timing of terrestrial core formation is necessary to test accretion models and for better understanding of the evolution of long-lived isotope systematics in the silicate Earth (e.g., Allègre et al., 1982; Kramers and Tolstikhin, 1997; Kramers, 1998). The different geochemical behaviour of Hf and W during metal/silicate differentiation (Hf strongly partitions into silicates, while W is concentrated in the metallic core) makes the short-lived ^{182}Hf-^{182}W-isotope system (half-life of 9 Ma) a very powerful clock of core formation. Harper et al. (1991) were the first to report differences between the ^{182}W/^{183}W ratios of the iron meteorite Toluca and a terrestrial W standard, thus proving the former existence of the now extinct ^{182}Hf nuclide at the beginning of solar system accretion (~4566 Ma ago; Manhès et al., 1988). Harper and Jacobsen (1996) subsequently confirmed and refined the ^{182}W deficit in the iron meteorite Toluca compared to the terrestrial standard to an absolute value of -3.9 ± 1.0 ε_{182W} (Fig. 1A). Using an initial solar system ^{182}W/^{183}W ratio of 1.851512 (i.e., the W-isotope composition of Toluca) and an initial ^{182}Hf/^{180}Hf ratio of 2×10^{-5}, Jacobsen and Harper (1995) calculated a total ^{182}W enrichment in chondrites of only $+0.3$ ε_{182W} after complete decay of ^{182}Hf (Fig. 1A). Thus, these authors concluded that the present-day enrichment of $+3.6$ ε_{182W} of the silicate Earth relative to their estimated present-day chondritic ^{182}W/^{183}W ratio implied very early terrestrial core formation (between 2 and 15 Ma after the collapse of the solar nebula, which we here equate with the beginning of accretion in the solar system).

The first W-isotope data for chondritic meteorites were reported by Lee and Halliday (1995, 1996), who obtained a more radiogenic average W-isotope ratio for the Allende and Murchison carbonaceous chondrites than the "chondritic" esti-

mate of Jacobsen and Harper (1995) and Harper and Jacobsen (1996). In fact, Lee and Halliday (1995, 1996) found no discernible difference between terrestrial ^{182}W/^{184}W and that of carbonaceous chondrites and proposed that Earth's core formed after ^{182}Hf became extinct. Lee and Halliday (1995) estimated an absolute minimum mean age for Earth's core of 62 ± 10 Ma after initial solar system accretion. This interpretation required revision of several aspects of models describing the mode of early terrestrial differentiation:

1. Late core formation is in conflict with a single solution to both terrestrial Pb-isotope paradoxes. If the first Pb-isotope paradox (i.e., accessible terrestrial silicate reservoirs plot to the right of the meteorite isochron in common Pb-isotope space) were solved with late core formation alone, as argued by Halliday and Lee (1999), the second Pb-isotope paradox (i.e., the mismatch between measured and inferred U/Th ratios of the midocean ridge basalt mantle) still remains unexplained (Kramers and Tolstikhin, 1997).

2. Terrestrial Xe-isotope systematics require termination of efficient mantle degassing when ^{129}I was still alive. Combined Pu-I-Xe-isotope systematics are most easily explained if large-scale degassing, related to mantle melting that resulted in metal/silicate differentiation, ended within 100 Ma of the beginning of accretion (Azbel and Tolstikhin, 1993). Ozima and Podosek (1999) even argued that taking into account that ~90% of the Earth's primordial Xe is missing from the terrestrial atmosphere, the atmospheric abundances of ^{129}Xe and ^{136}Xe (from ^{129}I and ^{244}Pu decay, respectively) required formation of the Earth 50 to 70 Ma after the collapse of the solar nebula. However, a mean age for core formation of 60 Ma after the collapse of the solar nebula implies substantial (i.e., 10 to 20%) core addition beyond 100 Ma if the terrestrial core flux followed predicted model functions (e.g., Wetherill, 1986; Jacobsen and Harper, 1995).

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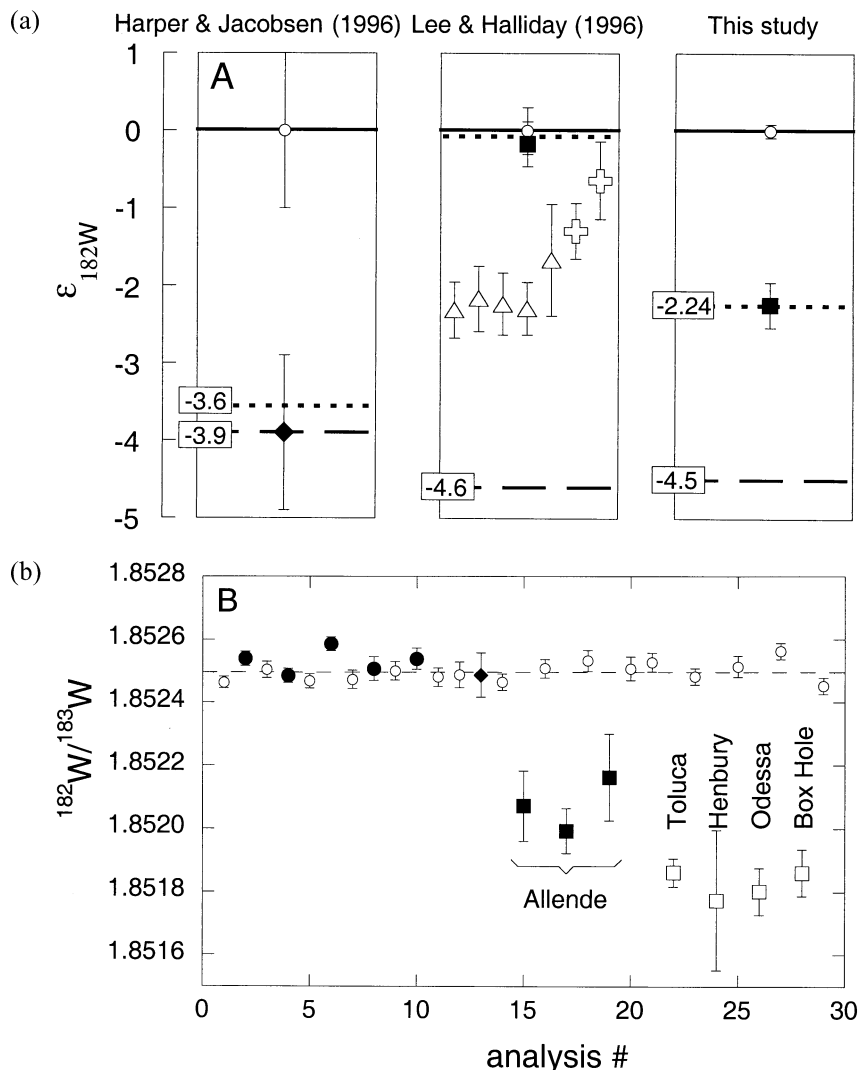
Fig. 1. (A) Bulk silicate Earth (solid lines), present-day chondritic (dotted lines), and initial solar system (stippled lines) ε_{182W} values determined by Harper and Jacobsen (1996), Lee and Halliday (1996), and in this study. The respective bulk silicate Earth W-isotope compositions of the individual studies were chosen as reference values (ε_{182W} = 0) to allow for direct comparison of the data. In all three studies, bulk silicate Earth is defined by measurements of terrestrial W standard solutions (small open circles) and confirmed by measurements of standard rocks in the study of Lee and Halliday (1996) (AGV-1 and WS-E; subsequently, Lee et al., 1997, also reported measurements of the Hawaiian basalt 1802-4A and the Atlantic midocean ridge basalt A 127-D-15) and this study (AGV-1 and Great Dyke sulphides). The present-day chondritic W-isotope compositions defined by Lee and Halliday (1996) and in this study are based on averages of W-isotope compositions of carbonaceous chondrites (filled squares; two independent analyses of Allende and one analysis of Murchison in Lee and Halliday's [1996] study confirming earlier measurements of the same carbonaceous chondrites [Lee and Halliday, 1995]; three independent analyses of Allende in this study). The chondritic W-isotope composition reported by Harper and Jacobsen (1996) was calculated assuming an initial solar system $^{182}Hf/^{180}Hf$ ratio of 2×10^{-5} (see text). All three studies used the W-isotope composition of iron meteorites as proxies for the initial solar system value. Five measurements of the W-isotope compositions of three enstatite chondrites (open triangles; Lee and Halliday, 2000a) and two ordinary chondrites (open crosses; Lee and Halliday, 2000b) are shown for comparison (see discussion in the text). (B) Measured $^{182}W/^{183}W$ ratios of Great Dyke sulphides (filled circles), the standard rock AGV-1 (filled diamond), Allende carbonaceous chondrites, and iron meteorites (see Table 1). All natural samples were interleaved with measurements of a W standard solution to check for memory effects (not observed) and to control instrumental stability during the study, which was excellent.

3. The Pd/Ag-isotope system is another short-lived clock (half-life of 7 Ma) with significant mother-to-daughter element fractionation during metal/silicate differentiation. The silicate Earth Ag-isotope composition is less radiogenic than that of the carbonaceous chondrite Allende (Hauri et al., 2000; Carlson and Hauri, 2001), and there is substantial variability in Ag-isotope composition of terrestrial material. Hauri et al. (2000) interpreted their findings to reflect terrestrial core formation within much less than 50 Ma after the collapse of the solar nebula.

4. A further constraint on the timing of core formation is afforded by the Mn/Cr-isotope system (half-life of only 3.5 Ma). There is substantial variation in Cr-isotope composition of different classes of chondrites. If, in terms of Cr-isotopes, the bulk Earth resembles carbonaceous chondrites, which show unradiogenic $^{53}Cr/^{52}Cr$ ratios compared to the silicate Earth value (Shukolyukov and Lugmair, 1998), Earth's core must have formed very early after the start of solar system accretion.

5. Recently reported detrital terrestrial zircons as old as 4404 Ma (Wilde et al., 2001) indicate existence of differentiated terrestrial crust only 160 Ma years after the start of accretion. Continued extensive accretion and core differentiation are difficult to envisage in the context of an Earth on which crust formation was already operational.

6. Finally, compared to the silicate Earth, lunar rocks show variable but more radiogenic W-isotope signatures of up to $+6$ ε_{182W} (Lee et al., 1997). Whilst the most radiogenic values are likely to be caused by Ta neutron capture (Leya et al., 2000), the more radiogenic W of the bulk Moon (compared to Earth) has probably evolved within the Moon itself (possibly because of the formation of its core). In that case, very early (<40 Ma after the collapse of the solar nebula) formation of the Moon is inevitable. However, early Moon formation within the giant-impact scenario requires rapid terrestrial accretion and, by definition, early terrestrial core formation (e.g., O'Neill, 2001). This is in conflict with the present interpretation of terrestrial W-isotopes, unless as a last resort, substantial continued accretion long after the giant impact is suggested (Halliday, 2000). However, a uniting feature of all accretion models is exponential decay of the accretion rate, such that rapid early accretion necessarily excludes substantial later slow accretion.

In view of the difficulty of accommodating all these constraints with a physically plausible model (Jones and Palme, 2000), we attempted to verify the solar system W-isotope reference framework by reanalysing W-isotopes of terrestrial and extraterrestrial material by multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS).

2. ANALYTICAL TECHNIQUES

2.1. Samples, Treatment, and Chemical Separation

As representative terrestrial samples, we chose the U.S. Geological Survey rock standard AGV-1; an in-house W standard, "ACQUIRE-W," prepared from high-purity, zone-refined W ribbon purchased from H. Cross Pdy, Ltd; and a sulphide concentrate from the late Archaean Great Dyke intrusion of Zimbabwe sampled at the Hartley Pt mine (made available to us by the Bundesamt für Geowissenschaften und Rohstoffe, Hannover, Germany). A description of the occurrence and mineralogy of the sulphide concentrate can be found in Oberthür et al. (1997).

Two sets of fragments of the Allende carbonaceous chondrite were obtained from two different sources: NMBE 50110 from the Natural History Museum in Bern, Switzerland, and Be-412-2 from the collection of the Physics Department, University of Bern, Switzerland. One set of fragments (NMBE 50110) was split into two aliquots, which were dissolved separately. None of the fragments had sawed or altered surfaces. No acid leaching or physical surface abrasion of the fragments was performed to avoid preferential dissolution of some components of the meteorites.

Samples of the Toluca and Odessa iron meteorites were obtained from the collection of the Physics Department, University of Bern, Switzerland, and those of the Henbury and Box Hole iron meteorites from the Queensland Museum, Brisbane, Australia. Minor surface corrosion of iron meteorites was removed by high–air pressure glass-shard blasting. Before digestion, iron meteorite samples were repeatedly washed in isopropanol alcohol by ultrasonic agitation to remove possible microscopic glass particles.

All samples were digested in previously unused but precleaned Teflon beakers by sequential attack in concentrated HF, 10 mol/L HCl, and 14 mol/L HNO_3 on a hot plate at 150°C. The dissolved samples were dried down and redissolved in 1 mL 10 mol/L HCl to break down possible fluoride complexes. After drying down, 1 to 2 mL of concentrated HNO_3 were added to the residues to visually check for total dissolution of the samples before W was separated by anion exchange. Visual inspection indicated complete dissolution such that we can exclude preferential leaching of mineral phases containing variably radiogenic W. Micron-sized components such as diamonds reported to be present in carbonaceous chondrites (e.g., Huss and Lewis, 1995) would have stayed undetected by this test but are unlikely to be important W hosts. Samples were subsequently taken back to dryness and finally dissolved in 2 to 3 mL 0.5 mol/L HCl + 1 mol/L HF (which is the loading mix "A" of the column separation).

Chemical separation of W was performed by anion exchange adapted from the protocol of Horan et al. (1998), which is a modification of the method by Kraus et al. (1955). Three cubic centimeters of Dowex AG1-X8 anion exchange resin (200 to 400 mesh) were loaded into 15-cc polypropylene columns and precleaned with 5 mL of mix "A," followed by two times 5 mL 1 mol/L HF + 9 mol/L HCl (mix "B") and finally 5 mL purified water (Milli-Q). Before sample loading, the resin was reequilibrated with 5 mL of mix "A." The sample was centrifuged in mix "A" and the supernate loaded onto the resin and purified by eluting three separate batches of 5 mL of mix "A" followed by a single elution of 4 mL of mix "B." The purified W was released from the resin with two batches of 5 mL of mix "B" and evaporated to dryness. Depending on the size of the dried residue, the sample was redissolved in mix "A" and passed through the same columns for a second time using the same elution scheme. After use, columns were cleaned by passing three batches of 7 mL of mix "B," two batches of 5 mL of mix "A," and two batches of 5 mL purified water and stored in 5 mL of mix "A." After five chemical separations, the resin was discarded and the column washed and packed with new resin. All terrestrial samples were processed first, followed by the Allende digestions and finally the iron meteorites. The aim of this sequence was to avoid contamination of terrestrial and chondritic samples by unradiogenic iron meteorite W.

2.2. Mass Spectrometry

All isotope measurements were performed on a Micromass IsoProbe MC-ICP mass spectrometer at the University of Queensland. Purified samples were dissolved in 1 to 2 mL 0.1 mol/L HF for aspiration by Cetac Aridus and MCN-6000. Uptake rates were approximately 25 μL/min, yielding measurement periods of 40 to 80 min. This allowed determination of 150 to 300 measurement cycles. Because ^{183}W is interference free, it was preferred in this study for normalisation following the original convention of Harper et al. (1991) rather than the ^{184}W normalisation. ^{184}W normalisation was introduced by Lee and Halliday (1995) because of a reported unidentified spectral interference on mass 183 in the baseline of their separated natural materials. An important feature of our data collection strategy was to measure ion currents of all abundant W-isotopes (i.e., masses 182, 183, 184, and 186) and to acquire statistics for all important ratios (i.e., $^{182}W/^{183}W$, $^{182}W/^{184}W$, $^{184}W/^{183}W$, $^{183}W/^{186}W$, and $^{184}W/^{186}W$) to validate data quality with measured stable W-isotope ratios (see Figs. 2A to 2C). Instrumental mass fractionation was corrected with power law using $^{184}W/^{183}W = 2.139758$ (Harper and Jacobsen, 1996). Figure 2A shows that fractionation-uncorrected (i.e., raw) stable W-isotope ratios of the ACQUIRE-W standard and all natural samples plot along the "theoretical" power law fractionation line, demonstrating its validity, within the experimental range of mass bias, for data correction. Rehkämper and Mezger (2000) already demonstrated that power and exponential laws yield mass bias–corrected data of equal quality and resolution on

(a) A — Forced fit: y = 1.5036x - 0.3473 — Odessa

(b) B — ACQUIRE-W: y = 1.5001x - 0.34696, MSWD = 1.15 — Allende: y = 1.5160x - 0.34739, MSWD = 0.003
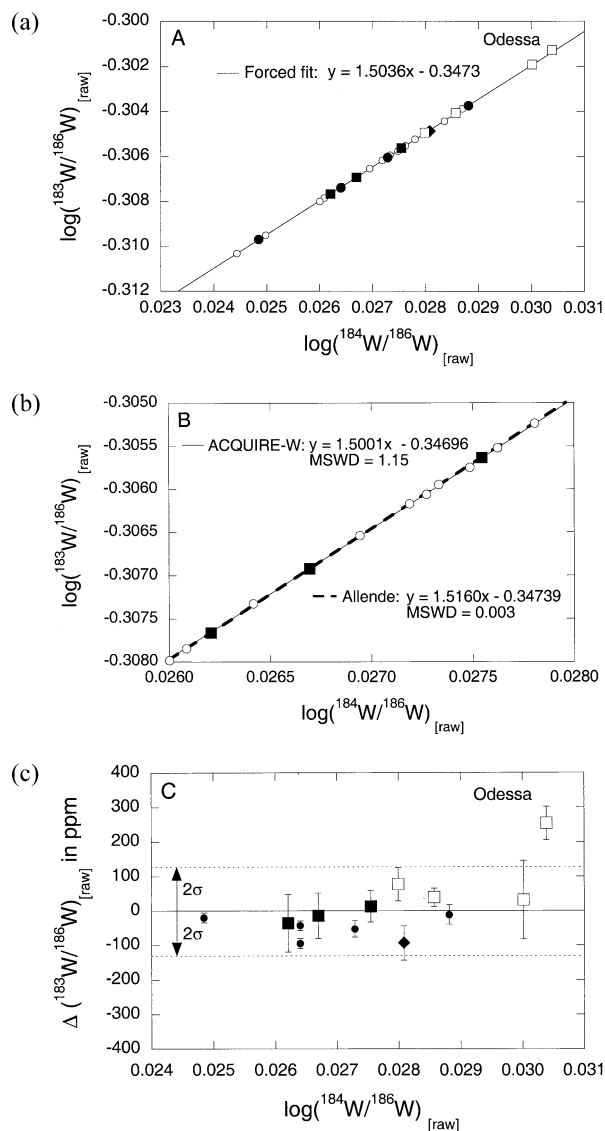
(c) C — Odessa

Fig. 2. (A) Plot of logarithms of Os-corrected but fractionation-uncorrected (i.e., raw) stable W-isotope ratios of all samples shown in Figure 1B (identical symbols). The fact that all standard and sample data plot along a well-defined regression line identical to the "theoretical" fractionation line with a slope of 1.5036 demonstrates instrumental stability and accuracy during this study and the validity of power law fractionation correction. (B) Detail of Figure 2A, including data for ACQUIRE-W standard and Allende carbonaceous chondrite only. The fractionation line defined by the Allende data is within uncertainties identical to that of the ACQUIRE-W standard. In addition, the slopes of Allende and ACQUIRE-W data are within uncertainties equal to the well-known theoretical value (Fig. 2A). The excellent conformity of Allende and ACQUIRE-W raw data demonstrates the accuracy of the small Os-interference in-run corrections for Allende data. (C) Deviation of measured from expected $^{183}W/^{186}W$ raw ratio (in ppm) as a function of $^{184}W/^{186}W$ raw ratio (logarithms). Expected $^{183}W/^{186}W$ raw ratios were calculated from the equation for the fractionation line defined by the ACQUIRE-W data (Fig. 2B). Accordingly, $\Delta(^{183}W/^{186}W)_{raw}$ (in ppm) is calculated as:

$$\Delta(^{183}W/^{186}W)_{raw} \text{ in ppm} = [(^{183}W/^{186}W)_{measured} / (^{183}W/^{186}W)_{expected} - 1] \times 10^6$$

Symbols are the same as in Fig. 1B. The solid (zero) line depicts the ACQUIRE-W standard $^{183}W/^{186}W$ raw ratio for any given $\log(^{184}W/^{186}W)$ value and the stippled lines are spaced at 2σ reproducibility.

this type of MC-ICP mass spectrometer. Small isobaric interferences of Os on masses 184 and 186 were corrected by monitoring ^{188}Os. ^{184}Os interferences on ^{184}W were 1 ppm for the Great Dyke sulphides; 7 ppm for AGV-1; 30 to 75 ppm for the iron meteorites; and 19, 108, and 140 ppm for the three Allende bulk rock fragments. ^{184}Os and ^{186}Os interferences were removed with $^{184}Os/^{188}Os$ and $^{186}Os/^{188}Os$ ratios that were adjusted for in-run mass fractionation iteratively obtained via the $^{184}W/^{183}W$ ratio. No correlation is found between the $^{184}Os/^{184}W$ and $^{182}W/^{183}W$ ratios. On an MC-ICP mass spectrometer, accurate mass interference corrections can apparently be performed for much larger interference-to-signal ratios, as demonstrated by Schönbächler et al. (2002) with ^{92}Mo corrections on ^{92}Zr. Despite ^{186}Os having a contribution from β decay of ^{190}Pt, a present-day chondritic $^{186}Os/^{188}Os$ ratio of 0.119834 (Shirey and Walker, 1998) was chosen for ^{186}Os interference correction on ^{186}W of all samples. The uncertainty of the "true" ^{186}Os abundance in natural samples (particularly iron meteorites) could only slightly but not significantly ($\sim$2 ppm) shift the measured $^{184}W/^{186}W$ ratio.

2.3. Data Presentation

Previous W-isotope studies reported their ^{182}W abundances relative to either ^{183}W or ^{184}W. Since both ^{184}W and ^{183}W are stable isotopes, $^{182}W/^{184}W$ ratios can easily be translated into $^{182}W/^{183}W$ ratios by multiplication with $^{184}W/^{183}W$ = 2.139758 (Harper and Jacobsen, 1996). However, different laboratories report slightly different W-isotope compositions, even of stable W-isotope ratios. This is largely due to the use of different fractionation corrections (including various "true" values of a particular W-isotope ratio) as well as uncertainties in oxygen isotope composition during negative thermal ionization mass spectrometry (N-TIMS) analyses (Harper and Jacobsen, 1996) and uncertainties in Faraday cup efficiencies affecting N-TIMS and MC-ICP-MS measurements in static multicollector mode. For absolute comparison of W data sets from different laboratories, an additional external offset correction would be necessary.

Here, we follow Horan et al. (1998), who proposed comparing data from different laboratories using ε_{182W} on a relative scale, where the terrestrial value from the respective study was used as reference (i.e., ε_{182W} = 0). All previous studies found terrestrial samples and W standards to be of constant W-isotope composition. Thus, in this study, ε_{182W} is defined as the part per 10^4 deviation of the $^{182}W/^{183}W$ ratio of a sample relative to the terrestrial value determined in the respective studies. For ease of comparison and to validate data quality, ε_{182W} is also tabulated as deviation of the $^{182}W/^{184}W$ ratio.

3. RESULTS

Our new high-precision W-isotope data for terrestrial samples, iron meteorites, and the carbonaceous chondrite Allende are given in Table 1 and shown in Figures 1B and 2A to 2C. We found excellent agreement between our measurements of AGV-1, Toluca, and Henbury with published data (Harper and Jacobsen, 1996; Lee and Halliday, 1996; Horan et al., 1998). Our data for the iron meteorites Odessa and Box Hole are within the range of all previously determined iron meteorites (for a summary, see Halliday and Lee, 1999). All analyses of terrestrial materials point to a homogeneous W-isotope composition of the silicate Earth (Table 1, Fig. 1B). However, our determinations of the $^{182}W/^{183}W$ ratios in the Allende carbonaceous chondrite are significantly less radiogenic than those previously reported (Lee and Halliday, 1995, Lee and Halliday, 1996). Three individual digestions of Allende yielded an average W-isotope composition of -2.24 ε_{182W} (Fig. 1A). If carbonaceous chondrites indeed contain less radiogenic W than was hitherto assumed, a cascade of implications follows for early differentiation in the solar system. As this is the most significant finding of our study, we next explore possible ex-

Table 1. W-isotope data.

Sample	$^{182}W/^{183}W$	2σ	$^{184}W/^{186}W$	2σ	$^{183}W/^{186}W$	2σ	ε_{182W}	2σ
Terrestrial								
[1] ACQUIRE-W	1.852464	19	1.079292	28	0.504372	14	−0.17	0.10
[3] ACQUIRE-W	1.852504	16	1.079351	17	0.504380	8	+0.05	0.09
[5] ACQUIRE-W	1.852468	22	1.079371	15	0.504394	7	−0.15	0.12
[7] ACQUIRE-W	1.852473	30	1.079312	22	0.504348	10	−0.12	0.16
[9] ACQUIRE-W	1.852501	30	1.079367	22	0.504335	10	+0.03	0.16
[11] ACQUIRE-W	1.852480	30	1.079340	22	0.504330	10	−0.08	0.16
[12] ACQUIRE-W	1.852487	41	1.079429	28	0.504374	12	−0.04	0.22
[14] ACQUIRE-W	1.852465	26	1.079349	17	0.504375	8	−0.16	0.14
[16] ACQUIRE-W	1.852508	30	1.079433	22	0.504399	10	+0.07	0.16
[18] ACQUIRE-W	1.852532	33	1.079453	24	0.504441	11	+0.20	0.18
[20] ACQUIRE-W	1.852507	37	1.079480	28	0.504444	12	+0.07	0.20
[21] ACQUIRE-W	1.852527	30	1.079424	19	0.504415	9	+0.17	0.16
[23] ACQUIRE-W	1.852482	26	1.079414	19	0.504403	10	−0.07	0.14
[25] ACQUIRE-W	1.852514	33	1.079382	24	0.504393	10	+0.10	0.18
[27] ACQUIRE-W	1.852563	26	1.079495	22	0.504425	10	+0.37	0.14
[29] ACQUIRE-W	1.852452	26	1.079336	19	0.504381	9	−0.23	0.14
Mean ACQUIRE-W	1.852495	17	1.079380	29	0.504387	16	0	0.09
[2] GD-sulphide	1.852539	22	1.079467	15	0.504412	7	+0.24	0.12
[4] GD-sulphide	1.852485	22	1.079366	15	0.504343	7	−0.05	0.12
[6] GD-sulphide	1.852586	22	1.079560	15	0.504462	7	+0.49	0.12
[8] GD-sulphide	1.852507	37	1.079387	30	0.504421	14	+0.07	0.20
[10] GD-sulphide	1.852539	33	1.079479	26	0.504442	12	+0.24	0.18
Mean GD-sulphide	1.852530	52	1.079460	100	0.504410	64	+0.19	0.28
[13] AGV-1	1.852487	70	1.079602	54	0.504508	25	−0.05	0.70
Grand BSE mean	1.852500	17	1.079408	32	0.504390	17	+0.03	0.09
Iron meteorites								
[22] Toluca	1.851862	44	1.079363	30	0.504404	13	−3.42	0.24
[24] Henbury	1.851774	222	1.079387	172	0.504429	58	−3.89	1.20
[26] Odessa	1.851802	74	1.078858	51	0.504187	24	−3.74	0.40
[28] Box Hole	1.851861	74	1.079206	51	0.504322	24	−3.42	0.40
Mean irons	—	—	1.079320	210	0.504390	110	—	—
Allende carbonaceous chondrite								
[15] NMBE 50110	1.852071	111	1.079369	73	0.504378	33	−2.29	0.60
[17] BE-412-2	1.851993	70	1.079320	50	0.504370	23	−2.71	0.38
[19] NMBE 50110	1.852162	137	1.079509	93	0.504440	42	−1.80	0.74
Mean Allende	1.852080	54	1.079360	210	0.504380	77	−2.24	0.29

W-isotopic compositions of terrestrial samples, four iron meteorites, and three digestions of the carbonaceous chondrite Allende. Numbers in square brackets refer to the sequence of analyses (Fig. 1B). ^{184}Os interference on ^{184}W and ^{186}Os interference on ^{186}W were corrected in run by monitoring the interference-free ^{188}Os signal (for details, see text). The W procedural blank determined by quadrupole inductively coupled plasma mass spectrometry was 47 pg for sample sizes of ∼1 g (i.e., terrestrial silicates) and ≤35 pg for Allende digests (∼500 mg) and ≤25 pg for iron meteorites and was thus negligible.

planations for the mismatch of W-isotope measurements of Allende.

4. DISCUSSION

4.1. Comparison of New and Previously Published Data for the Allende Chondrite

4.1.1. Sample contamination

The Allende $^{182}W/^{183}W$ analyses are not artefacts of contamination with iron meteorite W, as the W-isotope compositions of the iron meteorites were determined last in the analytical sequence (Fig. 1B). In any case, memory effects during analyses can be excluded because interleaved analyses of terrestrial samples (ACQUIRE-W standard) never deviated from the mean value, irrespective of the composition of the previously measured sample.

4.1.2. Sample heterogeneity

There is the possibility of severe W-isotope heterogeneity on hand-specimen scale. However, we obtained two separate fragments of Allende from two institutions that purchased their Allende samples from different sources and find no isotopic difference. Furthermore, Yin et al. (2002) recently published (in extended abstract form) a new W-isotope value of −2 ε_{182W}, in excellent agreement with our measurements. However, Yin et al's (2002) findings will only constitute bona fide support for our data when published in a peer-reviewed journal. Compared to these studies, there is substantial difference between the two published data sets for the Allende meteorite published by Lee and Halliday (1995, 1996). The average of the first determination of Allende is +0.98 ± 1.4 ε_{182W}, while the second determination yielded an average of −0.32 ± 0.37 ε_{182W}, which amounts to a 1.3-ε_{182W} difference. However, because the values agree within the large errors of the 1995 determination and because the more evolved enstatite chon-

Table 2. Detailed W-isotope data of Allende and model calculations.

Fractionation ratio	$^{184}W/^{183}W$		$^{183}W/^{186}W$		$^{184}W/^{186}W$	
	$\varepsilon^{182}W/^{183}W$	$\varepsilon^{182}W/^{184}W$	$\varepsilon^{182}W/^{183}W$	$\varepsilon^{182}W/^{184}W$	$\varepsilon^{182}W/^{183}W$	$\varepsilon^{182}W/^{184}W$
Sample						
			Allende carbonaceous chondrite			
NMBE 50110	–2.29	–2.26	–2.21	–2.01	–2.21	–2.01
BE-412-2	–2.71	–2.52	–2.27	–1.99	–2.27	–1.99
NMBE 50110	–1.80	–1.84	–2.11	–2.38	–2.11	–2.38
Mean	–2.24	–2.06	–2.23	–2.04	–2.23	–2.04
			Modelled ^{183}W interference			
Model 1	–2.24	–0.39	–3.12	–2.16	–2.05	0
Model 2	–2.24	–1.18	–2.46	–1.63	–1.65	0

W-isotope anomalies for our three Allende measurements reported as $\varepsilon^{182}W/^{183}W$ and $\varepsilon^{182}W/^{184}W$ using $^{184}W/^{183}W$, $^{183}W/^{186}W$, and $^{184}W/^{186}W$ ratios for fractionation correction. Statistics for the $^{182}W/^{184}W$ ratio were obtained in run and not calculated from the $^{182}W/^{183}W$ and $^{184}W/^{183}W$ ratios. Two hypothetical interference models were calculated to yield an $^{182}W/^{183}W$ anomaly of –2.24 ε relative to the terrestrial value using $^{184}W/^{183}W$ as the fractionation ratio. In model 1, the power law fractionation factor was 0.008, which required a 205 ppm isobaric interference on mass 183. Model 2 assumed less mass bias (fractionation factor of 0.005), which reduces the required interference to 165 ppm.

drites appear to have a constant W-isotope composition (Lee and Halliday, 2000a), we do not believe that sample heterogeneity could explain why our measurements are 224 ppm less radiogenic.

4.1.3. Incomplete sample digestion

Another possibility is that the sample preparation procedure caused the difference in measured isotope composition of Allende. However, we used a very similar sample digestion technique to that of Lee and Halliday (1995, 1996) (assuming that these authors dissolved their chondrite samples in a similar way to their lunar samples, as per Lee et al., 1997) so that incomplete sample dissolution (i.e., persistence of W in undigested residues) cannot explain the different isotope ratios. We specifically inspected our digests after redissolution in nitric acid and found no optically visible residues. One feature of our procedure is that we avoided leaching the meteorite samples (even in very weak acids) before dissolution to avoid preferential loss of W from components that are more easily attacked by HCl and HNO_3. It is, unfortunately, impossible to compare our procedure with those of Lee and Halliday (1995, 1996), as a detailed description of their analytical protocol for the carbonaceous chondrites was not reported.

4.1.4. Neutron capture effects

In chondritic meteorites, the production of ^{182}W from ^{181}Ta by cosmic ray–produced neutron capture may become crucial (Leya et al., 2000), and theoretically, differences in $^{182}W/^{183}W$ could have arisen from this process. However, the cosmic ray exposure (CRE) age of Allende is only ~6 Ma (Scherer and Schultz, 2000) and that of Murchison 0.58 Ma (Eugster et al., 1998). The Ta/W ratio in carbonaceous chondrites is ~0.16 (Wasson and Kallemeyn, 1988). Using the production rates given by Leya et al. (2000), we conclude that the contribution of neutron-produced ^{182}W to the total ^{182}W abundance for Allende and Murchison is negligibly small and could not have influenced the $^{182}W/^{183}W$ ratio. Neutron capture effects from cosmic ray irradiation on W can only slightly reduce the ^{182}W deficit in Toluca and other iron meteorites. More specifically,

Masarik (1997) concluded that the maximum change in the normalised $^{182}W/^{183}W$ ratio due to neutron capture reactions cannot account for more than ~25% of the ^{182}W deficit observed in Toluca by Harper and Jacobsen (1996). This is also the case for Henbury and Odessa, whose CRE ages are of the order of that of Toluca. The Box Hole CRE age is unknown.

4.1.5. Mass spectrometry

There are two aspects of W-isotope measurement that hold potential to explain a 224-ppm deviation in the $^{182}W/^{183}W$ ratio. First, interference of Os on masses 184 and 186 affects the estimate of mass bias, which can be corrected with the constant $^{184}W/^{183}W$ or $^{186}W/^{184}W$ ratios. We chose to normalise our data with $^{184}W/^{183}W$, while Lee and Halliday (1996) use the $^{186}W/^{184}W$ ratio, which has the obvious disadvantage of both masses being affected by Os, particularly 186, as the $^{186}Os/^{184}Os$ ratio is ~79. It is impossible to reconstruct from Lee and Halliday's (1995, 1996) data the alternative normalisation because these authors did not report the measured $^{184}W/^{183}W$ ratio. Regardless, it is possible to mass bias–correct our data with all three stable ratios ($^{184}W/^{183}W$, $^{183}W/^{186}W$, and $^{184}W/^{186}W$). As shown in Table 2, all these normalisations yield, within error, the same $^{182}W/^{183}W$ and $^{182}W/^{184}W$ ratios for Allende. This clearly demonstrates that the Os-correction applied in our procedure is robust. The second and more significant mass spectrometric problem would be an unidentified (molecular) interference on one or several of the W masses. Lee and Halliday (1995) reported an unidentified spectral interference on mass 183 in the baseline of their separated natural materials. None of their subsequent datasets for chondrites (Lee and Halliday, 1996, 2000a, 2000b) listed stable isotope ratios of mass 183. This means that unfortunately, it is impossible to test whether spectral interference in their measurements caused the discrepancy in the Allende data. However, the completeness of our data (Tables 1 and 2) allows testing the possibility of molecular interference. To obtain $^{182}W/^{183}W$ or $^{182}W/^{184}W$ ratios that are too low with our procedure (i.e., $^{184}W/^{183}W$ mass bias correction), we could only postulate a spectral interference on mass 183. Interfer-

ences on masses 182 and 184 would result in apparent high $^{182}W/^{183}W$ or $^{182}W/^{184}W$ ratios, because mass bias in MC-ICP-MS always favours ionisation of the heavy isotope. In Table 2, we show that the required interference on mass 183 depends on the extent of mass bias and ranges between 165 and 205 ppm for the range of mass bias experienced over the course of this study. Thus, if reported relative only to $^{182}W/^{183}W$ (not to $^{182}W/^{184}W$) and corrected only with $^{184}W/^{183}W$ (not with $^{186}W/^{184}W$ and $^{186}W/^{183}W$), an interference of this magnitude could indeed go unidentified and result in apparently wrong isotope data. However, as shown in Table 2, the effect of a mass-183 interference on mass bias estimate is easily exposed when the radiogenic isotope (^{182}W) is expressed relative to ^{184}W and if the data are normalised with the $^{186}W/^{184}W$ and $^{186}W/^{183}W$ ratios. Thus, interference on mass 183 can be identified by incoherent $^{182}W/^{183}W$ and $^{182}W/^{184}W$ ratios and unreproducible results for both ratios using different mass bias correction ratios. Our Allende data (Table 2) are internally fully consistent and yield, within error, exactly the same ^{182}W deficit, irrespective of whether expressed relative to ^{183}W or ^{184}W and no matter which normalisation is used.

The finding of consistent stable isotope ratios not only of the Allende data but of our entire data set is implicit in the observation of excellent colinearity on a plot (Figs. 2A and 2B) of $\log(^{183}W/^{186}W)_{raw}$ vs. $\log(^{184}W/^{186}W)_{raw}$, which in itself provides a strong measure of data quality. Since both ratios are stable, mass bias–uncorrected (but Os interference–corrected) data of all samples in this diagram must lie exactly along the fractionation line. Figure 2A shows that our samples, including the Allende measurements (Fig. 2B), define an excellent linear array reproducing the slope predicted by power law fractionation. Thus, this plot not only proves absence of molecular interferences but also demonstrates the validity of power law mass bias correction. Importantly, the mass bias experienced by the three Allende aliquots is well within the range of the standard (Fig. 2B), and there is no correlation between $^{182}W/^{183}W$ and extent of mass bias. The small differences between measured and expected stable isotope ratios are best expressed as deviations (in ppm) of one ratio (e.g., $^{183}W/^{186}W$) from that predicted by the experimental fractionation line defined by the standard (Fig. 2B). Comparison between predicted and observed ratios (Fig. 2C) reveals that stable W-isotope raw ratios of all samples determined in this study except those of the iron meteorite Odessa lie well within the uncertainty limits of the repeatedly measured ACQUIRE-W standard (Fig. 2C). Odessa therefore is identified as an analytical outlier and was not used for calculating the means of the stable W-isotope ratios of iron meteorites reported in Table 1. The three measurements of the Allende carbonaceous chondrite show excellent agreement of their stable W-isotope raw ratios with those of the AC-QUIRE-W standard (i.e., $\Delta[^{183}W/^{186}W]_{raw}$ of -15, -6, and $+6$ ppm), which is also a reflection of the accuracy of the small ^{184}Os and ^{186}Os interference corrections on ^{184}W and ^{186}W, respectively. We therefore conclude that our measured ^{182}W deficit of -2.24 ε is not a mass spectrometric artefact.

In summary, we are unable to offer a conclusive explanation for the difference in measured W-isotope ratios reported for the Allende meteorite by Lee and Halliday (1995, Lee and Halliday 1996) and this study (and Yin et al., 2002). However, in view of the internal consistency of our results, we regard it as unlikely that the discrepancy is an analytical artefact of our methodology. Furthermore, we note the excellent coincidence of our average value (-2.24 ε_{182W}) for Allende and that of enstatite chondrites (mean of -2.22 ε_{182W} = average of five measurements of three enstatite chondrites) reported by Lee and Halliday (2000a). According to Yin et al. (2002), ordinary chondrites too are characterised by an $\sim$2-ε_{182W} deficit relative to the terrestrial value. This may not be a fortuitous coincidence but could indicate a common Hf/W evolution of these meteorite classes. Thus, unlike with Mn-Cr systematics of chondrites, the choice of chondrite class to approximate the Earth may be relatively insignificant for Hf-W. We note that the enstatite chondrite internal isochron systematics are compatible with the chondritic evolution vector calculated from our Allende estimate (Figs. 1A and 2). Within the framework of our redetermined carbonaceous chondrite Hf-W evolution, the possibility exists that enstatite chondrites shared chondritic Hf-W evolution for the first $\sim$8 to 15 Ma, at which stage the enstatite chondrite parent body underwent metal/silicate differentiation (Fig. 3). In other words, both classes of chondrites would have common parentage. By contrast, Lee and Halliday (2000a), noting the mismatch with their solar system evolution (based on Allende and Murchison Hf-W systematics), proposed large-scale redistribution of (unradiogenic) W during collisions between planetesimals.

The debate regarding the correct determination of the Allende W-isotope composition will require further analyses by N-TIMS and MC-ICP-MS methodology. Despite the unresolved nature of this debate it is necessary, in the following, to briefly discuss the implications for early terrestrial and lunar differentiation processes in the framework of our less radiogenic W-isotope determinations for Allende, because the present-day solar system W-isotope composition is of such importance for planetary accretion and core formation models.

4.2. Revision of W Isotope Constraints on Early Terrestrial Differentiation

Following the well-accepted convention that chondrites are chemical and -isotopic proxies for the bulk Earth, the present-day $^{182}W/^{183}W$ ratio of the Earth's core can be calculated by simple mass balance. Because the present-day chondritic and bulk silicate Earth's $^{182}W/^{183}W$ are established, that of the core can be calculated as a function of the Hf/W ratios of chondrites and bulk silicate Earth (Fig. 4). Primitive chondrites show a nearly constant Hf/W ratio of 1.16 (Anders and Grevesse, 1989), while that of the bulk silicate Earth is considerably higher because of removal of W into the core and enrichment of Hf into the silicate mantle and crust. Estimates of the Hf/W ratio for the bulk silicate Earth range from $\sim$7 (Kramers, 1998) to $\sim$40 (Newsom et al., 1996), but most models use values between 10 and 20. A core $^{182}W/^{183}W$ ratio of 1.85205 can be calculated assuming redistribution of 90% of W from the bulk Earth into the core, resulting in a bulk silicate Earth Hf/W of 16.7. Assuming that core formation took place in a short, "catastrophic" event, its timing can be calculated from the chondritic evolution curve using the bulk silicate Earth Hf/W ratio (Fig. 4). For an initial solar system W-isotope composition of -4.5 ε_{182W} (given by the least radiogenic iron meteorites) the core formation time is 34 Ma after the start of solar system
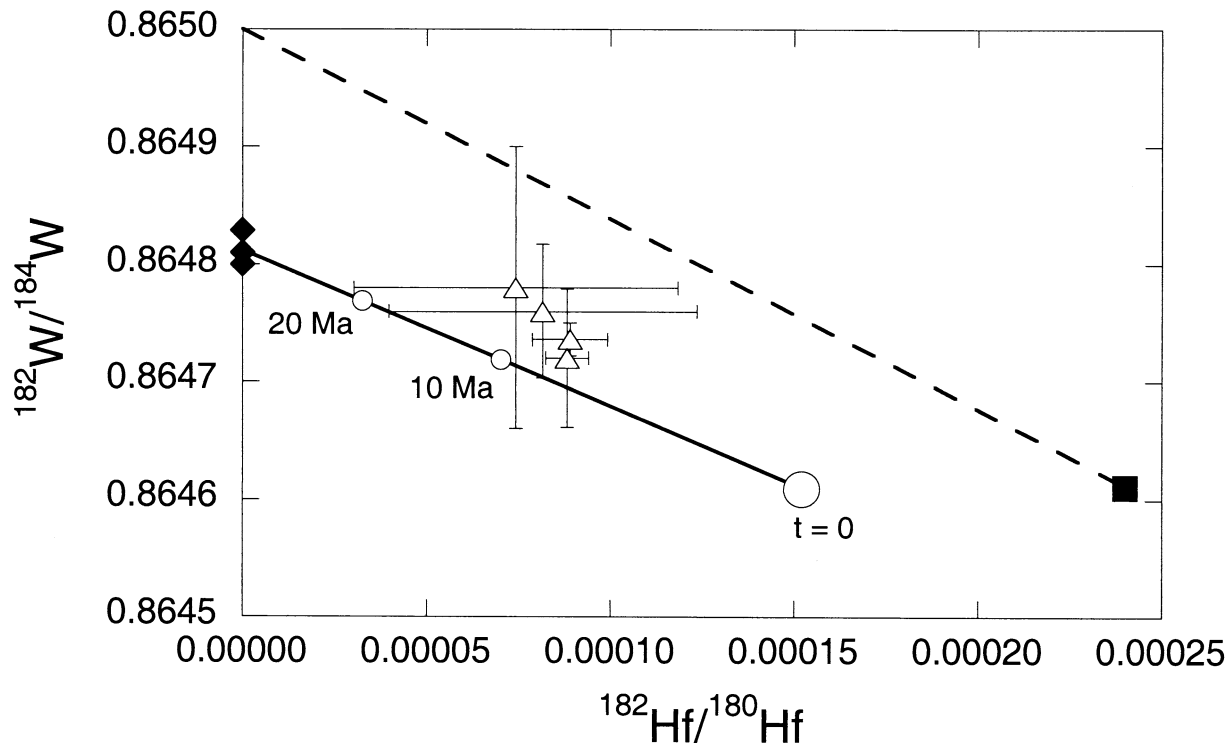
Fig. 3. Chondritic W-isotope evolution line of Lee and Halliday (1996) (filled square, stippled line) compared to that of this study (open circle, solid line) plotted in an $^{182}W/^{184}W$ vs. $^{182}Hf/^{180}Hf$ diagram. Because we determined ^{182}W anomalies relative to ^{183}W, not ^{184}W, our chondritic $^{182}W/^{184}W$ ratio (shown here for comparison) was simply calculated as a -2.24-ε_{182W} deficit relative to the terrestrial $^{182}W/^{184}W$ ratio of Lee and Halliday (1996). The inferred solar system initial (SSI) $^{182}Hf/^{180}Hf$ ratio can be calculated as

$$
\left(\frac{^{182}Hf}{^{180}Hf}\right)_{SSI} = \left[\left(\frac{^{182}W}{^{183}W}\right)_{CHOND} - \left(\frac{^{182}W}{^{183}W}\right)_{SSI}\right] / \left(\frac{^{180}Hf}{^{183}W}\right)_{CHOND}
$$

where $^{182}W/^{183}W_{SSI}$ is estimated from the least radiogenic W-isotope composition of iron meteorites (i.e., conservatively estimated as -4.5 ε_{182W} relative to the terrestrial $^{182}W/^{183}W$) and $^{180}Hf/^{183}W$ (atomic ratio) = Hf/W$_{CHOND}$ $\times$ $^{180}Hf/^{183}W$ = 2.76182, using a Hf/W$_{CHOND}$ ratio of 1.16 (Anders and Grevesse, 1989). Solving the above equation with the parameters listed above, we obtain a solar system initial $^{182}Hf/^{180}Hf$ ratio of 1.516×10^{-4}. The lines show radiogenic in-growth of ^{182}W by decay of ^{182}Hf with time (time scale given along our chondritic evolution line). There is a small difference in the slopes of the evolution lines, reflecting the fact that Lee and Halliday (1996) used a chondritic Hf/W ratio of 1.33 (Wasson and Kallemeyn, 1988), whereas we chose a value of 1.16 (Anders and Grevesse, 1989). Also plotted are data points derived from isochron regressions of four enstatite chondrite data sets (open triangles) and the averages of present-day enstatite chondrite whole rock $^{182}W/^{184}W$ (filled diamonds) reported by Lee and Halliday (2000a). The enstatite chondrite isochron data points plot closer to our chondritic Hf-W evolution line than to that of Lee and Halliday (1996) and present-day whole rock $^{182}W/^{184}W$ lie within the range of our carbonaceous chondrite value. The carbonaceous chondrite $^{182}Hf/^{180}Hf$ determined by Lee and Halliday (1996) is too high for enstatite chondrites, if the internal enstatite chondrite Hf-W isochrons are significant (for detailed discussion of alternative explanations, see Lee and Halliday, 2000a). No meaningful solution is found with Lee and Halliday's (1996) evolution line, unless disequilibrium between metal and silicate phases in enstatite chondrites is assumed. The small deviation of our chondritic evolution line with the enstatite chondrite data could be explained if our assumed Hf/W ratio is too high, and thus the obtained initial $^{182}Hf/^{180}Hf$ too low.

accretion. If W depletion is less pronounced, even younger core formation times are required (Fig. 4). In reality, core formation was not a single "catastrophic" event but a continuous process whose progress was limited by the accretion rate (e.g., Kramers, 1998). Because of the intimate link between accretion and core formation, we regard 34 Ma to also be a sound maximum estimate for the mean time of terrestrial accretion.

The largest component of uncertainty of the 34 Ma estimate is not due to the simplicity of the single-stage model. Rather, uncertainty in all core formation time estimates arises from the question of whether or not, in continuous core formation, metal

from newly accreted material (chondritic or differentiated) equilibrated with the Earth's evolving silicate mantle. Kramers (1998) demonstrated that if such equilibration occurred, its chief effect was to further deplete the mantle in metal phase content and siderophile elements. As a result, much smaller differences between terrestrial and chondritic W-isotope ratios than our 2.24-ε_{182W} estimate could still be reconciled with early accretion and core formation. This is because much of the radiogenic W that formed from Hf in the already depleted silicate mantle was later removed into the core with metal that arrived during the waning stages of accretion. Thus, because
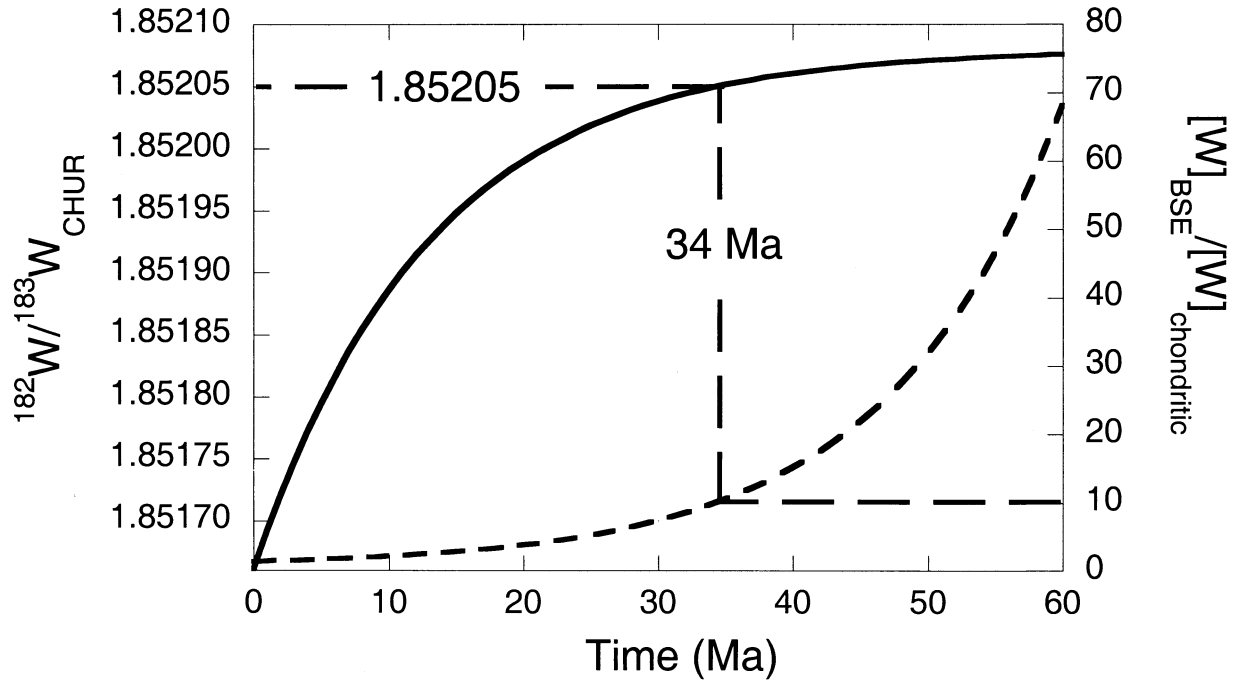
Fig. 4. Model of a catastrophic core formation event. The solid line describes the chondritic W-isotope evolution with time, using an initial solar system W-isotope composition of -4.5 ε_{182W} relative to present-day bulk silicate Earth (see Fig. 1A). The stippled line denotes, as a function of time, the W depletion in the bulk silicate Earth (expressed as $W_{BSE}/W_{chondrite}$) required to produce the bulk silicate Earth W-isotope composition. A Hf/W ratio of 16.7 for the bulk silicate Earth, which translates to a W depletion of 90% (see text), yields a catastrophic core formation age of 34 Ma after the start of solar system accretion. The corresponding core $^{182}W/^{183}W$ ratio is 1.85205.

the simple concept of instantaneous core formation neglects that possibility, our estimate of core formation at 34 Ma has to be regarded as a maximum time. Indeed, the 2.24-ε_{182W} difference between our Allende W-isotope composition and that of the silicate Earth is compatible with termination of terrestrial accretion before complete decay of substantial amounts of ^{182}Hf. A solar system initial $^{182}Hf/^{180}Hf$ ratio of 1.516×10^{-4} can be inferred from our Allende W-isotope composition by postulating that the solar system initial was -4.5 ε_{182W}. However, relative to our own iron meteorites data, which are less radiogenic (averaging ~ -3.6 ε_{182W}), we obtain a lower $^{182}Hf/^{180}Hf$ of 0.93×10^{-4}. This estimate is very similar to that obtained by Yin et al. (2002) from their combined chondrite isochron. A lower $^{182}Hf/^{180}Hf$ would mean that our estimate of core formation time (34 Ma) is a maximum.

Very early terrestrial accretion, as indicated by our data, permits early formation of the Moon by large impact and could explain lunar W-isotope variability as a feature that largely formed within the Moon itself. Thus, our redetermination of terrestrial, iron meteorite, and Allende W-isotope systematics removes most, if not all, of the inconsistencies with other -isotopic (Pb, Xe, Ag, Cr) and astrophysical constraints for the accretion and early differentiation of the planets in the solar system.

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