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Accretion of Primitive Planetesimals: Hf-W Isotopic Evidence from Enstatite Chondrites

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Enstatite chondrites have often been considered to be closely related to the material from which Earth accreted. However, tungsten isotopic data reveal clear differences. Moreover, the silicate and metal fractions define distinct initial $^{182}Hf/^{180}Hf$ corresponding to a 13.8 ± 5.3 million year apparent age difference. Internal reequilibration does not provide a ready explanation for this result. Larger scale redistribution of tungsten is more likely, such as may have occurred during collisions between planetesimals.

Enstatite chondrites formed in a highly reduced environment, possibly in the inner regions of the solar nebula (*1*, *2*). They are the only group of chondrites whose silicate fractions have oxygen isotopic compositions similar to those of Earth and the moon (*3*), prompting some to suggest a genetic relationship (*4*). The Mn-Cr isotopic data for enstatite chondrite leachates and residues define an initial Cr isotopic composition that is similar to that of silicate Earth and the moon (*5*, *6*), and this has been used to argue that the enstatite chondrite parent body (ECPB) may have formed at the same heliocentric distance. However, many features of enstatite chondrites are enigmatic and hard to explain. There are substantial compositional gaps between the enstatite chondrites and the Earth-moon system (*2*, *7*), and chemical evidence for heterogeneous accretion of the ECPB has been presented (*8*). Furthermore, the relationship with Earth is unlikely to be straightforward. For example, dynamic simulations suggest that localized feeding zones for the growth of planetesimals and planets are unrealistic (*9*). Rather, planetary accretion can sample a broad provenance (*9*, *10*).

The recently developed ^{182}Hf-^{182}W chronometer (half-life = 9 million years) is well suited for studying accretion in the inner solar system (*11–15*). Both Hf and W are highly refractory. However, chemically they are quite different, with Hf being strongly lithophile ("silicate-loving") and W moderately siderophile ("metal-loving"), such that fractionation between Hf and W occurs during metal-silicate differentiation and partial melting (*11*, *12*). Hence, excess ^{182}W in the W atomic abundance is found in meteorites that sample high Hf/W silicate reservoirs formed within the life-span of ^{182}Hf. This is as found in some eucrites, martian meteorites, lunar samples, and the silicate phases of ordinary chondrites (*13–15*). Conversely, a deficit in ^{182}W is found in early metals such as iron meteorites and the metal fractions of ordinary chondrites, because they have low Hf/W (*10*, *11*, *16*, *17*). Ordinary chondrites appear to define reasonable internal Hf-W isochrons with a linear functional relation between Hf/W and W isotopic compositions. Here we report data for enstatite chondrites and find different behavior implying systematic redistribution and mixing of W.

Four enstatite chondrites, including EH and EL groups, Abee (EH4), Indarch (EH4), ALHA81021 (EL6), and Hvittis (EL6), were selected for study. Experimental procedures (*18*) were as used previously (*15*). The Hf-W data for all four enstatite chondrites (Table 1) show a positive correlation between measured Hf/W ratios and the respective W isotopic compositions of individual fractions (Fig. 1), consistent with the former presence of ^{182}Hf. In detail, however, the metals and silicates display distinct characteristics (Fig. 1).

Portions of the magnetic (largely metal) fractions of each meteorite were leached in 6 M HCl (*18*). The leachates contain the easily soluble metal, sulfide, and minor phosphate fractions with low Hf/W (Table 1). The residues from this procedure mainly comprise small amounts of silicates and minor oxides, insoluble in 6 M HCl. The Hf-W data for all of these "magnetic fractions," that is, bulk metals, metal leachates, and metal residues, are collinear, intersecting the data for the carbonaceous chondrites, Allende and Murchison (*11*, *12*) (Fig. 1). These data are also collinear with the data for the ordinary chondrites (*15*), providing evidence that the metals are coeval and early (Web fig. 1) (*19*). A regression of the data for all enstatite chondrite metals, their leachates and residues, and the whole rock values of Allende and Murchison yields a slope (equal to initial $^{182}Hf/^{180}Hf$) of (1.85 ± 0.38) × 10^{-4} (Fig. 2), equivalent to that defined by the ordinary chondrites (~1.8 × 10^{-4}) (*15*). The regression results are the same but with larger uncertainties if the carbonaceous chondrites are excluded [(1.88 ± 0.73) × 10^{-4}]. The initial $^{182}Hf/^{180}Hf$ at the start of the solar system is thought to lie in the range (1.87 ± 0.16) × 10^{-4} to (2.75 ± 0.24) × 10^{-4} (*15*). On this basis, the metals in the enstatite chondrites formed within a few million years, at most, of the start of the solar system.

In contrast, the nonmagnetic fractions (predominantly silicates) for each sample lie to the right of and below the best-fit line defined by the magnetic (metal) fractions (Fig. 1). The data for the nonmagnetic frac-

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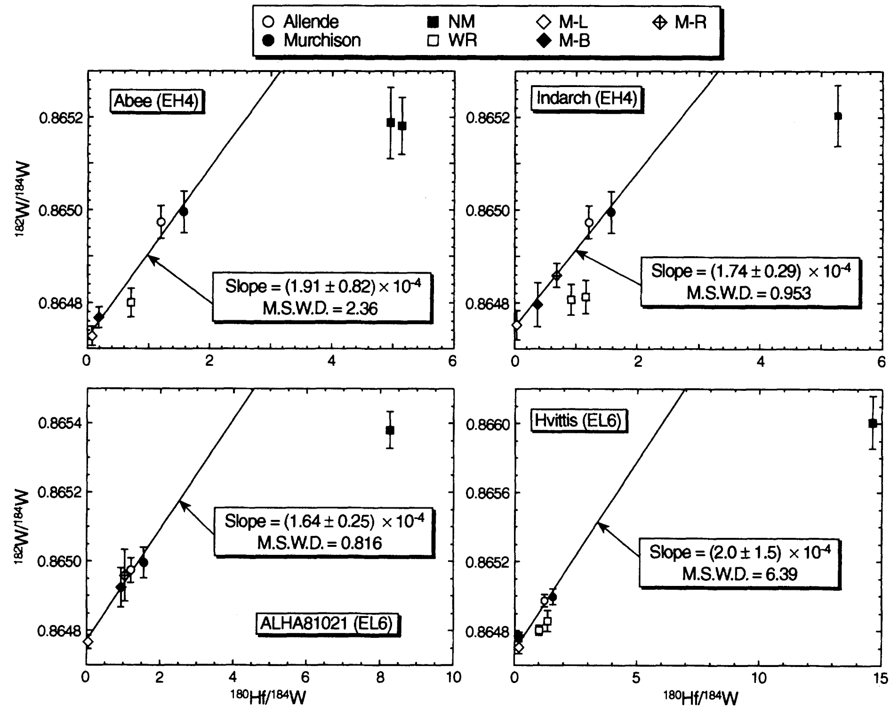

Fig. 1. Hf-W isochron plots for the four enstatite chondrites analyzed in this study. All the whole rock (WR) and nonmagnetic fraction (NM) data plot to the right of the isochron, defined by the magnetic fractions, i.e., metal leachate (M-L), bulk metal (M-B), and metal residue (M-R) and the two carbonaceous chondrites, Allende and Murchison (*11, 12*). M.S.W.D., mean square weighted deviation.

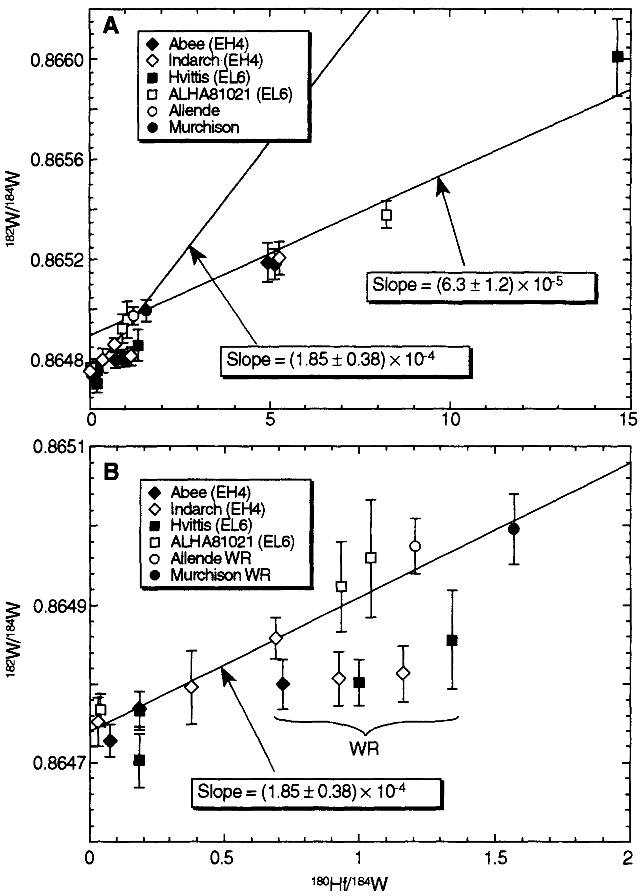

Fig. 2. The same Hf-W isochron plot as in Fig. 1 but combining all of the data from this study. The two straight lines shown in (**A**) were defined by (i) all of the magnetic fractions plus Allende and Murchison, with a slope of (1.85 ± 0.38) × 10^{-4}, and (ii) all of the nonmagnetic fractions plus Allende and Murchison, with a slope of (6.3 ± 1.2) × 10^{-5}. (**B**) The expansion of the lower left-hand corner of (A), highlighting the fact that all of the whole rock data deviate to the right of the straight line defined by the metallic fractions. The Hf-W data of ordinary chondrites (*15*) are available on *Science* Online (*19*).

tions of the meteorites define a shallower slope of (7.6 ± 1.3) × 10^{-5}, implying that the silicates formed or equilibrated later than the metals. This line includes Hvittis, which has a much higher Hf/W coupled with a larger W isotopic uncertainty. However, even ignoring this point, the slope (6.0 ± 2.0) × 10^{-5} remains the same within error. This best-fit line extrapolates toward the data for Allende and Murchison, as was found for the magnetic fractions. A combined regression of the data for all the nonmagnetic fractions and the Allende and Murchison whole rocks yields a slope of (6.3 ± 1.2) × 10^{-5} (Fig. 2). The difference in slope between the magnetic (largely metal) and nonmagnetic (largely silicate) fractions corresponds to a time difference of 13.8 ± 5.3 million years.

These data provide evidence for large-scale open-system behavior and mixing. The results for the silicates cannot reflect terrestrial contamination because all four meteorites appear to show the same effect and three are falls collected shortly after impact. There is no sign that a cryptic phase was missed in the analyses; indeed, the mass balance of separated fractions and whole rocks is consistent. Neither are the data explicable by closed-system redistribution. The data for the metals show little sign of reequilibration at a late stage (Fig. 2). Closed-system redistribution should retain chondritic W isotopic compositions for the bulk enstatite chondrites, whereas they display deficits in ^{182}W (−1.7 to −2.3 ε_W) despite having chondritic Hf/W. The ECPB contrasts with Earth, which has chondritic W (*11, 12*), suggesting that there is no connection between these bodies.

Because all four meteorites show the same systematics despite being of different petrographic and metamorphic type, EH4 and EL6, it seems likely that a larger scale open-system phenomenon is involved. Although no explanation is without difficulty, the data can be explained if the metal and silicate fractions differentiated separately and were then mixed in roughly average solar system proportions. This interpretation is consistent with previous studies that presented evidence of a heterogeneous accretion of the ECPB (*8*). The magnetic fraction would represent an early metal segregate, whereas the nonmagnetic (silicate) fraction represents material that continued to equilibrate with a separate chondritic reservoir until 8 to 19 million years after the start of the solar system. Collisions between planetesimals, each with their own enstatite chondrite-like metal and silicate fractions, would cause mixing in roughly chondritic proportions as observed. The enstatite chondrites carry sparse calcium-aluminum–rich inclusions (CAIs) with distinct O isotopic composition (*20*) and evidence of formerly live ^{26}Al (*21*). If much of the silicate represents wreckage from a differentiated planetesimal, diluted by other early solar system dust and debris, with, on average, carbonaceous chondritic W compositions, the rare CAIs would represent a fraction of the material picked up in space before mixing with metal. The fact that CAIs are scarce in enstatite chondrites would be consistent with the late occlusion of this material into the ECPB, ≥ 8 million years after the start of the solar system.

Support for such large-scale remixing on chondrite parent bodies has been found in noble gases. The feldspars in certain chondrites carry noble gas evidence of components that once resided at the surface of a parent body but have subsequently been remixed with other components such that the samples now have a chondritic chemical composition (*22*). Successive differentiation and remixing in chondritic proportions may have been a common result of early destruction and accretion of small bodies.

An alternative explanation is that the W in the silicates selectively equilibrated with a metamorphic fluid with less radiogenic W isotopic composition that passed through the parent bodies without perturbing the metals. There is good evidence for metamorphic alteration in the enstatite chondrites, although the Hf-W data are surprisingly systematic to be the result of such a process.

Finally, it is conceivable that the silicate and metal came from portions of the solar system with distinct initial ^{182}Hf/^{180}Hf. Heterogeneous distributions of radionuclides in the early solar system are supported by ^{26}Al (*21*) data. However, this model fails to explain why the silicate and metal fractions both appear to have been in W isotopic equilibrium with a bulk carbonaceous chondrite-like reservoir. So mixing of separately accreted, differentiated, and disrupted silicate and metal reservoirs would appear to be a likely explanation of the data. Further detailed studies of the achondrites, in particular the aubrites, should find evidence of reservoirs with anomalously radiogenic W for a given Hf/W. The degree to which open-system metamorphic equilibration has affected the systematics needs more thorough evaluation.

Table 1. Hf and W isotopic data. All the W isotopic measurements are normalized to ^{186}W/^{184}W = 0.927633 (*23*). The quoted 2σ errors refer to the least significant figures. The analytical uncertainty for the measured ^{180}Hf/^{184}W ratio varies between 0.1 and 0.5% from sample to sample, and a maximum value of 0.5% is chosen. The $\varepsilon_W = \{[(^{182}W/^{184}W)_{meas}/(^{182}W/^{184}W)_{std}] - 1\} \times 10^4$, the deviations in parts per 10^4 relative to the NIST-3163 W standard, which gives a mean ^{182}W/^{184}W = 0.865000 ± 18 (n = 30). EH4, H4-type enstatite chondrite; EL6, L6-type enstatite chondrite; M-L, metal leachate; M-B, bulk metal; M-R, metal residue; WR, whole rock; NM, nonmagnetic fraction; ppb, parts per billion.

Sample	Hf (ppb)	W (ppb)	^{180}Hf/^{184}W (atomic)	^{182}W/^{184}W ± 2σ error	ε_W ± 2σ error
			EH4		
Abee (Me 2474)					
M-L	38.07	589.7	0.07618	0.864728 ± 21	−3.14 ± 0.24
M-B	46.1	296.7	0.1834	0.864768 ± 22	−2.68 ± 0.26
WR	82.89	136.7	0.7156	0.864800 ± 31	−2.31 ± 0.36
NM-1	113.8	26.2	5.132	0.865182 ± 62	2.10 ± 0.70
NM-2	99.51	23.73	4.948	0.865188 ± 78	2.17 ± 0.90
Indarch (USNM 2835)					
M-L	5.39	195.9	0.03247	0.864752 ± 31	−2.86 ± 0.36
M-B	75.05	235.0	0.3770	0.864796 ± 47	−2.36 ± 0.52
M-R	164.1	281.6	0.6876	0.864859 ± 26	−1.63 ± 0.30
WR-1	112.5	114.4	1.161	0.864813 ± 36	−2.16 ± 0.42
WR-2	104.6	133.3	0.9249	0.864807 ± 34	−2.23 ± 0.40
NM	131.3	29.40	5.269	0.865204 ± 66	2.36 ± 0.76
			EL6		
ALHA81021					
M-L	17.67	508.2	0.04103	0.864767 ± 21	−2.69 ± 0.24
M-B	105.1	132.5	0.9357	0.864923 ± 57	−0.89 ± 0.66
M-R	108.4	122.4	1.045	0.864959 ± 74	−0.47 ± 0.86
NM	138.3	19.74	8.263	0.865380 ± 54	4.39 ± 0.62
Hvittis (Me 1470; USNM 6628)					
M-L	59.19	378.2	0.1847	0.864703 ± 34	−3.43 ± 0.40
M-B	58.7	372.8	0.1858	0.864766 ± 24	−2.71 ± 0.28
WR-1	159	144	1.31	0.864802 ± 29	−2.29 ± 0.34
WR-2	144.3	126.7	1.344	0.864856 ± 62	−1.66 ± 0.72
NM	254.1	20.48	14.64	0.86601 ± 15	11.6 ± 1.8

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