



# Rapid accretion and differentiation of iron meteorite parent bodies inferred from $^{182}\text{Hf}$ – $^{182}\text{W}$ chronometry and thermal modeling

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## ABSTRACT

New high-precision W isotope measurements are presented for 33 iron meteorites from 8 magmatic groups (IC, IIB, IID, IIIB, IIIE, IIIF, I VA and IVB), 2 non-magmatic groups (IAB–IIICD and IIE), and one ungrouped iron (Deep Springs). All magmatic irons have  $\varepsilon^{182}\text{W}$  values that are, within errors, equal to, or less radiogenic than, the Solar System initial of  $-3.47 \pm 0.20$ . A method was developed to correct the measured  $\varepsilon^{182}\text{W}$  values of magmatic iron meteorites for the presence of cosmogenic effects produced during space exposure to galactic cosmic rays. The corrected data provide new constraints on the timing of metal–silicate differentiation in iron meteorite parent bodies, which must have taken place within a few million years ( $<2$  to 6 My) of condensation of calcium–aluminum–rich inclusions (CAIs). Metal–silicate differentiation ages (from  $^{182}\text{Hf}$ – $^{182}\text{W}$  systematics) were combined with parent body sizes (from metallographic cooling rates) into a model of planetesimal heating by  $^{26}\text{Al}$ -decay, to constrain the accretion timescale of iron meteorite parent bodies. Accretion of iron meteorite parent bodies most likely occurred within 1.5 My of the formation of CAIs. The fast accretion times of iron meteorite parent bodies are consistent with dynamical models indicating that these objects may have originated in the terrestrial planet-forming region, where the accretion rates were high. Our W isotopic data for non-magmatic IAB–IIICD and IIE irons provide new constraints for their formation mechanisms. In particular, they support formation of IAB–IIICD iron meteorites by melting during a single collision event dated at 4–7 My after formation of the Solar System.

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## 1. Introduction

Several extant and extinct radiochronometers ( $^{187}\text{Re}$ – $^{187}\text{Os}$ ,  $^{107}\text{Pd}$ – $^{107}\text{Ag}$ ,  $^{53}\text{Mn}$ – $^{53}\text{Cr}$ ) have been used to constrain the time of formation of magmatic iron meteorites (Shen et al., 1996; Smoliar et al., 1996; Chen and Wasserburg, 1996; Carlson and Hauri, 2001; Sugiura and Hoshino, 2003). These systems indicate that accretion, differentiation, and crystallization of iron meteorite parent bodies occurred early, within the first several tens of My of the formation of the Solar System. However, they all have limitations to their application as fine scale chronometers for early Solar System events. Hafnium-182 is an extinct radionuclide which  $\beta^-$  decays into  $^{182}\text{Ta}$  with a half-life of 8.9 My (Vockenhuber et al., 2004). The latter is very unstable ( $t_{1/2} = 115$  d) and rapidly decays to  $^{182}\text{W}$ . The  $^{182}\text{Hf}$ – $^{182}\text{W}$  system is useful to date the relative timing of metal–

silicate differentiation in the early Solar System (Jacobsen and Harper, 1996; Lee and Halliday, 1996; Horan et al., 1998; Yin et al., 2002; Schoenberg et al., 2002; Kleine et al., 2002; Quitté and Birk, 2004; Lee, 2005; Kleine et al., 2005; Scherstén et al., 2006; Markowski et al., 2006a,b) because Hf is lithophile while W is moderately siderophile. If bulk planetesimals had chondritic compositions and metal–silicate differentiation occurred after complete decay of  $^{182}\text{Hf}$ , metallic cores should have chondritic  $^{182}\text{W}$  compositions. If differentiation occurred while  $^{182}\text{Hf}$  was still alive, a deficit in  $^{182}\text{W}$  in cores relative to chondrites should be produced. Thus, by studying the isotopic abundance of  $^{182}\text{W}$  in magmatic iron meteorites, which are thought to represent fragments of planetesimal cores, we can infer the timing of metal–silicate differentiation relative to condensation of refractory CAIs in the protosolar nebula.

Horan et al. (1998) performed the first extensive study of W isotopes in iron meteorites. They showed that magmatic iron meteorites have  $\varepsilon^{182}\text{W}$  values (relative deviation of the ratio of  $^{182}\text{W}$  to a stable W isotope from a terrestrial standard in parts per  $10^4$ ) between  $-5.1$  and  $-3.1$ . Recent studies have shown that some iron meteorites, such as Tlacotepec, have very negative  $\varepsilon^{182}\text{W}$  values ( $-4.4$  to  $-4.0$ ) (Quitté and Birk, 2004; Lee, 2005; Scherstén et al., 2006;

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Markowski et al., 2006a,b), lower than the initial solar value of  $-3.47 \pm 0.20$  defined by CAI and chondrite isochrons (Kleine et al., 2005). Taken at face value, the implication would be that metal-silicate differentiation in these iron meteorite parent bodies predated the formation of CAIs, which goes against the current paradigm that CAIs are the oldest condensed material in the Solar System.

Exposure to galactic cosmic radiation (GCR) can modify the W isotopic compositions of iron meteorites (Masarik, 1997; Leya et al., 2003) through capture of secondary thermal neutrons. This can lower  $\varepsilon^{182}\text{W}$  values and yield false negative ages relative to CAIs (Masarik, 1997; Leya et al., 2003). Markowski et al. (2006b) measured the W isotopic compositions along depth profiles in Grant (IIIB) and Carbo (IID) iron meteorites. They demonstrated that the anomalously low  $\varepsilon^{182}\text{W}$  values in these meteorites were produced by interactions with GCR. Thus in those samples,  $\varepsilon^{182}\text{W}$  cannot be interpreted in terms of  $^{182}\text{Hf}$  decay alone. It is conceivable that the very negative  $\varepsilon^{182}\text{W}$  values measured in Tlacotepec have also been produced by exposure to GCR, given the long exposure age ( $945 \pm 55$  Ma) of this sample (Voshage and Feldmann, 1979). A major challenge in establishing the  $^{182}\text{Hf}$ – $^{182}\text{W}$  system as a reliable chronometer is to find a way to accurately correct for the cosmogenic effect. Knowledge of exposure ages alone is not sufficient because the effect of irradiation by GCR is modulated by the depth of burial in the pre-atmospheric object (Masarik, 1997).

We studied Hf–W systematics in iron meteorites using an improved method, allowing variations of less than 0.1  $\varepsilon$ -unit on  $^{182}\text{W}$  to be resolved (Foley et al., 2005; Qin et al., 2007; Qin et al., 2008). Increasing the precision of W isotopic measurements in iron meteorites can improve the time resolution of core segregation processes, and provide a potential means of correcting cosmogenic and nucleosynthetic effects. Several aspects of our approach distinguish this work from previous studies:

- (i) This study focused on a subset of samples with well characterized  $^{41}\text{K}$ – $^{40}\text{K}$  exposure ages (Voshage and Feldmann, 1979; Voshage et al., 1983; Voshage, 1984).
- (ii) A precision of  $\sim \pm 0.1$  or better on  $\varepsilon^{182}\text{W}$  was achieved, which is comparable to or better than the most recent studies (Scherstén et al., 2006; Markowski et al., 2006a), but represents a  $\sim 2$ – $5$  fold improvement compared to earlier efforts (Jacobsen and Harper, 1996; Lee and Halliday, 1996; Horan et al., 1998; Yin et al., 2002; Schoenberg et al., 2002; Kleine et al., 2002; Quitté and Birck, 2004; Lee, 2005).
- (iii) A new method is presented for estimating  $\varepsilon^{182}\text{W}$  of magmatic iron meteorites prior to GCR exposure.
- (iv) The time of core–mantle differentiation, as inferred from  $^{182}\text{Hf}$ – $^{182}\text{W}$  systematics, was used in a thermal model of planetesimal differentiation to constrain the time of accretion of iron meteorite parent bodies.

## 2. Methods

The methods used for purifying W and analyzing its isotopic composition have been presented in detail elsewhere (Foley et al., 2005; Qin et al., 2007) and will be briefly reviewed here. Iron meteorite samples were first leached in 11 N HCl–1 N HF to remove surface-sited terrestrial contamination from various sources. The cleaned samples were then dissolved in aqua regia and evaporated to dryness and redissolved in 11 N HCl. Chemical separation was achieved by passing the samples through one cation exchange column and several anion-exchange columns (Qin et al., 2007). This protocol can accommodate sample sizes up to 1.7 g so that large quantities of clean W (usually 500–2000 ng) can be retrieved for isotopic analyses. The final W solutions were analyzed on a Micromass Isoprobe multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS) located at the Field Museum, Chicago. The measurements were normalized to  $^{186}\text{W}/^{183}\text{W} = 1.98594$  (Völkening et al., 1991) using the

exponential law. This law describes well the fractionation occurring in a MC-ICPMS (Maréchal et al., 1999). The NIST 3163 W reference material was used as the W isotope standard. Both the samples and standards were run at ion intensities of  $3\text{--}8 \times 10^{-11}$  A for  $^{184}\text{W}$ , obtained with 30–80 ppb solutions. The sample and standard solutions were introduced into the ICP source in the form of aerosols using an Aridus desolvating nebulizer. The W concentration of the sample was always matched with that of the bracketing standard within 3% because we noticed that a mismatch in the W concentration can affect the accuracy of the isotope measurements (Qin et al., 2007). The sample measurements were interspersed between those of the standard, and the internally normalized W isotope composition of the sample was corrected using the mean of the two bracketing standard analyses. All isotope ratios are presented using the  $\varepsilon$  notation, always using  $^{183}\text{W}$  as the denominator isotope. A total of 13–20 ( $n$ ) repeats were obtained for each sample and were used to calculate averages and 95% confidence intervals as follows,

$$\varepsilon = \frac{1}{n} \sum_{k=1}^n \varepsilon_k \pm \sqrt{\frac{1}{n-1} \sum_{k=1}^n (\varepsilon_k - \bar{\varepsilon})^2 \frac{t_{0.95, n-1}}{\sqrt{n}}} \quad (1)$$

where  $t_{0.95, n-1}$  is student's  $t$ -value corresponding to a two-sided 95% confidence interval for  $n-1$  degrees of freedom.

The absolute  $^{182}\text{W}/^{183}\text{W}$  and  $^{184}\text{W}/^{183}\text{W}$  ratios (after normalization to  $^{186}\text{W}/^{183}\text{W} = 1.98594$ ) of the NIST 3163 W reference material averaged over a period of two years are  $1.85174 (\pm 43, 2\sigma)$  and  $2.14123 (\pm 63, 2\sigma)$ , respectively. These values agree within error with those reported previously by negative thermal ionization mass spectrometry ( $1.85128 \pm 35$  and  $2.14078 \pm 13$ ) and MC-ICPMS ( $1.85163 \pm 8$  and  $2.14076 \pm 7$ ) (Völkening et al., 1991; Lee and Halliday, 1995).

## 3. Results

### 3.1. $\varepsilon^{182}\text{W}$ results

Iron meteorites from both magmatic (IC, IIAB, IID, IIIAB, IIIE, IIIF, I VA and IVB) and non-magmatic (IAB–IIICD and IIE) groups were studied (Table 1). All samples show deficits in  $\varepsilon^{182}\text{W}$  of  $-4.2$  to  $-2.3$  relative to the terrestrial W reference NIST 3163, a proxy for the composition of the bulk silicate Earth (Fig. 1). These values are also significantly lower than those measured in bulk chondrites ( $-1.9 \pm 0.2$ ) (Yin et al., 2002; Schoenberg et al., 2002; Kleine et al., 2004). This range of variation is consistent with previous work, and demonstrates that  $^{182}\text{Hf}$  was alive at the time of metal-silicate differentiation in these meteorites (Jacobsen and Harper, 1996; Lee and Halliday, 1996; Horan et al., 1998; Yin et al., 2002; Schoenberg et al., 2002; Kleine et al., 2002; Quitté and Birck, 2004; Lee, 2005; Kleine et al., 2005; Scherstén et al., 2006; Markowski et al., 2006a). Resolvable isotopic variations are present both within and between iron meteorite groups.

Some of the samples measured in this study have also been analyzed in previous work, including Nocolche (IC) (Scherstén et al., 2006), Arispe (IC) (Lee, 2005; Scherstén et al., 2006; Markowski et al., 2006a), Bendego (IC) (Scherstén et al., 2006), El Burro (IIA) (Scherstén et al., 2006), Carbo (IID) (Markowski et al., 2006a,b), Henbury (IIIAB) (Horan et al., 1998; Scherstén et al., 2006; Markowski et al., 2006a), Grant (IIIB) (Lee, 2005; Markowski et al., 2006b), Nelson County (IIIF) (Markowski et al., 2006a), Duchesne (IVA) (Scherstén et al., 2006), Tawallah Valley (IVB) (Horan et al., 1998; Markowski et al., 2006a), Cape of Good Hope (IVB) (Horan et al., 1998; Lee, 2005; Scherstén et al., 2006; Markowski et al., 2006a), Santa Clara (IVB) (Markowski et al., 2006a), Hoba (IVB) (Scherstén et al., 2006), Tlacotepec (IVB) (Horan et al., 1998; Quitté and Birck, 2004; Lee, 2005; Kleine et al., 2005; Scherstén et al., 2006; Markowski et al., 2006a), and Watson (IIE) (Snyder et al., 2001; Markowski et al., 2006a). There is good agreement with the present work except for Tlacotepec (Kleine et al., 2005) and Nocolche (Scherstén et al., 2006) that can be explained by differences in the degree of shielding from GCR.

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