

HAFNIUM-TUNGSTEN ISOTOPE SYSTEMATICS OF BULK CHONDRITES. J. L. Hellmann¹ and R. J. Walker¹, ¹Department of Geology, University of Maryland, College Park, Maryland, 20742, USA (hellmann@umd.edu).

Introduction: The short-lived ^{182}Hf - ^{182}W system ($t_{1/2} \sim 8.9$ Myr) is widely used for constraining the timing of metal-silicate differentiation of planetesimals [e.g., 1] (i.e., formation of iron meteorites) as well as for high temperature thermochronology of chondrites and their components [e.g., 2-5]. Importantly, ^{182}W model ages of early metal-silicate segregation of iron meteorites strongly depend on the Hf/W ratio and the associated W isotopic composition estimated for their bulk parent bodies and their precursor materials. To date, all studies have assumed that iron meteorite parent bodies evolved with a Hf/W ratio similar to that of carbonaceous chondrites, samples that likely formed in the outer solar system beyond the orbit of Jupiter. However, a recent study concluded that the different ordinary chondrite parent bodies, which originate from the inner solar system, evolved with distinct Hf/W ratios [2]. Furthermore, it was inferred that the ordinary chondrite precursor reservoir, prior to nebular metal-silicate fractionation, exhibited a significantly lower Hf/W ratio than the value determined for carbonaceous chondrites [2]. This, in turn, suggests that W model ages of non-carbonaceous (NC) iron meteorites originating from the inner solar system may be too old.

To address this issue and further explore the variability of Hf-W isotope systematics of different nebular reservoirs, we determine W isotope compositions and $^{180}\text{Hf}/^{184}\text{W}$ ratios of bulk enstatite, ordinary, and carbonaceous chondrites. In the future course of this study, we will considerably increase the number of samples from all major chondrite classes, which will tighten the constraints on the timing of planetesimal accretion and differentiation, and improve our understanding about the chemical evolution of the early solar nebula. In addition to this, we will gain insights about the distribution of metal on the sample scale, and assess the level of Hf/W heterogeneity in individual chondrites in comparison to their parent bodies.

Samples and analytical methods: Five bulk chondrites were investigated: St. Mark's (EH5), Richardton (H5), Saratov (L4), Allende (CV3), and Murchison (CM2). The enstatite and ordinary chondrites (1-2 g pieces) were crushed and ~1 g powder aliquots were taken for analysis of Hf and W concentrations, and W isotope composition. Additionally, 0.5 g of the Allende powder MS-A (~100 g), 4 g of Murchison (~9 g), and 0.5-1 g of the terrestrial rock standards BHVO-2 and JB-2 were processed similarly to the enstatite and ordinary chondrites

following previously established procedures [e.g., 2, 3]. In brief, sample powders were dissolved in HF-HNO₃-HClO₄, and aliquots were taken for determination of Hf and W concentrations by isotope dilution. From the remaining sample solution, W was separated using a two-stage anion exchange chromatography procedure, and W isotope compositions were measured using the *Neptune Plus* MC-ICPMS at the University of Maryland. Results are reported in $\epsilon^{182}\text{W}$ as the parts-per-10⁴ deviation from the $^{182}\text{W}/^{184}\text{W}$ of bracketing terrestrial standards.

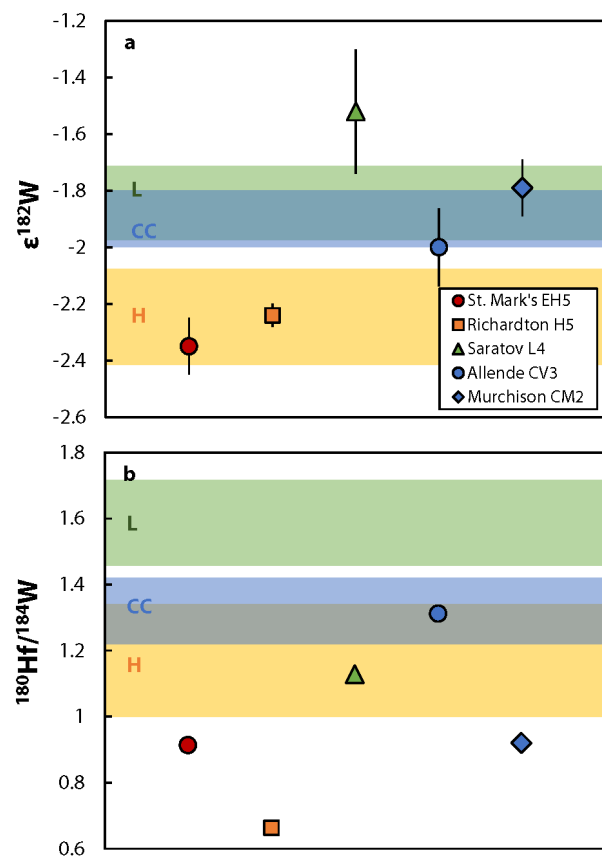


Figure 1. Tungsten isotopic compositions (a) and Hf/W ratios (b) of bulk enstatite (red), ordinary (H – orange, L – green), and carbonaceous (CC – blue) chondrites. Colored bars represent the inferred compositions of the bulk parent bodies, respectively [2, 6].

Results: Analyses of both BHVO-2 and JB-2 yielded W isotopic compositions and Hf/W ratios similar to previously published data [e.g., 4, 7], demonstrating accuracy of our isotope measurements. The Hf-W isotope systematics of Allende are also

indistinguishable from values reported by previous studies [3, 4], and agree with the W isotope composition and Hf/W ratio inferred for the carbonaceous chondrite reservoir (Fig. 1). By contrast, while the W isotope composition of Murchison is similar to that of Allende, its Hf/W ratio is significantly lower. Both ordinary chondrites exhibit Hf/W ratios that are lower than the values inferred for their parent bodies. Whereas the W isotopic composition of Richardton (H5) matches the inferred value of the H chondrite parent body, the W isotopic composition of Saratov (L4) is elevated relative to that of the L chondrite parent body (Fig. 1). The EH5 chondrite St. Mark's displays the lowest W isotope composition of all chondrites analyzed in this study, and also its Hf/W ratio is among the lowest values. Importantly, St. Mark's Hf-W isotope systematics agree very well with previously published Hf-W data for bulk EH chondrites [8].

Discussion: Metal-silicate heterogeneity among chondrites. Chondrites derive from a multitude of parent bodies that formed in distinct regions of the accretionary disk and under vastly different conditions. Ultimately, nebular and parent body processes resulted in largely different metal-to-silicate ratios among the chondrite classes and their sub-groups. While most carbonaceous chondrites contain little or no metal, enstatite and ordinary chondrites exhibit variable, and in some cases large proportions of metal. Given that siderophile W is predominantly hosted in metal, whereas lithophile Hf is hosted in silicate, heterogeneous distribution of metal grains may result in largely different Hf/W ratios also among samples from the same chondrite group. Thus, the significantly lower Hf/W ratios of some of the bulk chondrites might reflect the overabundance of metal relative to the average parent body composition. In the future, we will further quantify the variability of Hf/W ratios among bulk chondrites within the different chondrite sub-groups.

Implications from low Hf/W ratio of enstatite chondrites. The very unradiogenic W isotope composition of St. Mark's, in combination with its low Hf/W ratio (Fig. 1), suggests that the EH chondrite parent body evolved with a Hf/W ratio that was significantly lower than that of carbonaceous chondrites. If this low Hf/W ratio applies not only to an enstatite chondrite parent body, but also to early differentiated planetesimals that accreted in the inner solar system, the metal-silicate segregation ages of the respective iron meteorites would shift towards younger ages by up to ~0.7 Myr (Fig. 2). If true, some NC iron meteorites (*i.e.*, IVA, IIIIE) from the inner solar system would exhibit comparatively young crystallization ages of ~2-3 Ma after formation of Ca-Al-rich inclusions (CAIs), similar to most carbonaceous (CC) iron

meteorites from the outer solar system [1]. By contrast, some of the oldest NC iron meteorites (*i.e.*, IC, IIAB) only shift marginally towards younger ages (by ~0.1-0.2 Myr), with the result that they remain significantly older than all CC iron meteorites (Fig. 2). This is a critical issue because based on these iron meteorite ages, it has been argued that the early solar nebula remained spatially separated into an inner (NC) and outer (CC) disk reservoir between ~1 and ~4 Ma after CAI formation, associated with the early and rapid growth of Jupiter's core. Ultimately, although some NC iron meteorites may be younger than previously reported [9], utilizing the low Hf/W ratio of enstatite chondrites for calculating NC iron meteorite crystallization ages is not in contrast to the early spatial separation of the NC and CC nebular reservoirs.

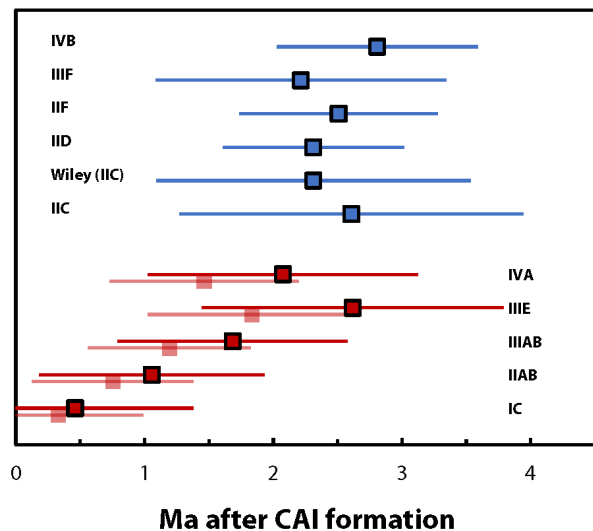


Figure 2. Model ages of metal-silicate segregation in CC (blue) and NC (red) iron meteorite parent bodies. Carbonaceous iron meteorite model ages were calculated assuming a carbonaceous chondrite-like Hf-W isotopic evolution. Model ages of NC iron meteorites were calculated assuming both carbonaceous chondrite-like (transparent symbols) and enstatite chondrite-like (solid symbols) Hf-W isotopic evolution. Tungsten isotopic compositions of iron meteorites used for age calculations are from [9].

References: [1] Kruijer T. S. et al. (2014) *Science*, 344, 1150-1154. [2] Hellmann J. L. et al. (2019) *GCA*, 258, 290-309. [3] Kruijer T. S. et al. (2014) *EPSL*, 403, 317-327. [4] Budde G. et al. (2016) *PNAS*, 113, 2886-2891. [5] Archer G. J. et al. (2019) *GCA*, 245, 556-576. [6] Kleine T. et al. (2004) *GCA*, 68, 2935-2946. [7] Tappe et al. (2020), *EPSL*, 547, 116473. [8] Lee D.-C. and Halliday A. N. (2000) *Science*, 288, 1629-1631. [9] Kruijer T. S. et al. (2017) *PNAS*, 114, 6712-6716.