

Hf-W CHRONOMETRY OF ORDINARY CHONDRITES AND THE TIMING OF SOLAR NEBULA METAL-SILICATE FRACTIONATION.

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Introduction: Ordinary chondrites derive from three different parent bodies (H, L and LL) that, upon their accretion underwent thermal metamorphism and subsequent cooling. A key characteristic of ordinary chondrite groups is that they have distinct metal-to-silicate ratios and bulk Hf/W [1], which may suggest that the accretion conditions were different for each parent body. Dating ordinary chondrites using the short-lived Hf-W chronometer ($t_{1/2} \sim 8.9$ Myr) not only provides insights into the thermal evolution of their parent bodies [e.g., 2], but also into the mechanism and timescales involved in the accretion of these bodies in the solar nebula. For instance, Hf-W chronometry of H chondrites indicates that their time-integrated Hf/W ratio is lower than that of carbonaceous chondrites, pointing to a process that fractionated Hf and W in the solar nebula [2]. With the aim of better understanding the timing and nature of such nebular Hf/W fractionations, we initiated a Hf-W isochron study on separates of equilibrated L and LL chondrites of petrologic types 4 to 6. Such internal Hf-W isochrons not only provide the initial $^{182}\text{Hf}/^{180}\text{Hf}$ of a chondrite—which records the time of Hf-W closure during thermal metamorphism—but also precisely constrains its initial $^{182}\text{W}/^{184}\text{W}$ value. Here we present our first Hf-W results for 3 L chondrites (Tennasilm, L4; Saratov, L4; Kunashak, L6) as well as high-precision $\epsilon^{182}\text{W}$ metal data for several L and LL chondrites.

Methods: The samples were gently crushed and sieved, and chondrite metals were removed using a handmagnet. The silicate fractions were separated into weakly magnetic (WM) and non-magnetic (NM) components. After digesting the chondrite fractions in $\text{HNO}_3\text{-HCl-HF}$ (metals) or HF-HNO_3 (silicates) on a hotplate, 2-10% aliquots were taken to determine Hf and W concentrations by isotope dilution. For unspiked samples, W was separated by anion exchange chromatography [3] and W isotope compositions were measured on a Neptune *Plus* MC-ICPMS at Münster. Results are reported in $\epsilon^{182}\text{W}$ as the parts-per- 10^4 deviation from the $^{182}\text{W}/^{184}\text{W}$ of terrestrial bracketing standards. In comparison to previous studies [e.g., 1], both the silicate and particularly the metal data are considerably more precise with an external reproducibility on $\epsilon^{182}\text{W} \sim 0.05 \epsilon$ for most metal samples (95% conf.).

Results: The metal separates show strong deficits in $\epsilon^{182}\text{W}$ ranging from *ca.* -3.3 to *ca.* -2.8 for L chondrites and *ca.* -3.1 to *ca.* -2.3 for LL chondrites, in both cases consistent with the very low $^{180}\text{Hf}/^{184}\text{W}$ of these fractions ($\sim 0.01\text{-}0.04$). In contrast, the WM and NM fractions of the L chondrites show more radiogenic $\epsilon^{182}\text{W}$ values coupled with higher Hf/W ratios, resulting in a total spread in $\epsilon^{182}\text{W}$ of $\sim 5 \epsilon$ -units for Tennasilm (L4) and Saratov (L4) and $\sim 28 \epsilon$ -units for Kunashak (L6). The Hf-W data of the three chondrites yield well defined isochrons with precise slopes, resulting in Hf-W isochron ages of ~ 3 Myr (L4) Myr and ~ 9 Myr (L6) after CAI. The isochron intercepts are essentially defined by the metal data points of the chondrites which provide precise estimates of their initial $\epsilon^{182}\text{W}$.

Discussion: *Thermal history of the L chondrite parent body.* Our results suggest that L6 chondrites have younger Hf-W ages than L4 chondrites, implying higher metamorphic peak temperatures and slower cooling in chondrites of higher petrologic type. A similar systematic was previously observed for H chondrites, and would be consistent with a concentrically layered, ‘onion-shell’ structure for the L chondrite parent body after it had undergone thermal metamorphism followed by subsequent cooling [2,4]. However, additional Hf-W ages for a more comprehensive set of L chondrites are necessary to fully assess the initial structure of the L chondrite parent body.

Hf-W evolution of chondrite reservoirs. In a diagram of initial $\epsilon^{182}\text{W}$ vs. time, the L4 chondrites, together with H4 chondrites [2] and Allende (CV3) chondrules and matrix [5], cluster around a common initial $\epsilon^{182}\text{W}$ and Hf-W age corresponding to $\sim 2\text{-}3$ Myr after CAI. This observation suggests that different ordinary and carbonaceous chondrite groups evolved with a uniform Hf/W ratio up to that point in time. In contrast, the initial $\epsilon^{182}\text{W}$ of Kunashak (L6) is significantly higher than that of H6 chondrites [2], but their Hf-W ages are similar ($\sim 9\text{-}10$ Myr). Thus, these L and H chondrites had evolved with distinct Hf/W ratios, most likely established by a nebular metal-silicate fractionation just prior to parent body accretion. Further evidence for such a Hf/W fractionation among different ordinary chondrite groups comes from the relatively elevated $\epsilon^{182}\text{W}$ of up to *ca.* -2.4 obtained for the LL metals, which suggest that the LL chondrites derive from a reservoir with elevated Hf/W relative to L and H chondrites. Of note, the distinct Hf/W ratios inferred from the Hf-W isotopic evolution are consistent with the variable measured Hf/W ratios of ordinary chondrite groups [1]. Collectively, the Hf-W data provide evidence for a nebular metal-silicate fractionation just prior to accretion of ordinary chondrite parent bodies. However, additional Hf-W isochron data of L and LL chondrites are needed to fully assess the significance and to precisely date the timing of these nebular fractionation event.

References: [1] Kleine T. et al. 2009. *GCA* 73:5150-5188. [2] Kleine T. et al. 2008. *EPSL* 270:106-118. [3] Kruijer T. S. et al. 2014. *EPSL* 403:317-327. [4] Tieloff M. et al. 2003. *Nature* 422:502-506. [5] Budde G. et al. 2016. *PNAS* 113:2886-2891.