**CONSTRAINING THE TIMESCALE OF SOLAR NEBULA METAL-SILICATE FRACTIONATION USING Hf-W CHRONOMETRY OF ORDINARY CHONDRITES.** J.L. Hellmann[1], T.S. Kruijer[1] and T. Kleine[1], [1]University of Münster, Institut für Planetologie, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany (jan.hellmann@uni-muenster.de).

**Introduction:** Ordinary chondrites derive from at least three different parent bodies (H, L and LL) that exhibit different metal-to-silicate ratios. Given that chondrule formation was associated with metal-silicate fractionation [*e.g.,* 1], it seems likely that the distinct metal-to-silicate ratios of ordinary chondrite subgroups also were established during chondrule formation. Moreover, as chondrules probably accreted into chondrite parent bodies shortly after their formation [1,2], chondrule formation, metal-silicate fractionation and chondrite parent body accretion all may be directly related to each other. However, the timing of metal-silicate fractionation among ordinary chondrites is not known, and so it remains unclear whether or not this process was coeval to chondrule formation.

Here we use the short-lived $^{182}$Hf-$^{182}$W chronometer ($t_{1/2}$ ~8.9 Myr) to investigate the timescale of metal-silicate fractionation among ordinary chondrites. Owing to their distinct metal-to-silicate ratios, ordinary chondrites have different bulk Hf/W, and so each subgroup should have followed distinct Hf-W isotopic evolutionary paths, determined by the time of metal-silicate fractionation and the Hf/W ratio that results.

Ordinary chondrites exhibit a range of metamorphic conditions, from unequilibrated (petrologic type 3) to equilibrated samples (types 4–6). A prior study has shown that the Hf-W ages of equilibrated H chondrites become increasingly younger with increasing petrologic type, consistent with an 'onion shell' structure of the H chondrite parent body, in which H6 chondrites are located at greater depth and cooled slower than H4 chondrites [3,4]. As Hf-W isochrons not only provide the initial $^{182}$Hf/$^{180}$Hf of a chondrite – which records the time of Hf-W closure during thermal metamorphism [3] – but also constrain its initial $^{182}$W/$^{184}$W, the Hf-W isotopic evolution of ordinary chondrite groups can be examined through isochrons for samples of different petrologic type from a given parent body. Here we report Hf-W isochrons for equilibrated H, L and LL chondrites of petrologic types 4 to 6, and use these data to assess the timescales of metal-silicate fractionation and parent body accretion. In addition, these data provide insights into the thermal history and structure of ordinary chondrite parent bodies.

**Samples and Methods:** A total of 10 ordinary chondrites was studied, including three L chondrites (Tennasilm, L4; Saratov, L4; Kunashak, L6), four LL chondrites (NWA 7545, LL4; NWA 6935, LL5; Tuxtuac, LL5; NWA 5755, LL6), and new data for fractions of three H chondrites (Ste. Marguerite, H4; ALH 84069, H5; Estacado, H6) studied previously [3]. The samples were crushed to different grain sizes (40 and 250 µm), and then subdivided into fractions of different magnetic susceptibility using a hand magnet. This resulted in metal separates (M) and several silicate-rich fractions ranging from weakly magnetic (WM) to nonmagnetic (NM). After digesting the chondrite fractions in $HNO_3$-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 [5] and W isotope compositions were measured on a Neptune *Plus* MC-ICPMS at Münster. Results are reported in $\varepsilon^{182}$W as the parts-per-$10^4$ deviation from the $^{182}$W/$^{184}$W of bracketing terrestrial standards. Compared to previous work [*e.g.*, 3], both the silicate and especially the metal data are considerably more precise with an external reproducibility of ±0.05 $\varepsilon^{182}$W for most metal samples (95% conf.).

**Results:** The metal separates show deficits in $\varepsilon^{182}$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 $^{180}$Hf/$^{184}$W of these fractions (<0.04). In contrast, the WM and NM fractions of the L and LL chondrites show more radiogenic $\varepsilon^{182}$W values coupled with higher Hf/W ratios, resulting in total spreads in $\varepsilon^{182}$W of up to ~28 ε-units (Fig. 1).

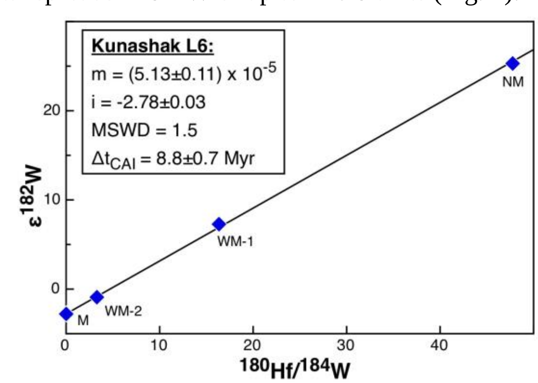


**Fig. 1.** $^{182}$Hf-$^{182}$W isochron for the Kunashak (L6). m = initial $^{182}$Hf/$^{180}$Hf. i = initial $\varepsilon^{182}$W.

**Discussion**: *Hf-W isochrons.* The Hf-W data of all studied L and H chondrites yield well-defined isochrons and provide precise initial $^{182}$Hf/$^{180}$Hf and Hf-W ages relative to CAIs (see Fig. 1 for an example). Note that the isochron intercepts are essentially defined by the metal data points of the chondrites, which provide precise estimates of their initial $\varepsilon^{182}$W. By contrast, for most LL chondrites, well-defined Hf-W isochrons are only obtained for the silicate dominated WM and NM fractions, whereas the LL metals typically plot significantly below the intercept $\varepsilon^{182}$W defined by the silicate fractions (see Fig. 2 for an example). This offset is most likely attributable to an earlier Hf-W closure for the LL metals compared to the silicate-dominated WM and NM fractions. This is not unexpected, because the metal content in LL chondrites is quite low [6], and so large metal grains probably were not in direct contact with high-Ca pyroxenes (the major host of Hf that was originally hosted in nearly metal-free chondrules), hampering efficient exchange of radiogenic $^{182}$W, and leading to a higher closure temperature of the metals. Irrespective of this, the silicate-dominated fractions of the LL chondrites define precise Hf-W isochrons.

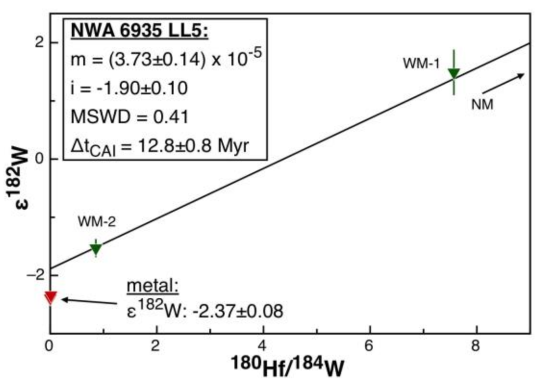


**Fig. 3.** $^{182}$Hf-$^{182}$W isochron for the NWA 6935 LL5 chondrite. Data of metal separates were excluded from isochron regression. m = initial $^{182}$Hf/$^{180}$Hf. i = initial $\varepsilon^{182}$W.

*Thermal history of ordinary chondrite parent bodies.* Our results show that type 6 ordinary chondrites generally have younger Hf-W ages than type 4 samples, implying slower cooling in chondrites of higher petrologic types. These systematic variations are consistent with a concentrically layered 'onion-shell' structure of chondrite parent bodies after they had undergone thermal metamorphism followed by subsequent cooling, as previously suggested for H chondrites [3, 4]. However, additional Hf-W ages for a more comprehensive set of L and LL chondrites are necessary to fully assess the initial structure of their parent bodies.

*Hf-W evolution of chondrite reservoirs.* In a plot of initial $\varepsilon^{182}$W *vs.* time (Fig. 3), all type 4 chondrites (including H, L and LL samples) cluster around a common initial $\varepsilon^{182}$W and Hf-W age of ~3-4 Myr after CAIs. In contrast, for type 6 chondrites the initial $\varepsilon^{182}$W are variable and decrease from LL6 to L6 to H6, yet they all have similar Hf-W ages of ~9–11 Myr after CAIs. Thus, different groups of ordinary chondrites evolved with distinct Hf/W ratios, where LL chondrites are characterized by the highest and H chondrites by the lowest Hf/W. This is consistent with the variable silicate-to-metal ratios of ordinary chondrites, which also decrease in the order LL>L>H, indicating that the distinct Hf/W ratios of the ordinary chondrites most likely result from metal-silicate fractionation. As the Hf-W evolution lines for each ordinary chondrite group intersect with each other at ~2–3 Myr after CAIs (Fig. 3), the distinct bulk Hf/W of the H, L, and LL chondrite reservoirs were established at this time. Prior to this event the primitive ordinary chondrite reservoir(s) first evolved with a uniform Hf/W ratio, which was similar to the ratio observed for H chondrites. This is consistent with the solar Fe/Si ratio of H chondrites [7] and suggests that the higher Hf/W and silicate-to-metal ratios of the L and LL chondrites compared to H chondrites reflect the loss of metal.

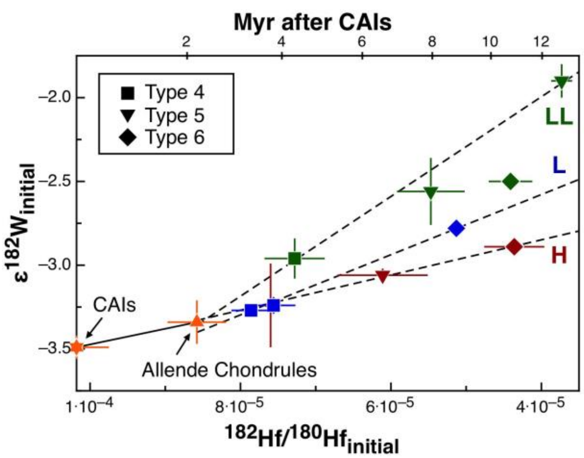


**Fig. 2.** Tungsten isotope evolution diagram for H (red), L (blue) and LL chondrites (green). Regression-derived evolution lines (*dashed*) show that each chondrite group evolved with a distinct time-integrated $^{180}$Hf/$^{184}$W after ~2-3 Myr after CAIs. Also shown are data points for CAIs [5] and for Allende matrix and chondrule separates [1].

The timescale of metal-silicate fractionation among ordinary chondrites is remarkably consistent with the Hf-W age of Allende (CV3) chondrules and matrix [1] (Fig. 3) as well as most Al-Mg ages of chondrules (~2 Myr after CAIs) [*e.g.*, 8]. Collectively, our results thus indicate that chondrule formation, nebular metal-silicate fractionation and chondrite parent body accretion were coeval at *ca.* 2-3 Myr after CAI formation.

**References:** [1] Budde G. et al. (2016) *PNAS*, *113*, 2886–2891. [2] Alexander C.M.O. et al. (2008) *Science*, *320*, 1617–1619. [3] Kleine T. et al. (2008) *EPSL*, *270*, 106–118. [4] Trieloff M. et al. (2003) *Nature*, *422*, 502–506. [5] Kruijer T.S. et al. (2014) *EPSL*, *403*, 317–327. [6] Kong P. and Ebihara M. (1996) *EPSL*, *137*, 83–93. [7] Palme H. et al. (2014) *in ToG (vol. 2.2)*, 15–36. [8] Kita N.T. and Ushikubo T. (2012) *MAPS*, *47*, 1108–1119.