CHRONOLOGY OF MELTING AND DIFFERENTIATION ON THE UREILITE PARENT BODY INFERRED FROM Hf-W SYSTEMATICS. G. Budde[1], T. S. Kruijer[1], M. Fischer-Gödde[1], A. J. Irving[2], and T. Kleine[1]. [1]Institut für Planetologie, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Straße 10, 48149 Münster, Germany (gerrit.budde@uni-muenster.de). [2]Department of Earth and Space Sciences, University of Washington, Seattle, WA 98195, USA.

Introduction: Ureilites are ultramafic achondrites consisting mainly of olivine and pyroxene with interstitial graphite and metal. They represent mantle residues of a partially melted, carbon-rich asteroid, left behind after extraction of both metallic and basaltic partial melts [*e.g.*, 1]. As such, ureilites can provide unique insights into the early stages of planetary melting and differentiation. The chronology of ureilites and the timescale of melting and differentiation in the ureilite parent body (UPB) are poorly constrained. To date the most precise chronological constraints are provided by Al-Mg and Mn-Cr ages for feldspathic clasts from two polymict ureilites [2]. These ages (~5 Ma after CAI) provide a minimum estimate for the timing of UPB differentiation and more specifically may reflect the time of basaltic melt extraction on the UPB or, alternatively, protracted cooling of basaltic melts within the crust of the UPB some time after melt extraction [3].

The short-lived Hf-W chronometer ($t_{1/2}$ = 8.9 Ma) is well-suited to investigate the timescales of planetary differentiation, and especially of core formation [*e.g.*, 4]. Lee et al. [5] reported the first Hf-W data for ureilites, demonstrating that ureilites are characterized by ^{182}W deficits relative to chondrites, consistent with an early differentiation of the UPB. Although that study reported variable $^{182}W/^{184}W$ for ureilites—corresponding to a total spread in Hf-W model ages of ~10 Ma—these differences were not resolved, making the Hf-W age of UPB differentiation uncertain. In order to better constrain the timescale of UPB differentiation we initiated a high-precision W isotope study on a comprehensive set of ureilite specimens (from Northwest Africa and Antarctica) and present here our results for 12 monomict ureilites. To gain further insights into the history of metal in the ureilites, the Hf-W data are supplemented by highly siderophile element (HSE) concentration data.

Methods: Bulk ureilite samples (~1 g) were carefully cleaned, powdered in an agate mortar and digested in Savillex beakers using HF–HNO_3. Small aliquots were taken for the determination of HSE concentrations and Hf and W concentrations by isotope dilution. The remaining sample solution was further treated with inverse aqua regia in Carius tubes at 230 °C to destroy abundant carbon compounds. Methods for the separation of W by anion exchange chromatography and the determination of Hf/W followed [6] and [7].

The W isotope measurements were performed on the Neptune *Plus* MC-ICPMS at the Institute for Planetology at the University of Münster (see [6] for details). The W isotope data are reported in $\varepsilon^{18i}W$ as the parts per 10^4 deviation from terrestrial $^{18i}W/^{184}W$. The accuracy and precision of the W isotope measurements were monitored by repeated analyses of the terrestrial DTS-2B standard, which was processed together with the ureilites. The DTS-2B measurements yielded a mean $\varepsilon^{182}W = 0.03 \pm 0.07$ (2 s.d., n=22) for ~30 ng W consumed per analysis.

The HSE aliquots were purified by cation exchange chromatography and the isotope dilution measurements were made on the XSeries 2 Q-ICPMS in Münster.

Results: All investigated ureilites have subchondritic Hf and W concentrations and $^{180}Hf/^{184}W$ (<0.1 for most samples). The new W isotope data reveal resolved differences in present-day $\varepsilon^{182}W$ values of the ureilites, which range from *ca.* –3.2 to *ca.* –2.8. Fig. 1 shows that there is no obvious correlation between $\varepsilon^{182}W$ and $^{180}Hf/^{184}W$, however. All investigated ureilites exhibit terrestrial $^{183}W/^{184}W$, indicating that nucleosynthetic W isotope anomalies are absent in these samples. The measured $\varepsilon^{182}W$ values can therefore be interpreted in terms of chronology.

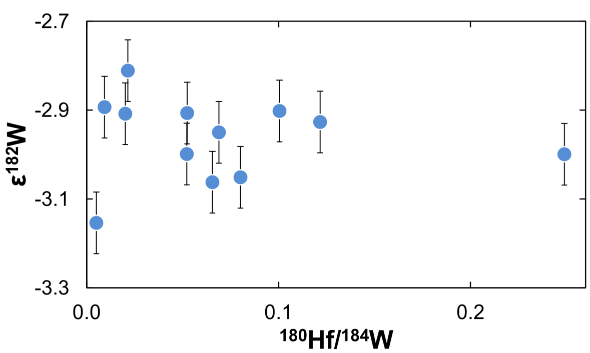

Fig. 1. Hf-W isochron diagram for ureilites.

The ureilites investigated for this study have subchondritic Pd/Ir between ~0.2 and ~0.4, within the typical range of most ureilites [8]. Fig. 2 shows that there is no correlation between $\varepsilon^{182}W$ and Pd/Ir, indicating that there is no simple link between HSE fractionation and timing of metal-silicate fractionation. On the basis of HSE systematics, Rankenburg et al. [8] inferred the presence of two distinct metal components in the ureilites, which were variably mixed during ureilite petrogenesis. Fig. 2 shows that such mixing processes do not seem to have been responsible for generating the observed variability in ε^{182}W values.

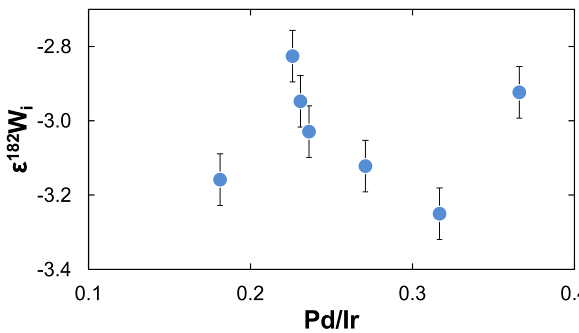

Fig. 2. Initial ε^{182}W *vs.* Pd/Ir for ureilites.

Discussion: The depletions in W and Hf relative to chondrites indicate that ureilites lost both a W-bearing metallic melt as well as a Hf-bearing silicate melt. As is evident from the low Hf/W of most ureilites, extraction of Hf seems to have been more efficient than that of W. Tungsten probably was strongly partitioned into a C-rich metallic liquid, which was only partially extracted and is present today as grain boundary metal [9]. Given the evidence for Hf/W fractionation associated with both metal and silicate melting in the UPB, the W isotope data can potentially constrain the timing of both melting events.

Perhaps the tightest time constraint is given by the lowest ε^{182}W value observed among the ureilites, because this value provides a strict upper limit for the onset of melting and metal-silicate separation in the UPB. The lowest initial ε^{182}W among the investigated ureilites is *ca.* –3.25, corresponding to a Hf-W model age of ~2 Ma after CAI formation, indicating that melting started within the first ~2 Ma of the solar system. Such early melting would be consistent with ^{26}Al being the dominant heat source for differentiation of the UPB. Using simple thermal modeling of asteroids heated internally by ^{26}Al [10], a metal-silicate separation age of ~2 Ma can be linked to an accretion age of ~1 Ma, suggesting that the UPB accreted within the first ~1 Ma of the solar system. This estimate is in good agreement with an accretion age of ~0.6 Ma inferred from more sophisticated modeling of the thermal evolution and melt extraction on the UPB [3].

The chronological significance of the variable ε^{182}W observed among the ureilites is more difficult to assess. The variable ε^{182}W values indicate that melting and differentiation of the UPB was not a single event at a well-defined point in time. The ε^{182}W values of the investigated ureilites range between *ca.* –3.2 and *ca.* –2.8, corresponding to two-stage Hf-W model ages between approximately 2 and 7 Ma after CAI. Such a time span for melting is in good agreement with Mn-Cr and Al-Mg ages of feldspathic clasts in polymict ureilites of ~5 Ma after CAI formation [2]. It is unclear, however, as to whether the variable ε^{182}W reflect distinct, more local events of metal-silicate separation, or if they are the result of two distinct melting events during global differentiation of the UPB. Assuming that the first melt to form in the UPB was a S-rich metallic melt, extraction of that melt would have resulted in elevated ^{180}Hf/^{184}W in the ureilite source region for some time until a basaltic melt was subsequently extracted, resulting in the low Hf/W observed today in the ureilites. In the time period between extraction of a S-rich metallic melt and extraction of a basaltic melt, the ureilite source region may have evolved with variable elevated Hf/W, potentially resulting in the observed variability of ε^{182}W values. However, it remains unclear whether the time span between these two proposed melt extraction events was long enough, and whether the variation of ^{180}Hf/^{184}W was large enough, to produce the observed range in ε^{182}W values.

Conclusions: The new Hf-W data demonstrate that melting within the UPB started within the first ~2 Ma of the solar system, implying parent body accretion within the first ~1 Ma after CAI formation. The early melting required by our new data is in good agreement with ^{26}Al being the dominant heat source for differentiation of the UPB. The W isotope results reveal resolved differences in ε^{182}W values of ureilites, corresponding to model ages of metal-silicate separation between approximately 2 Ma and 7 Ma after CAI. However, the differences in ε^{182}W may not reflect distinct events of metal segregation, but may instead result from elevated and variable Hf/W persisting in the ureilite source regions between extraction of a S-rich metallic melt and a basaltic melt. It thus will be critical to assess whether the two partial melts were extracted almost simultaneously or rather separated by a time span of several hundred thousand years.

References: [1] Goodrich C. A. et al. (2004) *Chemie der Erde*, 64, 283–327. [2] Goodrich C. A. et al. (2010) *EPSL*, 295, 531–340. [3] Wilson L. et al. (2008) *GCA*, 72, 6154–6176. [4] Kleine T. et al. (2009) *GCA*, 73, 5150–5188. [5] Lee D.-C. et al. (2009) *EPSL*, 288, 611–618. [6] Kruijer T. S. et al. (2012) *GCA*, 99, 287–304. [7] Kleine T. et al. (2012) *GCA*, 84, 186–203. [8] Rankenburg K. et al. (2008) *GCA*, 72, 4642–4659. [9] Goodrich C. A. et al. (2013) *GCA*, 112, 340–373. [10] Qin L. et al. (2008) *EPSL*, 273, 94–104.