HAFNIUM-TUNGSTEN CHRONOLOGY OF CR CHONDRITES.

G. Budde, T. S. Kruijer, and T. Kleine, Institut für Planetologie, University of Münster, Wilhelm-Klemm-Straße 10, 48149 Münster, Germany (gerrit.budde@uni-muenster.de).

Introduction: Precisely constraining the duration of chondrule formation is important for understanding the origin of chondrules, and for assessing the timescale over which primitive planetesimals formed in the early solar system. Previous studies have shown that most chondrules formed at ~2 Ma after the formation of Ca-Al-rich inclusions (CAIs) (see [1] for an overview), but chondrules from CR chondrites appear to be significantly younger [2,3]. However, these relatively young ages, which were predominantly obtained using the ^{26}Al-^{26}Mg system [3], do not necessarily require a late formation. They could also reflect disturbance during alteration on the CR parent body, or result from an ^{26}Al-poor composition in the CR precursor material [4,5]. Thus, it is important to determine the time of CR chondrite formation using other chronometers.

Compared to the Al-Mg system, the ^{182}Hf-^{182}W system ($t_{1/2}$ = 8.9 Ma) is far more robust against resetting by parent body processes. This makes the Hf-W system ideally suited to assess as to whether CR chondrules formed later than other chondrules. Moreover, as chondrule formation was associated with metal-silicate separation [*e.g.*, 1], and because CR chondrites contain abundant Fe-Ni metal, the formation of CR chondrules can be dated via metal-silicate Hf-W isochrons.

We present precise Hf-W ages for four different CR chondrites. In addition, we also determined high-precision (non-radiogenic) W and Mo isotope compositions for individual components of CR chondrites. These data provide important insights into the genetic links between these components, which in turn allows assessing the chondrule formation mechanism [1,6]. Finally, the Hf-W data have important implications for assessing as to whether ^{26}Al was homogeneously distributed in the early solar system.

Methods: We obtained Hf-W and Mo isotope data for bulk samples, magnetic separates, and individual components (metal, chondrules) from four CR2 chondrites (Acfer 097, GRA 06100, NWA 1180, NWA 801). The analytical methods followed our established procedures [1,6], and all isotope measurements were made using the Neptune *Plus* MC-ICP-MS at Münster. The Mo and W isotope data are internally normalized to ^{98}Mo/^{96}Mo and either ^{186}W/^{183}W ('6/3') or ^{186}W/^{184}W ('6/4'), and are reported as ε-unit deviations (*i.e.*, 0.01%) relative to the bracketing solution standards. Repeated analyses of terrestrial rock and metal standards (BHVO-2, NIST 129c) define an external reproducibility (2 s.d.) for the W and Mo isotope ratios of ~0.1 and 0.2–0.4 ε-units, respectively.

Nucleosynthetic isotope anomalies in CR components: The analyzed samples show variable anomalies in ε^{183}W (~0.1–0.7), where the metal fractions have the lowest and the silicate-dominated fractions the highest excesses in ε^{183}W. The ε^{183}W variations are correlated with measured Mo isotope variations (ε^{92}Mo: ~2–10), and are attributable to the uneven distribution of a presolar carrier enriched in *s*-process nuclides. Of note, metal and silicates show complementary nucleosynthetic isotope anomalies, indicating that relative to the bulk meteorite, metals are enriched in an *s*-process carrier, whereas silicates are depleted in this carrier. This finding is consistent with the isotopic complementarity observed for Allende chondrules and matrix [1,6] and provides further evidence that the major components of (carbonaceous) chondrites are genetically linked and formed together from one common reservoir of solar nebula dust.

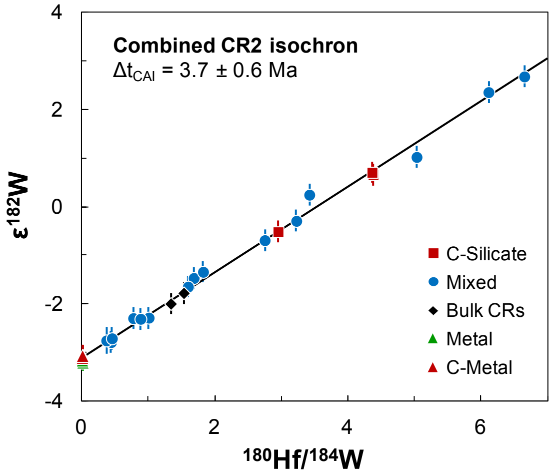

Fig. 1. Combined isochron for the investigated CR2 samples (after a small correction for nucleosynthetic W isotope anomalies). C: Chondrule (silicate/metal).

Timescale of chondrule formation: After correction of measured ε^{182}W for nucleosynthetic isotope anomalies [1], all analyzed samples plot on well-defined isochrons. Note that this correction (for the ^{186}W/^{183}W-normalized values) is <0.05ε for most samples and thus smaller than the analytical uncertainty. All four CR chondrites have indistinguishable Hf-W ages and combined define an age of 3.7±0.6 Ma after

CAI formation (Fig. 1). This age is in excellent agreement with the mean Al-Mg age for CR chondrules of 3.7±0.3 Ma [3], as well as a Pb-Pb age of 3.7±0.6 Ma (corrected to $^{238}U/^{235}U$ = 137.786) obtained for six chondrules from the CR2 chondrite Acfer 059 [2]. Thus, three different chronometers provide consistent ages for the formation of CR chondrules (Fig. 2), demonstrating that they formed ~1–2 Ma later than chondrules from ordinary chondrites, which formed at ~2 Ma after CAI formation [*e.g.*, 7]. Collectively, these data suggest that the CR chondrite parent body accreted later than several other chondrite parent bodies. This later accretion may indicate that CR chondrites derive from a greater heliocentric distance, as is evident from their ^{15}N-enriched composition. The relatively late formation of CR chondrites is also consistent with the idea that carbonaceous chondrites initially accreted in the outer solar system, beyond the orbit of Jupiter [6,8].

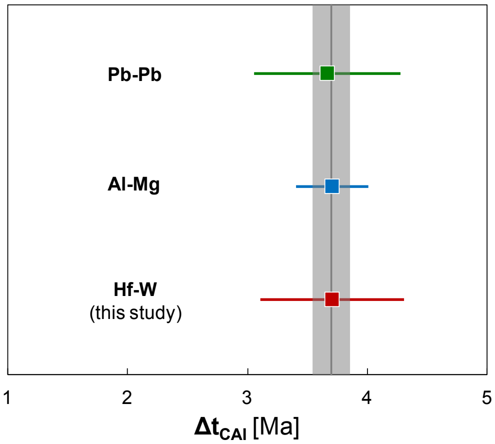

Fig. 2. Pb-Pb [2], Al-Mg [3], and Hf-W ages for CR chondrites are in excellent agreement. The gray bar represents the weighted mean of the three ages.

Implications for the distribution of ^{26}Al in the solar nebula: The Hf-W age for CR chondrites not only constrains the chronology of chondrule formation, but also provides insights into the distribution of ^{26}Al within the solar nebula. There are now four different types of samples, spanning the entire effective lifetime of ^{26}Al (~5 Ma), that have been dated with both the Hf-W and Al-Mg systems: bulk CAIs, CV chondrules [1,9], CR chondrules [this study, 3], and angrites (D'Orbigny and Sahara 99555). For all four samples the Hf-W and Al-Mg ages are in excellent agreement, and in a diagram of initial $^{26}Al/^{27}Al$ versus $^{182}Hf/^{180}Hf$ all samples plot on a well-defined correlation line (Fig. 3). The slope (12.9±1.4) of this correlation is in very good agreement with the expected slope of 12.6±0.4, as defined by the ratio of the ^{26}Al and ^{182}Hf decay constants, demonstrating that these samples formed from a reservoir with common initial $^{26}Al/^{27}Al$ and $^{182}Hf/^{180}Hf$ as defined by bulk CV CAIs.

Although the Al-Mg and Hf-W ages are concordant, small ^{26}Al heterogeneities may still exist that could not be resolved using Hf-W chronometry. However, the minimal observed scatter of the data points from the regression line narrows the permissible degree of ^{26}Al heterogeneity to <10–20%. This finding is in disagreement with the high level of heterogeneity proposed in some previous studies, based on the comparison of Al-Mg and Pb-Pb ages [4] or correlated ^{26}Mg and ^{54}Cr variations in meteorites [5]. Instead, given that CAIs, CV and CR chondrites, as well as angrites represent material that formed at different times and derive from distinct reservoirs in the solar protoplanetary disk, the concordance of Al-Mg and Hf-W ages provides strong evidence for a disk-wide homogeneous distribution of ^{26}Al in the early solar system (most likely to better than ±10%). Consequently, this demonstrates that different initial $^{26}Al/^{27}Al$ in meteorites and (most) meteoritic components have chronological significance.

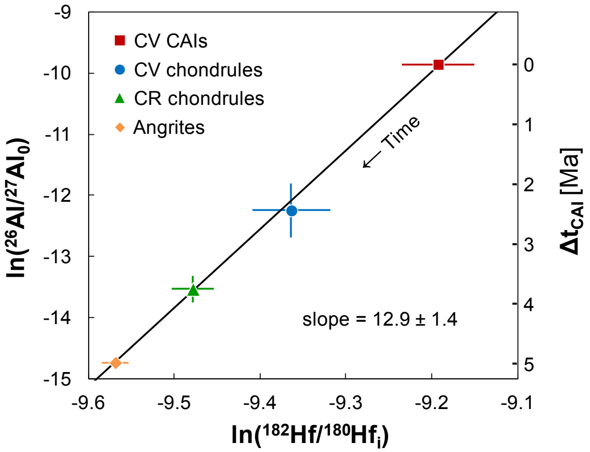

Fig. 3. Initial $^{26}Al/^{27}Al$ vs. $^{182}Hf/^{180}Hf$ for different solar system materials. Data for CAIs and angrites are from [4, 10, and references therein]. Other data sources are provided in the text.

References: [1] Budde G. et al. (2016) *PNAS*, 113, 2886–2891. [2] Amelin Y. et al. (2002) *Science*, 297, 1678–1683. [3] Schrader D. L. et al. (2016) *GCA*, in press (10.1016/j.gca.2016.06.023). [4] Schiller M. et al. (2015) *EPSL*, 420, 45–54. [5] Larsen K. K. et al. (2011) *ApJ*, 735, L37. [6] Budde G. et al. (2016) *EPSL*, 454, 293–303. [7] Kita N. T. et al. (2013) *MAPS*, 48, 1383–1400. [8] Warren P. H. (2011) *EPSL*, 311, 93–100. [9] Nagashima K. et al. (2016) *GCA*, in press (10.1016/j.gca.2016.10.030). [10] Kruijer T. S. et al. (2014) *EPSL*, 403, 317–327.