

HAFNIUM-TUNGSTEN AGE OF ALLENDE CHONDRULES AND MATRIX. G. Budde, T. Kleine, T. S. Kruijer, and K. Metzler. Institut für Planetologie, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Straße 10, 48149 Münster, Germany (gerrit.budde@uni-muenster.de).

Introduction: Chondrules probably formed as free-floating melt droplets during transient heating events in the solar nebula [e.g., 1]. They are the major constituent of most chondrites, in which they occur embedded in a matrix of fine-grained silicates, oxides, and sulfides along with other components (e.g., CAI, AOA). Chondrules and matrix appear to be chemically complementary, indicating that they formed together from a single reservoir [e.g., 1]. However, the origin of chondrules is not well understood and this is partly because their chronology is poorly known. Al-Mg ages for chondrules from primitive ordinary chondrites indicate formation ~ 2 Ma after CAI [2], but chronological information about the formation of chondrules from carbonaceous chondrites is sparse. On the basis of Pb-Pb ages for single chondrules from the CV3 chondrite Allende it has been argued that chondrule formation began contemporaneously with CAI formation and continued for ~ 3 Ma [3]. However, until now only very few chondrules from carbonaceous chondrites have been dated, so that it is not known when the majority of these chondrules had formed.

To determine the formation time of chondrules, we applied the short-lived ^{182}Hf - ^{182}W system to matrix and chondrule separates from Allende. Our approach is to date a large number of chondrules to ultimately constrain the time at which the majority of the chondrules had formed. We, therefore, did not attempt to date individual chondrules—which would not be possible with the Hf-W system—but focus on distinct chondrule fractions, each consisting of a large number of chondrules.

Methods: We have analyzed two matrix and three chondrule fractions (each consisting of 10^2 – 10^3 chondrule fragments and intact chondrules) from Allende. In addition, two different powders of bulk Allende (MS-A, MS-B) were analyzed repeatedly. Matrix and chondrule fractions were prepared either by the freeze-thaw disaggregation technique (M1, C1) or by sieving and hand-picking from a gradually crushed ~ 40 g slice of Allende (M2, C2, C3). All chondrule fractions were carefully purified by hand-picking, sonicated in acetone, and then ground to a fine powder. Samples were digested in Savillex beakers using HF-HNO₃(-HClO₄), followed by inverse aqua regia. Hafnium and W concentrations were determined by isotope dilution on small aliquots of the sample solutions. Methods for the separation of W by anion exchange chromatography followed [4] and [5].

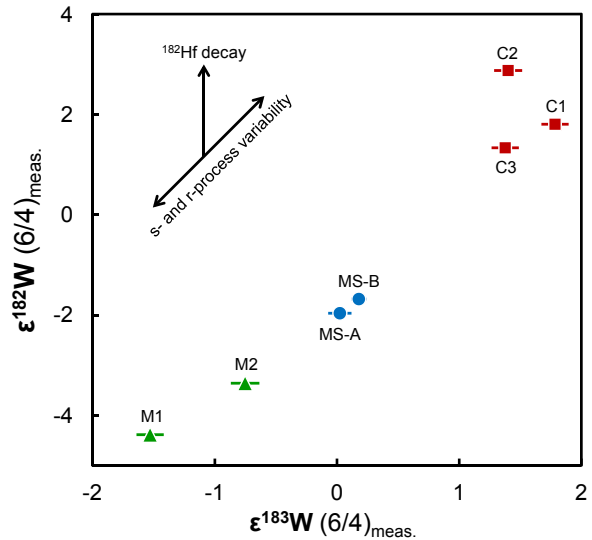


Fig. 1. Measured $\epsilon^{182}\text{W}$ vs. $\epsilon^{183}\text{W}$ for matrix (M) and chondrule (C) separates from Allende, as well as two bulk rock samples (MS-A, MS-B).

The W isotope compositions were measured on a Neptune Plus MC-ICP-MS in the Institut für Planetologie at the University of Münster [6]. The W isotope data are normalized to either $^{186}\text{W}/^{183}\text{W}$ (6/3) or $^{186}\text{W}/^{184}\text{W}$ (6/4) and reported as ϵ -unit deviation (i.e., 0.01%) relative to the bracketing standards. Repeated analyses of the terrestrial BHVO-2 rock standard, which was digested, processed through the full chemical separation, and analyzed together with each set of samples, yielded a mean $\epsilon^{182}\text{W}$ (6/4) of -0.01 ± 0.07 (2 s.d., $n=8$) for ~ 30 ng W consumed per analysis.

Results: The chondrule and matrix fractions display large nucleosynthetic $\epsilon^{183}\text{W}$ anomalies (Fig. 1), indicating a deficit in s-process W nuclides (or an r-excess) in the chondrules and a complementary s-excess (or r-deficit) in the matrix. In contrast, bulk Allende shows only small if any $\epsilon^{183}\text{W}$ anomalies (Fig. 1). Compared to bulk Allende, the matrix is characterized by lower Hf/W and $\epsilon^{182}\text{W}$, whereas the chondrules display higher and variable Hf/W and $\epsilon^{182}\text{W}$. The chondrule fractions have quite constant W but variable Hf concentrations, resulting in elevated and variable Hf/W. After correction for nucleosynthetic W isotope anomalies [6], the chondrule and matrix fractions define an isochron corresponding to an age of 3.9 ± 1.0 Ma after CAI formation (Fig. 2), and an absolute age of 4564.0 ± 0.9 Ma relative to the angrite D'Orbigny [5].

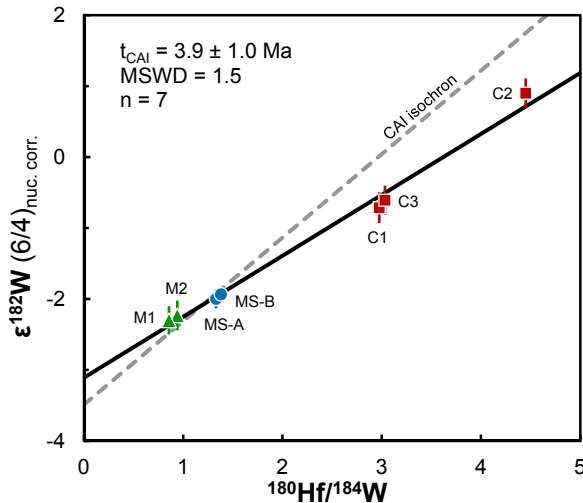


Fig. 2. Hf-W isochron for matrix (M) and chondrule (C) separates from Allende after correction for nucleosynthetic W isotope anomalies. Also shown is the bulk CAI isochron (dashed line) from [6].

Discussion: Several observations indicate that the Hf-W isochron defined by the matrix and chondrule fractions provides the time of Hf/W fractionation during chondrule formation. First, the peak metamorphic temperature of Allende of ~ 550 °C [7] is well below the Hf-W closure temperature of ~ 800 – 900 °C [8], indicating that diffusion of radiogenic ^{182}W during metamorphism was negligible. Second, bulk CAI from Allende plot on a well-defined Hf-W isochron [6], whose slope is steeper than that of the chondrule-matrix isochron (Fig. 2). If the Hf-W system in Allende would have been reset by parent body processes, then the CAI isochron should also be affected. This is not observed, however. Note that the CAI isochron corresponds to an absolute age of ~ 4568 Ma, indicating that the CAI remained closed systems for Hf-W since their formation [6]. Third, there has been minimal redistribution of elements between matrix and chondrules, even for mobile elements such as Sr [9]. The complementary Hf/W ratios of matrix and chondrules, therefore, have been established during chondrule formation and do not result from parent body processes. Finally, the preservation of large and complementary nucleosynthetic W isotope anomalies between matrix and chondrules indicates limited diffusional exchange of W by parent body processes. We, therefore, interpret the Hf-W age to date the formation of Allende chondrules.

Pb-Pb ages for individual Allende chondrules range from 4564.7 ± 0.3 to 4567.3 ± 0.4 Ma and have been interpreted to indicate that chondrule formation occurred over an extended period of ~ 3 Ma after CAI formation [3]. A multi-chondrule fraction from Allende

has a Pb-Pb age of 4564.4 ± 0.9 Ma (recalculated from [10] using the U isotope composition of chondrites [11]), in very good agreement with the Hf-W age of 4564.0 ± 0.9 Ma obtained here. Note that each of the chondrule fractions we analyzed consists of 10^2 – 10^3 chondrules. Thus, the most straightforward interpretation of the chronological data is that the majority of Allende chondrules formed at 4564.0 ± 0.9 Ma (as given by the Hf-W age), while some chondrules formed earlier and perhaps as early as CAI (as evident from Pb-Pb ages for individual Allende chondrules).

The Hf-W age of Allende chondrules is also in good agreement with a Pb-Pb age of 4563.8 ± 0.7 Ma for a chondrule from the CR chondrite Acfer 059 (recalculated from [12] using the U isotope composition of chondrites [11]). Taken together, the chronological data suggest that formation of carbonaceous chondrite chondrules peaked at ~ 4 Ma after CAI formation, which is ~ 2 Ma later than formation of most ordinary chondrite chondrules [2]. However, more precise chronological studies on chondrules are necessary to firmly establish a time difference between the formation of different chondrule populations.

Conclusions: Hf-W data for chondrule and matrix fractions from Allende indicate that the majority of Allende chondrules formed 4 ± 1 Ma after CAI formation. However, some chondrules might have formed earlier, perhaps as early as CAI, as indicated by Pb-Pb chronometry. Chondrules and matrix in Allende display large and complementary nucleosynthetic W isotope anomalies, but bulk Allende does not. Matrix and chondrules, therefore, must have formed from a single, isotopically normal reservoir, as has been inferred previously from the complementary chemical compositions of matrix and chondrules [1]. The observed nucleosynthetic W isotope heterogeneity most likely has been induced due to uneven mixing of presolar components between chondrule precursors and matrix (perhaps by grain size sorting), followed by instantaneous accretion after chondrule formation.

References: [1] Palme H. et al. (2015) *EPSL*, 411, 11–19. [2] Kita N.T. et al. (2013) *MAPS*, 48, 1383–1400. [3] Connelly J.N. et al. (2012) *Science*, 338, 651–655. [4] Kruijjer T.S. et al. (2012) *GCA*, 99, 287–304. [5] Kleine T. et al. (2012) *GCA*, 84, 186–203. [6] Kruijjer T.S. et al. (2014) *EPSL*, 403, 317–327. [7] Cody G.D. et al. (2008) *EPSL*, 272, 446–455. [8] Kleine T. et al. (2008) *EPSL*, 270, 106–118. [9] Bland P.A. et al. (2005) *PNAS*, 102, 13755–13760. [10] Connelly J.N. & Bizzarro M. (2009) *Chemical Geology*, 259, 143–151. [11] Goldmann A. et al. (2015) *GCA*, 148, 145–158. [12] Amelin Y. et al. (2002) *Science*, 297, 1678–1683.