POSSIBLE URANIUM ISOTOPIC HETEROGENEITY IN ALLENDE CHONDRULES AND ITS IMPACT ON Pb-Pb AGES: A FIRST CASE OF U AND Pb ISOTOPES FROM A SINGLE CHONDRULE. M. H. Huyskens[1], Q.-Z. Yin[1], M. E. Sanborn[1], Y. Amelin[2], R. Merle[2], and K. Yamashita[3]. [1]Department of Earth and Planetary Sciences, University of California-Davis, One Shields Avenue, Davis, CA, USA, (mhuyskens@ucdavis.edu), [2]Research School of Earth Sciences, The Australian National University, Canberra ACT 0200, Australia. [3]Graduate School of Natural Science and Technology, Okayama University, Japan.

Introduction: The $^{238}U/^{235}U$ ratio was long thought to be invariable in the Earth and other solar system materials. With advances in measurement precision and accuracy this view has changed and significant variations were first shown in calcium-aluminum-rich inclusions (CAIs) [1]. Since this initial report [1], many Earth and other solar system materials have been measured. While most show meteorite values equal to the redefined terrestrial average value, there are a few examples of chondrites and achondrites showing some variation [2-4]. It has been shown that terrestrial weathering could induce variations in $^{238}U/^{235}U$ and some meteorites that were not fresh falls do show a disequilibrium $\delta^{234}U$ signature [2]. Such a feature is not expected in antique, non-weathered meteorites. If we limit the data to the observed fresh falls, and recovered finds at secular equilibrium based on the measured $^{234}U/^{238}U$, then we do see some variation among meteorites that are unaffected and independent of terrestrial variations. Knowing the U isotopic composition is especially important since our knowledge of the age of many planetary materials is based on the U-Pb decay system. Due to low U content and limited sample availability, it is unfeasible or even impossible to measure the $^{238}U/^{235}U$ composition with adequate precision in the same material for U-Pb dating, since current analytical methods require ≥3 ng of U for precise $^{238}U/^{235}U$ determination. For U-Pb geochronology of chondrules, this amount of U is usually not available in a single chondrule given a typical concentration of 10-25 ppb [5, 6] and a typical diameter of <1 mm [7]. Thus, the $^{238}U/^{235}U$ composition is often assumed based on the solar system average with the assumption that all chondrules have the same U isotopic composition. However, to this date, it is not clear if the U isotopic composition of chondrules is homogeneous. Brennecka et al. [6] addressed this question by separating chondrules based on size and magnetic properties. In order to have enough material for a precise measurement, hundreds of chondrules had to be dissolved for each of the six groups determined in that study. Thus, the information of potential isotopic heterogeneity for individual chondrules is lost. Here, we report the U isotopic composition for the the large (>10 mm) chondrule A25-2 from the CV3 chondrite Allende weighing ~3.6 g, for which Pb isotopic data have been previously reported [8].

Methods: Several large fragments of the mega chondrule A25-2 were acquired for the study and the attached matrix material was carefully removed. The pure chondrule material was crushed in an agate mortar and a total of 461 mg was divided and dissolved in three separate Parr dissolution vessels in a mixture of HF-HNO_3 at 190°C for 4 days. After evaporation and redissolution in 6 M HCl, the three fractions were recombined and spiked with the ^{233}U-^{236}U spike IRMM-3636 with a $^{236}U/^{235}U$ of ~6. The sample then underwent several evaporation and redissolution cycles to ensure sample-spike equilibration. Uranium was separated using anion chemistry followed by UTEVA chemistry. The U isotopic composition was determined on a Thermo *Neptune Plus* MC-ICP-MS in low resolution mode for high precision. The Faraday cups were paired with 10^{11} Ω resistors, except for the ^{235}U cup, which was connected to a 10^{12} Ω resistor. A solution blank was measured before and after each sample and the average of this signal was subtracted from the sample signals.

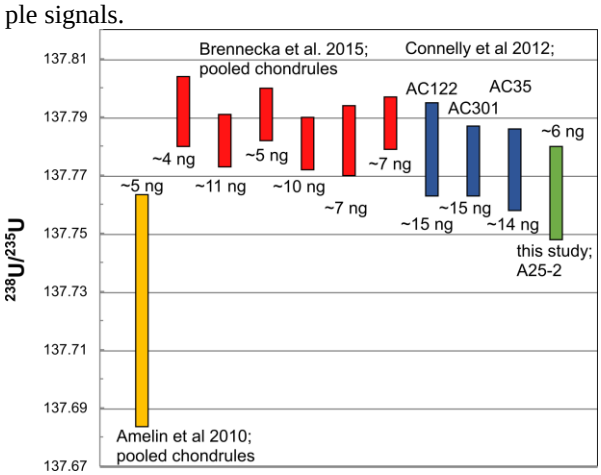

Fig. 1: Compilation of all currently determined $^{238}U/^{235}U$ ratios for Allende chondrules and the amount of U consumed for each analysis.

The data was corrected for instrumental mass dependent fractionation using an exponential law based on the known ^{233}U-^{236}U ratio of IRMM-3636 [9]. Samples were tightly bracketed with the Uranium isotopic standard CRM 112a using a similar concentration and sample/spike ratio. All reported values are relative to a

$^{238}U/^{235}U$ ratio of CRM 112a of 137.837 [10]. The sample was measured twice in different analytical sessions. To determine the accuracy of the procedure, the terrestrial rock standards BCR-2 and BHVO-2 underwent the same procedures as the sample.

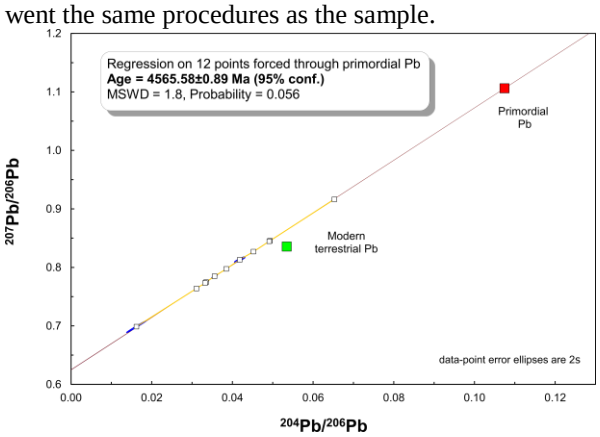

Fig. 2: Isochron regressions from HF leachates and residues of Allende megachondrule. Ages calculated using the determined $^{238}U/^{235}U$ ratio of 137.764. Data from [8] were filtered following the procedure used by [12]: data points that plot marginally below the line between the most radiogenic Pb data and primordial Pb are removed. For clarity, the data points are represented by squares. The individual error ellipses are smaller than the symbol for the majority of the data.

Results: The chondrule A25-2 has a $^{238}U/^{235}U$ ratio of 137.764±0.016. Within the same analytical sessions the solution standard IRMM-184 yielded a $^{238}U/^{235}U$ ratio of 137.681±0.011 (n=5, MSWD=1.3) compared to 137.683±0.020 [11] and the terrestrial rock standards BCR-2 and BHVO-2 showed a $^{238}U/^{235}U$ ratio of 137.803±0.019 (vs. 137.800 ±0.006 [4]) and 137.806± 0.018 (vs. 137.794±0.003 [4]), respectively. Recalculating the age of the chondrule A25-2 [8] using the determined U isotopic composition results in an age of 4565.58±0.89 (2σ, considering Pb and U analytical uncertainty, Fig. 2).

Discussion: Currently, there are still very limited data available for the U isotopic composition of chondrules. Due to the small size and low U concentration, measurements of individual chondrules are limited to abnormally large chondrules, of which only four are reported to date, including this study. These four chondrules have identical U isotopic composition within the uncertainty with a weighted average of 137.773±0.007 (n=4; MSWD= 0.65 [12, this study]), when recalculated to the same $^{238}U/^{235}U$ ratio of CRM 112a of 137.837 [10]. However, there are some noticeable variations between individually measured large chondrules and pooled smaller chondrules, where [6] reported an averaged value of 137.786± 0.004 (n=5) and [5] a value of 137.724±0.040 (Figure 1). Considering that there might be variation in the U isotopic composition among individual chondrules, correcting Pb-Pb ages with an averaged $^{238}U/^{235}U$ ratio can lead to biased ages. With the entire range of $^{238}U/^{235}U$ ratios for chondrules reported thus far, the additional uncertainty of the Pb –Pb age would be 1.26 Ma. When excluding the value reported by [5], which is the most extreme value reported so far, and relatively imprecise compared to more recent measurements, the additional uncertainty reduces to 0.59 Ma. This additional uncertainty is a minimum estimate and has to be considered where determination of the U isotopic composition in an individual chondrule is not feasible.

Conclusion: This study represents the first case where both Pb and U isotopic compositions were measured from the same chondrule. The large chondrule A25-2 from the CV3 chondrite Allende yielded a U corrected Pb-Pb age of 4565.58±0.89 Ma. This age is within the range of reported Pb-Pb ages for chondrules from Allende [8, 12-15]. Based on the currently available data, U isotopic compositions of individual chondrules might vary. To date only chondrules from the Allende CV3 chondrite have been measured for the U isotopic composition. This is a highly biased dataset and U isotopic composition of chondrules from other chondrite groups will need to be determined to establish its homogeneity or heterogeneity.

For Pb-Pb ages of chondrules, where determination of the U isotopic composition is not possible, the range of $^{238}U/^{235}U$ variations should be considered. This leads to an additional uncertainty of 0.59 Ma. This additional uncertainty is relatively large compared to the typical analytical uncertainty on Pb-Pb dates alone (down to ~0.3 Ma and possibly lower). However, including this uncertainty component is necessary to assure that the ages are accurate within their total uncertainty limits until the issue of U isotopic homogeneity or heterogeneity is solved.

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