TOWARDS A NEW ABSOLUTE CHRONOLOGY FOR THE EARLY SOLAR SYSTEM. J. N. Connelly[1], M. Bizzarro[1], M. Ivanova[2], and A. N. Krot[3,1]. [1]Centre for Star and Planet Formation, Geological Museum, Copenhagen University, Øster Voldgade 5-7, 1350, Copenhagen K, Denmark. [2]Vernadsky Institute, 19 Kosygin Str., 119991 Moscow, Russia. [3]Hawai'i Institute of Geophysics and Planetology, 1680 East-West Rd, Honolulu, HI, 96822, USA.

Introduction: The ages of calcium-aluminum inclusions (CAIs) and chondrules underpin our understanding of the timing and nature of critical events in the first ca. 5 million years of solar system formation. Only the double decay U-Pb system, where ^{235}U decays to ^{207}Pb and ^{238}U decays to ^{206}Pb, provides the necessary ca. ± 0.25 Myr resolution for absolute ages of these inclusions. The different decay rates of ^{235}U and ^{238}U produces present-day ratios of radiogenic ^{207}Pb *vs*. radiogenic ^{206}Pb that relate to time lapsed (t) since the last closure through the equation:

$$\frac{^{207}Pb^R}{^{206}Pb^R} = \frac{^{235}U(e^{\lambda_1 t}-1)}{^{238}U(e^{\lambda_2 t}-1)}$$

With the decay constants (λ_1, λ_2) known, calculation of an age by this so-called Pb-Pb chronometer requires knowledge of the $^{238}U/^{235}U$ ratio, which has long been assumed to be fixed at 137.88. This was proven incorrect by [1] for at least CAIs, thereby requiring independent measurement of the $^{238}U/^{235}U$ ratio for all materials dated by the Pb-Pb system. We have undertaken a study to directly determine the Pb and U isotopic composition of a set of CAIs and chondrules to provide a suite of robust absolute ages for the formation of these inclusions from CV meteorites.

Pb Isotopes: All meteorites and their components are contaminated to some degree by terrestrial Pb irrespective of how quickly they are recovered after their fall to Earth and how carefully they are curated. More intensive washing procedures has proven necessary to routinely successfully address the problem of terrestrial contamination. This has been combined with dramatic improvements in laboratory blanks and mass spectrometry that has allowed for accurate and sufficiently precise analyses to be conducted on sub-10 pg size samples of Pb by thermal ionization mass spectrometery (TIMS). These improvements have been complemented by strategic stepwise dissolution to parse the Pb into different aliquots with the aim to define a linear array that verifies that the remaining Pb corresponds to a binary mix of radiogenic and either initial Pb or any other single component of Pb and provides the radiogenic $^{207}Pb/^{206}Pb$ ratio of the sample when this condition is satisfied [2]. We analyze all Pb isotopic analyses using a Thermo-Fisher Triton TIMS using a high-efficiency Si-gel activator, an equal atom ^{202}Pb-^{205}Pb double spike and mainly using a peak-jumping routine to sequentially measure each Pb isotope on an axial secondary electron multiplier – ion counting system [2].

U Isotopes: We have known since early 2010 that the $^{238}U/^{235}U$ ratio of 137.88 is not inappropriate for most if not all meteoritic materials [1]. The challenge immediately became to determine this ratio accurately for limited amounts of U (typically less than 10 ng) while deriving errors less than 200 ppm, corresponding to an age uncertainty related to the U isotopic ratio below +/- 0.3 Myr. To improve the counting statistics and thereby improve precision, we opted to use the Thermo-Fisher Neptune Plus in low resolution mode that provided a sensitivity of 2500 V/ppm of U. Despite a three step U purification procedure (1 ml UTEVA, 1 ml anion and 0.12 ml anion columns), we were unable to avoid unpredictable interferences on the minor ^{235}U peak as well as the spike masses of ^{233}U and ^{236}U in low resolution mode – an effect that translated into false anomalies of ^{235}U of up to 1000's of ppm and far outside of errors. The molecular interferences are inferred to be a combination of matrix cations, gas species and/or organics from the resins used to isolate U. While this problem is obvious when analyzing small (< 5 ng U), it must also exist when analyzing larger amounts of U but the effect will be less obvious due to the larger sample/interference ratio. We have specifically noted a correlation between the potential for interferences on either ^{235}U or the spike masses of ^{233}U or ^{236}U related to samples of CAIs with high rare earth element contents.

To systematically avoid this issue for samples of all sizes, we have had to develop a four-stage chemical separation procedure for U and analyze all samples on on the high mass side of the peak with a resolving power of 2500. We use the standard bracketing method with three standards before and after each unknown and with on peak zeros measured as full analyses before every standard and unknown. We report all $^{238}U/^{235}U$ ratios relative to the standard 112a (or its derivative 145b) with a ratio of 137.84 [3].

Results: We have derived ages based on both U and Pb isotope measurements for two more CAIs from the CV3 chondrite Efremovka. Inclusion 22E is a fine-grained spinel-hibonite-rich CAI having a nearly monomineralic porous core composed of micron-sized euhedral hibonite grains. The core is surrounded by a mantle of concentrically-zoned objects with a spinel + hibonite ± perovskite core, melilite ± anorthite mantle, and Al,Ti-diopside rim. The abundance of melilite increases towards the CAI periphery. 22E is mineralogically similar to fine-grained spinel-rich CV CAIs formed by gas-solid condensation from a gas depleted in refractory rare earth elements [4]. As such, it is an ideal candidate to provide a benchmark primary age of formation for CAIs and, by inference, the solar system. Inclusion 31E is a coarse-grained igneous (Type B) CAI composed of melilite, Al,Ti-diopside, spinel, and Fe-Ni metal. Corrected for their respective U isotopic ratios, the ages of 22E and 31E are overlapping at 4567.34 ± 0.30 and 4567.17 ± 0.24 Ma, respectively.

Using our refined U analytical methods, we have also measured the U isotopic ratios of a range of inner solar system materials: whole rocks of Ivuna (CI), Gujba (CB), Allende (CV), enstatite chondrite, eucrite Juvinas, angrite SAH 99555, and basaltic achondrite NWA 2976, and several chondrules from Allende. These objects have variable $^{54}Cr/^{52}Cr$ ratios, indicating that they formed in distinct regions of the disk. By contrast, the lack of $^{238}U/^{235}U$ variability in these same materials establishes that the bulk inner solar system has a uniform U isotope composition, which we estimate to be 137.79 ± 0.01. Using this value for chondrules, we have determined Pb-Pb ages for three CV3 Allende chondrules that range from 4567.14 ± 0.24 to 4565.52 ± 0.38 Ma.

Discussion: At present, there are five absolute ages for CAIs in the peer-reviewed literature [5−9] but only the age of 4567.18 ± 0.50 Ma by [9] for the large CAI SJ101 from the CV3 chondrite Allende is based on a measured U isotopic ratio. As such, it is the only robust age currently available in the literature and the other ages [5−8] can effectively be disregarded.

Both ages presented here for Efremovka CAIs overlap the age of CAI SJ101 [9]. A weighted average age for these three CAIs is 4567.21 ± 0.24, which we take as the current best estimate of the age of CAIs and, by extension, the solar system. The oldest age for a single chondrule of 4567.14 ± 0.24 overlaps the weighted average age of CAIs, thereby requiring that the chondrule forming process was underway contemporaneously with the formation of CAIs. The younger ages here and previously published for single and multiple chondrule fractions confirm that the chondrule forming process or that chondrule re-working lasted for at least 1.6 Myr.

The isotopic measurement of small amounts of U is highly susceptible to interferences on the minor ^{235}U isotope as well as the spike isotopes especially when measured by MC-ICP-MS at low resolution. While the resulting anomalies become less pronounced for larger amounts of U, we note deviations outside of error emerging from the limited published data that we attribute to this affect. For example, we notice that the $^{238}U/^{235}U$ ratio of 137.751 ± 0.018 for NWA 2976 has been reported by [10] is close but outside of errors of our measurement of 137.783 ± 0.011.

The development of U isotopic analyses for sample limited materials is the last step required to erect the first assumption free absolute chronometric framework for the first 5 Myr of the solar system. The emerging picture is one of discordance between ages from the U-Pb and Al-Mg systems, an observation that we attribute to an inhomogeneous distribution of ^{26}Al within the inner solar system [11]. There is a better agreement for the Hf-W short-lived chronometers implying homogeneity of ^{182}Hf in the precursor materials to planets and planetesimals within the inner solar system.

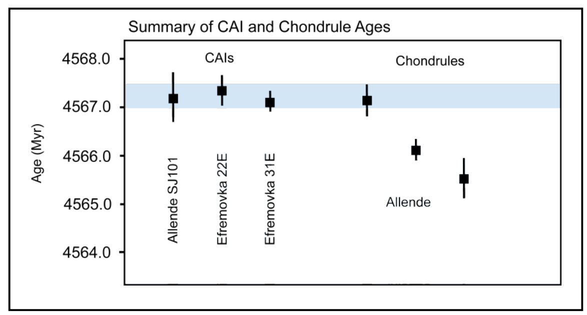

Figure 1: Summary of absolute ages for CAIs and chondrules for which we have reliable estimates of the U isotopic composition (age for SJ101 from [8]).

References: [1] Brennecka G. A. et al. (2010) *Science, 327,* 1103−1105. [2] Connelly J. N. and Bizzarro M. (2009) *Chemical Geology, 259,* 143−151. [3] Condon D. et al. (2010) *GCA, 74,* 7127−7143. [4] Krot A. N. et al. (2004) *GCA, 39,* 1517−1553. [5] Amelin Y. et al. 2002 *Science, 297,* 1678−1683. [6] Bouvier A. et al. (2007) *GCA, 71,* 1583−1604. [7] Connelly J. N. et al., (2008) *ApJ, 675,* L121−L124. [8] Bouvier A. and Wahdwa M. (2010*) Nature Geoscience, 3,* 637−641. [9] Amelin Y. et al. (2010) *EPSL, 300,* 343-350. [10] Bouvier A. et al. (2011) *GCA, 75,* 5310−5323. [11] Larsen K. et al. (2011) *ApJ, 735,* L37−L44.