TOWARDS RECONCILING EARLY SOLAR SYSTEM CHRONOMETERS: THE $^{238}U/^{235}U$ RATIOS OF CHONDRITES AND D'ORBIGNY PYROXENES. G. A. Brennecka[1*], M. Wadhwa[1], P. E. Janney[1] and A. D. Anbar,[1,2], [1]School of Earth and Space Exploration, Arizona State University (*brennecka@asu.edu) [2]Department of Chemistry and Biochemistry, Arizona State University.

Introduction: Recent work has shown variability in the $^{238}U/^{235}U$ ratio in calcium-aluminum-rich inclusions (CAIs), primarily from the decay of extant ^{247}Cm ($T_{1/2}$ ~15.6 Ma) in the early Solar System [1]. This has implications for the precise Pb-Pb dating of meteorites since it can no longer be assumed that the $^{238}U/^{235}U$ ratio in these objects has a constant value of 137.88. In particular, the highly precise Pb-Pb age of 4564.42±0.12 Ma for the D'Orbigny angrite [2] has been used as an anchor for several high-resolution extinct chronometers. This age is based on an internal isochron from pyroxene and whole rock fractions and assumes a $^{238}U/^{235}U$ ratio of 137.88 in these fractions. In this work, we have analyzed the U isotopic composition of D'Orbigny pyroxenes to ascertain the accuracy of this Pb-Pb age. Additionally, we have measured U isotopes in bulk samples of different types of chondrites to determine if redox, thermal or aqueous processing could measurably fractionate $^{238}U/^{235}U$ ratios in these objects.

Methods: All chemical processing was performed under clean laboratory conditions in the Isotope Cosmochemistry and Geochronology Laboratory (ICGL) at Arizona State University (ASU). Bulk samples (ranging from 5.3 to 10.7 g) of the Abee (EH), Monroe (H4) and Nulles (H6) chondrites, as well as a pyroxene separate (174 mg) from the D'Orbigny angrite were completely dissolved using HNO_3, HF, and HCl; approximately 2% of each dissolved sample was reserved for trace element (rare earth element, Th and U) measurements. Uranium was separated from the remaining sample solutions for measurement of the $^{238}U/^{235}U$ ratio, following procedures discussed previously [1,3]. Uranium isotope measurements were performed on a ThermoFinnigan Neptune multicollector inductively coupled plasma mass spectrometer (MC-ICPMS) in the ICGL using a ^{236}U:^{233}U double-spike to correct for instrumental mass bias. We additionally measured trace element concentrations and Th/U ratios on the Thermo X-series quadrupole ICPMS in the Keck Laboratory for Biogeochemistry at ASU.

Results: The measured U isotopic compositions of the samples are shown in Fig. 1 and are reported as $^{238}U/^{235}U$ ratios calculated relative to the U isotope standard SRM950a, which is assumed to have a $^{238}U/^{235}U$ value of 137.88 [1,3,4]. The chondrite meteorites analyzed in this study have indistinguishable $^{238}U/^{235}U$ values: Abee = 137.835±0.028, Monroe = 137.837±0.011, and Nulles = 137.831±0.013. The reported errors are ±2SD, based on multiple runs of each of these samples. The D'Orbigny pyroxene fraction has a $^{238}U/^{235}U$ ratio of 137.822±0.028. Given the small amount of U in this sample, only a single run could be performed. Therefore, in this case, the error is ±2SD based on repeat measurements of the SRM950a standard made during the same analytical session as the D'Orbigny pyroxene sample, and run at the same concentration as this sample. The $^{232}Th/^{238}U$ ratios for Abee, Monroe, Nulles and D'Orbigny pyroxenes are 1.1, 3.3, 3.0, and 5.6, respectively (2SD errors are ±2%).

Discussion and Conclusions: *Can redox, thermal or aqueous processing fractionate the $^{238}U/^{235}U$ ratio?* Common mechanisms for isotope fractionation in other elements can include redox, thermal and low-temperature aqueous processes. If redox processes fractionate the $^{238}U/^{235}U$ ratio in meteoritic materials (as they are known to do in terrestrial samples [3]), objects that formed in different redox environments (e.g., enstatite chondrites, which formed under reducing conditions, and ordinary chondrites, which formed under relatively more oxidizing conditions) could have different $^{238}U/^{235}U$ values. If thermal processes fractionate $^{238}U/^{235}U$, objects formed in the same redox environment but subjected to different temperature histories (e.g., ordinary H chondrites of different metamorphic grades) could be expected to exhibit different $^{238}U/^{235}U$ values. Finally, if low-temperature aqueous processes fractionate $^{238}U/^{235}U$, then meteorites that experienced such processing (e.g., CM chondrites) might show different $^{238}U/^{235}U$ values compared to those that did not (e.g., ordinary chondrites).

The chondritic meteorites analyzed have experienced a range of redox, thermal and aqueous processing. Abee belongs to the EH chondrite group that formed in an extremely reducing environment [5]. Monroe (H4) and Nulles (H6) belong to the ordinary chondrite group that formed under relatively higher *f*O2 conditions than enstatite chondrites [5]; however, while these two samples belong to the same meteorite class, they represent different thermal histories. In our previous work [1], we analyzed the Murchison (CM) chondrite, which has experienced extensive aqueous alteration (e.g., [6-8]), and the Allende (CV) chondrite, which has experienced a complex history of aqueous processing followed by thermal metamorphism [9,10].

As can be seen in Fig. 1, the U isotope compositions of all these chondrites are identical to each other within the errors. As such, it is evident that within the analytical uncertainties, the redox, thermal and aqueous processes experienced by these meteorites have not affected their U isotopic compositions.

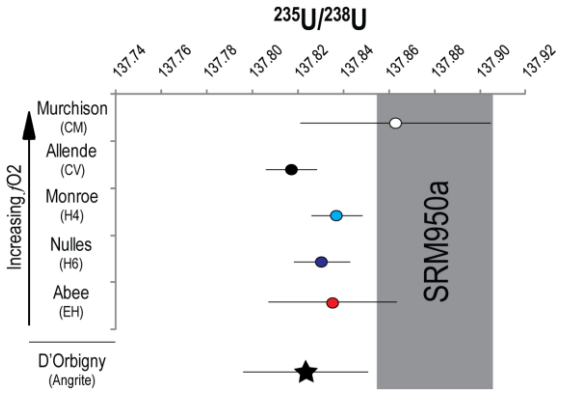

Figure 1 – Measured $^{238}U/^{235}U$ ratios in bulk samples of various chondrites and in the D'Orbigny pyroxene fraction; data for Murchison and Allende are from [1].

D'Orbigny: Implications for its Pb-Pb age and its role as an anchor for extinct chronometers. The high-precision relative ages of early Solar System events based on extinct chronometers must be "anchored" by an absolute age from Pb-Pb dating. An accurate and precise Pb-Pb age of that anchor is therefore critically important for mapping the relative ages from the extinct chronometers on to an absolute time scale. In several recent studies, the short-lived ^{26}Al-^{26}Mg, ^{53}Mn-^{53}Cr, and ^{182}Hf-^{182}W systems have been anchored to the Pb-Pb age of the D'Orbigny angrite (e.g., [11,12]), and thus, the ages based on these extinct chronometers depend on the accuracy of the Pb-Pb date of the D'Orbigny anchor.

Based on the $^{238}U/^{235}U$ ratio of 137.822±0.028 reported here in the pyroxene fraction of the D'Orbigny angrite, the previously reported Pb-Pb age of 4564.42±0.12 [2] for this meteorite (which assumed an invariant $^{238}U/^{235}U$ ratio of 137.88) will need to be adjusted by -0.6±0.3 Ma. Therefore, the recalculated Pb-Pb age for D'Orbigny is 4563.8±0.4 Ma. As an example of the application of this revised age as an anchor, the Al-Mg model age of the CAI from the NWA 2364 CV chondrite is 4568.6 ± 0.5 Ma (compared to 4569.2 ± 0.2 Ma when using the Pb-Pb age reported by [2]). This Al-Mg age is now in excellent agreement with the Pb-Pb age of 4568.7 ± 0.2 Ma for this CAI [13].

Live ^{247}Cm in the early Solar System. Correlations between U isotopic ratios and Th/U ratios have recently been used as evidence of extant ^{247}Cm in the early Solar System [1]. Thus far, this evidence has been confined to CAIs of the Allende meteorite [1]. In Fig. 2, we have plotted the U isotope compositions versus the Th/U ratios measured by us (this study and [1]) in bulk chondrites and the D'Orbigny pyroxenes. Although these data define a narrow spread in Th/U and U isotopic ratios, within the errors, they do fall along the same trend as that defined by the data from Allende CAIs [1] and are consistent with the decay of live ^{247}Cm in the early Solar System.

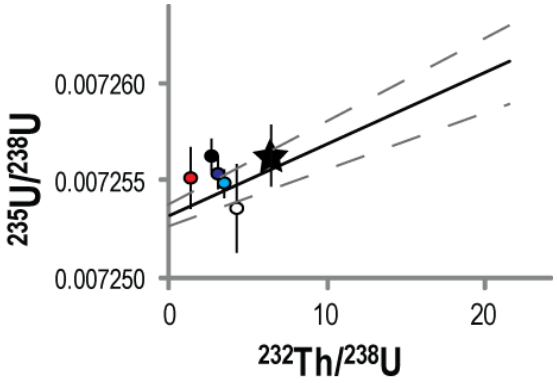

Figure 2 – The U isotopic composition (plotted as $^{235}U/^{238}U$) versus the $^{232}Th/^{238}U$ ratio for bulk samples of chondrites and for D'Orbigny pyroxenes (symbols are the same as in Fig. 1). For Murchison and Allende, U isotopic data are from [1], Th/U ratios are from [14]. The black line is the best fit regressed through the Allende CAI data, with the dashed lines representing 2SD errors on this best fit line [1].

References: [1] Brennecka G.A. et al. (in press) *Science*. [2] Amelin Y. (2008) *GCA, 72*, 221-232. [3] Weyer S. et al. (2008) *GCA 72*, 345-359 [4] Chen J. and Wasserburg G.J. (1980) *Geophys. Res. Letters 7*, 275-278. [5] Wadhwa M. (2008) *Reviews in Min. & Geochem., 68*, 493-510. [6] Fuchs L.H. et al. (1973) *Smithsonian Cont. to the Earth Sciences, 10*, 1–39. [7] Johnson C.A. & Prinz M. (1993) *GCA, 57*, 2843–2852. [8] Browning L B. et al. (1996) *GCA, 60*, 2621–2633 [9] Scott E.R.D. et al. (1995) *Meteoritics, 30*, 576. [10] Krot A.N. (2008) *GCA, 72*, 2534-2555. [11] Burkhardt C., et al. (2008) *GCA, 72*, 6177-6197. [12] Wadhwa M. et al. (2009) *GCA, 73*, 5189-5201. [13] Bouvier A. and Wadhwa M. (2009) *LPS XV*, A2184. [14] Rochell A. & Jochum P.K. (1993) *EPSL, 117*, 265-278.