Importance of uranium isotope variations for chronology of the Solar System's first solids. Y. Amelin[1], A. Kaltenbach[2], T. Iizuka[1], C.H. Stirling[2], T.R. Ireland[1], M. Petaev[3] and S.B. Jacobsen[3], [1]Research School of Earth Sciences, Building 61, Mills Road, The Australian National University, Canberra ACT 0200 Australia (yuri.amelin@anu.edu.au), [2]Centre for Trace Element Analysis and Department of Chemistry, University of Otago, PO Box 56, Union Place, Dunedin, New Zealand, [3]Department of Earth & Planetary Sciences, Harvard University, 20 Oxford St., Cambridge, MA 02138, USA.

Introduction: The $^{238}U/^{235}U$ ratio must be known for accurate determination of ^{207}Pb-^{206}Pb ages. This ratio was thought to be invariant [1-3] until recent discoveries of uranium isotope variations in terrestrial rocks [4-5] and in Ca-Al-rich refractory inclusions (CAIs) in carbonaceous chondrites [6]. The ^{207}Pb-^{206}Pb age of CAIs has been used as our best absolute age for the beginning of the Solar System's formation, but their Pb isotopic ages don't fit well in the emerging consistent pattern of the early Solar System chronology [7,8]. It is possible that some of the differences in formation time intervals between various early Solar System objects, obtained from extinct nuclide chronologies and from ^{207}Pb-^{206}Pb dates [7,8], are caused by variations of the $^{238}U/^{235}U$ ratios.

We performed a combined high precision $^{238}U/^{235}U$ and $^{238,235}U$-$^{206,207}Pb$ study of the Allende CAI SJ101 [9], and a U isotopic study of chondrules and representative whole rock samples of the same meteorite. The CAI SJ101A is a rather typical forsterite-bearing (FoB) inclusion in mineralogy and chemical composition, but has a more complex internal structure than most FoB CAIs [9]. The Group II REE pattern and major element ratios close to the solar values suggest that precursors of this CAI could have formed by non-equilibrium condensation in a closed system of solar composition.

Methods: A 76 mg aliquot of crushed material from a slice cut from the central part of the CAI, a group of >50 chondrules prepared for an earlier study [10], and five fragments, randomly taken from interior portion of an Allende specimen cut into thin slices, were analyzed for U isotope composition at the University of Otago, using the analytical procedures of [3,4]. The samples were spiked with a high purity ^{233}U-^{236}U mixed tracer, and analyzed without acid leaching, in order to prevent possible U isotope fractionation induced by laboratory treatment. Isotopic compositions were measured on a Nu Plasma MC-ICPMS with a DSN-100 desolvating nebulizer by simultaneous detection of uranium isotopes. A concentrated solution was analyzed on-peak over a 60-120 s acquisition period to increase the minor ^{235}U ion beam signal to an intensity that is sufficiently large (typically >1 x 10^{-12} A) for measurement on a stable Faraday collector to maximize the signal to noise ratio and minimizing errors [3]. The measured isotope ratios were corrected for the contributions of natural U isotopes in the ^{233}U-^{236}U spike and instrumental mass fractionation, by normalization against $^{236}U/^{233}U$. The $^{236}U/^{233}U$ ratio was calibrated against the U standard CRM 145, assuming the $^{238}U/^{235}U$ value of 137.88. The $^{144}Nd/^{238}U$ ratio was measured in a 80 mg aliquot of powdered sample using GV Platform XS quadrupole mass spectrometer at Harvard University.

U-Pb analyses were performed on nine ca. 5 mg aliquots of crushed CAI, using procedures, including rigorous multi-step acid leaching, similar to those used for angrites [11] and Efremovka CAI E60 [12]. All residues and leachates were spiked with mixed ^{202}Pb-^{205}Pb-^{229}Th-^{233}U-^{236}U tracer before digestion. Pb and U were analyzed on a Finnigan MAT-261 TIMS at the Australian National University as Pb^+ in static multi-collector mode on Faraday cups, and as UO_2^+ on an electron multiplier, respectively. Twenty 300 picogram loads of the NIST SRM-981 standard, spiked with the same tracer as the meteorite samples, yielded 0.05904 (±0.22%, 2 s.d.) for $^{204}Pb/^{206}Pb$, 0.91475 (±0.020%, 2s.d.) for $^{207}Pb/^{206}Pb$, and 2.16803 (±0.032%, 2 s.d.) for $^{208}Pb/^{206}Pb$.

Results: A ^{207}Pb-^{206}Pb isochron for seven acid-washed fractions (excluding two fractions rich in dark, more altered material) of the CAI SJ101A yield an age of 4567.22 ± 0.21 Ma, assuming a $^{238}U/^{235}U$ value of 137.88 (Fig.1). This date is identical to the date of E60, a FoB-type CAI from the CV chondrite Efremovka [12], and are consistent within 95% confidence intervals with the ages of several other CAIs from Allende [13,14], but is distinctly younger than some of the recently reported Pb-Pb ages of CAIs from the CV chondrites NWA 2364 [15] and Allende [16].

The $^{238}U/^{235}U$ ratio of 137.917±0.043 in CAI SJ101 (Fig. 2) marginally overlaps at the 95% confidence limits with the mean value of 137.861±0.014 for three terrestrial mafic and ultramafic rocks, and is well resolved from the mean value of 137.788±0.017 for Allende bulk rock fragments and a chondrule fraction.

Discussion: The difference of 0.129±0.046 in $^{238}U/^{235}U$ between the CAI SJ101 and bulk Allende meteorite and chondrules implies an increase in the ^{207}Pb-^{206}Pb age difference of 1.35±0.49 Ma compared to the age interval calculated assuming identical $^{238}U/^{235}U$. Using the measured $^{238}U/^{235}U$ in the chondrule and CAI age calculations, instead of assuming a constant value, increases the age difference between the CAI SJ101 and the Allende chondrule age in [10] from 0.62±1.02 Ma to 1.97±1.13 Ma and makes the interval clearly resolved. The age difference between the CAI SJ101 and the Allende chondrule age in [13] increases from 1.77±0.50 to 3.12±0.70 Ma. The CAI-chondrule Pb-Pb age difference of 2-3 Ma, calculated with the measured $^{238}U/^{235}U$, is close to the CAI-chondrule time interval estimated using the ^{26}Al-^{26}Mg and ^{182}Hf-^{182}W extinct nuclide chronometers, thus resolving one of the major inconsistencies in the emerging pattern of early Solar System chronology [7,8,12].

The $^{238}U/^{235}U$ ratio in meteorites can be lowered if their parent bodies contained live ^{247}Cm [1-3]. Stirling et al. [2,3] have established an upper limit for a Solar System initial $^{247}Cm/^{235}U$ of less than 8×10^{-5}, using Nd/U as a proxy for Cm/U. However, recent reports of low $^{238}U/^{235}U$ in CAIs [17,18] are attributed to the possible presence of significantly higher levels of ^{247}Cm in the early Solar System. We assess whether ^{247}Cm could have contributed to the observed difference in $^{238}U/^{235}U$ between the CAI SJ101 and bulk Allende by comparing their $^{144}Nd/^{238}U$ ratios, following [2,3]. Nd and U concentrations of 9.25 ppm and 62.37 ppb, respectively, measured in a representative whole rock powder sample of the CAI SJ101 yield the $^{144}Nd/^{238}U$ value of 58.7. This is ca. twice as high as the bulk Allende values of 25-30 [2,3] and would require CAI SJ101 to have a higher relative abundance of ^{235}U, and thereby a lower $^{238}U/^{235}U$, than the bulk sample to be consistent with the former presence of "live" ^{247}Cm. This, however, is contrary to the reported observations. The observed difference in $^{238}U/^{235}U$ is, therefore, caused by some other mechanism, possibly isotope fractionation, a redox processes, or a nucleosynthetic isotope anomaly, rather than ^{247}Cm decay.

Our data support growing understanding that $^{238}U/^{235}U$ variations in planetary materials are pervasive, caused by more than one mechanism, and are large enough to make significant changes in ^{207}Pb-^{206}Pb ages at the current precision of dating. We suggest that achieving accurate ages in any geo- and cosmochronological study using the $^{238,235}U$-$^{206,207}Pb$ isotopic chronometer must include precise determination of the $^{238}U/^{235}U$ ratio. A necessary first step towards a consistent U-Pb chronology free from biases induced by U isotope variations is establishing a common reference point – a single large, homogeneous U isotope standard that will be accepted and widely used by the geochronology and cosmochronology communities.

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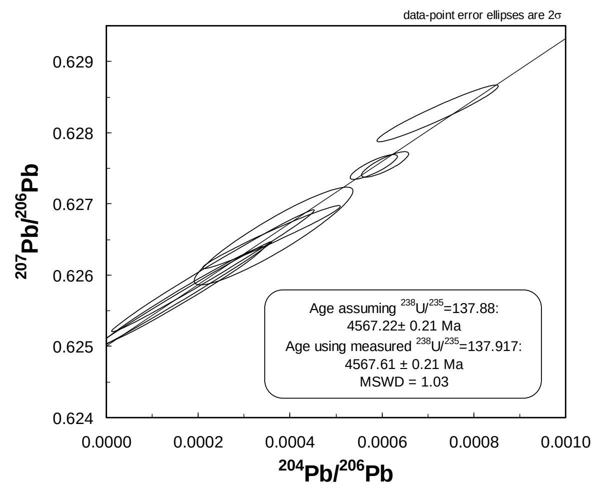

Fig. 1. Pb-isotopic data for acid-washed fractions from Allende CAI SJ101, plotted in a $^{207}Pb/^{206}Pb$ vs. $^{204}Pb/^{206}Pb$ isochron diagram.

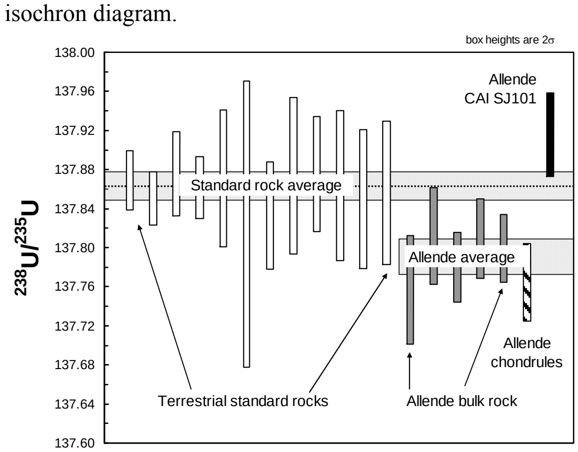

Fig. 2. Uranium isotopic compositions of USGS standard rocks BCR-2, BHVO-2 and DTS-2, fragments of the Allende meteorite, an aliquot of an assorted Allende chondrule population, and Allende CAI SJ101.