U-Pb chronology of the Solar System's oldest solids with variable $^{238}\text{U}/^{235}\text{U}$

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Abstract

Accurate determination of the absolute ages of the oldest Solar System objects – chondrules and Ca-Al-rich inclusions (CAIs), requires knowledge of their $^{238}\text{U}/^{235}\text{U}$ ratios. This ratio was assumed to be invariant in all U-Pb dating of meteorites so far, but the recent discovery of U isotope variations in CAIs (Brennecka et al. 2010a) shows that this assumption is invalid. We present the first combined high precision U and Pb isotopic data for a CAI, and U isotopic data for chondrules and whole rock fractions of the Allende meteorite. The Pb-Pb isochron age of the CAI SJ101 is 4567.18 ± 0.50 Ma, calculated using the measured $^{238}\text{U}/^{235}\text{U} = 137.876 \pm 0.043$ (2σ), reported relative to $^{238}\text{U}/^{235}\text{U} = 137.837$ of the CRM 145 standard. Our best current estimate of the average terrestrial value is: $^{238}\text{U}/^{235}\text{U} = 137.821 \pm 0.014$. The error in the age includes uncertainties in the Pb-Pb isochron intercept and in the $^{238}\text{U}/^{235}\text{U}$ ratio. Allende bulk rock and chondrules have $^{238}\text{U}/^{235}\text{U} = 137.747 \pm 0.017$ (2σ), distinctly lower than the CAI. The difference in the $^{238}\text{U}/^{235}\text{U}$ ratio of 0.129 ± 0.046 (2σ) between the CAI and chondrules and bulk meteorite increases the ^{207}Pb - ^{206}Pb age difference by ~ 1.4 million years, and eliminates apparent disagreement between the CAI-chondrule formation time interval determinations with the U-Pb and extinct nuclide (^{26}Al - ^{26}Mg and ^{182}Hf - ^{182}W) data. We discuss standardization of $^{238}\text{U}/^{235}\text{U}$ measurements for U-Pb geochronology and cosmochemistry, elemental and isotopic fractionation induced by intensive acid leaching, ages of CAIs in the context of $^{238}\text{U}/^{235}\text{U}$ variability, and possible causes of U isotopic variations in CAIs and meteorites.

Keywords

Chondrites, chondrules, refractory inclusions, absolute age, U-Pb, uranium isotopes

1. Introduction

Recent discoveries in astronomy and planetary science have overturned the previously accepted paradigm of planetary system formation by gradual cooling of a collapsed molecular cloud, and sequential condensation of ever larger lumps of matter, growing from mineral grains to planets. Instead, the early solar nebula is now seen as a dynamic assembly of hot and cold domains, differentiating planetesimals and pristine dust, which coexisted and interacted for a period of less than 10 million years (Ma). Understanding the interaction between these domains is impossible without accurate knowledge of the sequence and duration of the early processes occurring in the Solar System. The time markers for these processes are provided by abundances of short-lived (now extinct) isotopes, and by accumulation of radiogenic Pb isotopes from the decay of U and Th.

Two types of mm-sized solid aggregates: refractory calcium-aluminium rich inclusions (CAIs), and igneous spherical objects composed of ferromagnesian silicate minerals, glassy mesostasis, and Fe,Ni-metal (chondrules), are among the first solids that formed during the accretion of our Solar System. Their temporal relationships have been the subject of many recent studies (Amelin et al. 2002, Bizzarro et al. 2004, Thrane et al. 2006, Amelin and Krot 2007, Bouvier et al. 2007, Connelly et al. 2008a, Jacobsen et al. 2008, Burkhardt et al. 2008, Bouvier and Wadhwa 2009, Krot et al. 2009, Nyquist et al. 2009, Villeneuve et al. 2009) using extinct ^{26}Al - ^{26}Mg and ^{182}Hf - ^{182}W , and extant $^{238,235}\text{U}$ - $^{206,207}\text{Pb}$ isotopic chronometers. These studies confirm that CAIs are the oldest macroscopic solids formed in the accreting solar nebula, and show that chondrule formation started shortly after CAI formation and completed within 3-5 Ma. The oldest differentiated asteroids also formed within this time interval. However, two unresolved problems remain: whether the apparent age difference between CAIs and chondrules is real (Davis 2009), and what causes a deviation in ages of CAIs from the emerging consistent pattern of the early Solar System chronology (Burkhardt et al. 2008, Davis 2009, Amelin et al. 2009, Nyquist et al. 2009, Kleine et al. 2009).

Among the causes of possible inaccuracy in $^{207}\text{Pb}/^{206}\text{Pb}$ ages of meteorites and their components are variations in the $^{238}\text{U}/^{235}\text{U}$ ratio. Early reports of large excesses of ^{235}U (Arden 1977, Tatsumoto and Shimamura 1980), attributed to decay of extinct ^{247}Cm (half-life = 15.6 My, Fields et al. 1971), were refuted by subsequent more precise and accurate studies (Chen and Wasserburg 1981, Friedrich et al. 2004, Stirling et al. 2005, 2006). This ratio was thought to be

invariant in the Earth and early Solar System at the limits of analytical precision of the time, and a constant $^{238}\text{U}/^{235}\text{U}=137.88$ was adopted for use in all geochronological studies (Steiger and Jäger 1977), largely based on absolute $^{238}\text{U}/^{235}\text{U}$ measurements for uranium ores by Cowan and Adler (1976). However, the question was re-opened by recent discoveries of U isotope variations in some terrestrial rocks (Stirling et al. 2007, Weyer et al. 2008, Bopp et al. 2009), particularly in surface samples formed in low-temperature environments, and in some CAIs from carbonaceous chondrites (Brennecka et al. 2010a). The magnitude of $^{235}\text{U}/^{238}\text{U}$ variations in CAIs reported in the latter study is such that it would infer adjustments to the $^{207}\text{Pb}/^{206}\text{Pb}$ age of up to 5 Ma, but hitherto there have been no geochronological studies where the U isotopic variations are assessed along with their corresponding Pb isotope ratios.

In the present study, we report combined high precision $^{238}\text{U}/^{235}\text{U}$ and $^{238,235}\text{U}-^{206,207}\text{Pb}$ measurements of the CAI SJ101 from the CV chondrite Allende, and a U isotopic study of chondrules and representative whole rock samples of the same meteorite. The detected U isotopic variations are used to correct the ages and age intervals.

2. Sample and techniques

The CAI SJ101 is a rather typical forsterite-bearing (FoB) inclusion in mineralogy and chemical composition, but has a more complex internal structure than most other CAIs of that type (Petaev and Jacobsen 2009). This CAI has a Group II rare earth element (REE) distribution (see Ireland and Fegley 2000 for a review of Group II rare earth element patterns), being depleted in very refractory elements and having major element ratios close to the solar values. This suggests that precursors of this CAI could have formed by non-equilibrium condensation from a gas with compositions close to solar, or slightly depleted in the most refractory elements (Petaev and Jacobsen 2009).

SJ101 is a large (6.34 g, ~2.5x1.5 cm), potato-shaped CAI that has been extracted almost intact from an Allende end piece. The CAI was cut perpendicular to its longest axis into two pieces weighing 2.41 and 3.83 g. A slice from the larger piece, free from matrix overgrowths, has been coarsely crushed for destructive analyses. A 76 mg aliquot of crushed CAI material, a 197 mg sample comprising >50 chondrules prepared for an earlier study (Amelin and Krot 2007) and five ca. 440 mg whole rock fragments, randomly taken from the interior portion of an Allende

specimen cut into ca. 3 mm slices, were analysed for U isotope composition at the Centre for Trace Element Analysis at the University of Otago, using the analytical procedures of Stirling et al. (2005, 2006, 2007). Lead isotopic analyses were performed at the Australian National University using analytical procedures reported in Amelin (2008a, b; 2009).

The U-isotopic and U-Pb procedures and the U-Pb data are described in detail in the Electronic Supplementary Material ES1. In brief, samples for U isotopic analyses were spiked with a high purity ^{233}U - ^{236}U mixed tracer, and analysed without acid leaching, to prevent possible U isotope fractionation induced by laboratory treatment. Uranium was chemically extracted from the sample matrix and purified using TRU.Spec and UTEVA.Spec ion exchange resins (Eichrom). Uranium isotopic compositions were measured using a Nu Plasma multiple-collector inductively coupled plasma mass spectrometer (MC-ICPMS) with a DSN-100 desolvating nebuliser by simultaneous detection of all U isotopes. A concentrated solution was analysed 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 ($>1 \times 10^{-12}$ A) for measurement on a stable Faraday collector, thus maximising the signal to noise ratio and minimising errors (Stirling et al. 2006). The measured isotope ratios were corrected for both the contributions of natural U isotopes present in the ^{233}U - ^{236}U spike and instrumental mass fractionation (by normalization against $^{236}\text{U}/^{233}\text{U}$). The $^{236}\text{U}/^{233}\text{U}$ ratio of the mixed spike tracer was calibrated against the U metal standard CRM 145, assuming CRM 145 has a $^{238}\text{U}/^{235}\text{U}$ value of 137.837 ± 0.015 (Richter et al. 2010). Repeat $^{238}\text{U}/^{235}\text{U}$ measurements of <10 ng loads of CRM 145, spiked in the same way as the samples, yielded a long-term reproducibility of 0.024% (2 s.d.).

U-Pb analyses were performed on a Finnigan MAT 261 thermal ionisation mass spectrometer (TIMS). The results of analyses of twenty 300 picogram loads of the NIST SRM-981 standard, spiked with the same ^{202}Pb - ^{205}Pb - ^{229}Th - ^{233}U - ^{236}U mixed tracer as the meteorite samples, are presented in Table ES2. Nine aliquots of crushed CAI with a total mass of 45 mg were analysed using procedures, including multi-step acid leaching, and data treatment, similar to those used for angrites (Amelin 2008a,b) and Efremovka CAI E60 (Amelin et al. 2009). The nine aliquots were analysed in three batches, using slightly different washing schemes in order to test the efficiency of removal of non-radiogenic Pb, and possible effects on fractionation between U and Pb. All three batches (A003, A004 and A005) were washed in 0.5M HNO_3 with ultrasonic

agitation (first wash), and in hot 7M HNO₃ and 7M HCl (second wash). Batch A004 was additionally leached in hot 9M HBr for 14 hours (third wash).

The concentrations of Nd and U along with other trace and major elements were determined with an accuracy of ~ 1-2% by a GV Platform XS quadrupole ICP-MS at Harvard University on an 80 mg aliquot of SJ101. The concentrations of major elements in this aliquot are nearly identical to the bulk composition measured by EMPA of a complete polished section cut through the SJ101 inclusion (see Table 2 in Petaev and Jacobsen 2009).

3. Results

U isotope data are presented in Table ES3 and Fig.1, and are described in detail in Supplementary Material ES1. A terrestrial reference value of $^{238}\text{U}/^{235}\text{U}=137.821\pm0.014$ (MSWD=0.32), measured during the same instrument session as the Allende samples, was determined from multiple analyses of three USGS standard rocks: basalts BCR-2 and BHVO-2, and dunite DTS-2b. The $^{238}\text{U}/^{235}\text{U}=137.876\pm0.043$ in the CAI SJ101 marginally overlaps the “terrestrial” value at the 95% confidence limits. This value is used in Pb isotopic age calculation for this CAI throughout this paper. Five whole rock fragments of Allende yield a mean $^{238}\text{U}/^{235}\text{U}=137.751\pm0.021$ (MSWD=1.07], which is in excellent agreement with the average value of 137.750 ± 0.021 (2 S.E.) determined for two independent bulk samples of Allende reported in Stirling et al. (2006) (following the conversion of $\epsilon^{235}\text{U}$ notation into absolute $^{238}\text{U}/^{235}\text{U}$ values). The Allende chondrule fraction has a $^{238}\text{U}/^{235}\text{U}=137.724\pm0.040$, and is identical, within error, to the whole rock value for Allende. Taken together, the Allende whole rock and chondrule fractions yield a $^{238}\text{U}/^{235}\text{U}=137.747\pm0.017$ (MSWD=1.07), which is distinctly lower than the “terrestrial” and CAI values.

U-Pb data for acid leachates and residues are presented in Table ES4, and discussed in detail in the Supplementary Material ES1. One of the fractions (#6) which mainly consisted of dark, probably altered material, yielded Pb isotopic data that deviate from the data for all the other fractions, and a highly discordant U-Pb system. The data for this fraction are excluded from isochron regressions. The first (ultrasonic) washes contain Pb with $^{206}\text{Pb}/^{204}\text{Pb}$ between 13 and 24. The second (hot 7M HNO₃ and 7M HCl) washes contain Pb with slightly higher $^{206}\text{Pb}/^{204}\text{Pb}$ between 19 and 79. The Pb isotopic composition is much more radiogenic in the third (hot 9M

HBr) washes ($^{206}\text{Pb}/^{204}\text{Pb}$ between 550 and 1400), and in the residues ($^{206}\text{Pb}/^{204}\text{Pb}$ between 1400 and 3000). Non-radiogenic Pb in the CAI SJ101 is a mixture of initial Pb with an isotopic composition close to primordial Pb (Tatsumoto et al. 1973), and easily leachable Pb resembling modern crustal Pb (Stacey and Kramers 19975), probably from surface contamination. To better understand the effects of acid leaching on the U-Pb system, the leachates and residues were numerically recombined using measured U and Pb concentrations and Pb isotopic ratios. Recombined concentrations and isotopic ratios are presented in the Table ES2 along with measured ratios.

The total content of uranium in the nine analysed fractions of CAI SJ101 is between 59 and 71 ppb. Concordance of the U-Pb isotopic systems in recombined bulk analyses within 5% (within 1.5% considering batches A003 and A005 only) is consistent with closed system behaviour. A Pb-Pb isochron for the residues and third washes are plotted in Fig. 2. The isochron dates of the third washes (4567.72 ± 0.70 Ma) and complementary residues (4566.06 ± 0.63 Ma) of the sample batch A004 diverge outside 95% error limits, whereas the residues of the batches A003 and A005 yield an intermediate value of 4567.26 ± 0.19 Ma. We consider this as evidence for fractionation between radiogenic ^{207}Pb and ^{206}Pb induced by extensive leaching in hot 9M HBr. That leaching step also induced excess fractionation between U and radiogenic Pb, expressed by considerably larger negative discordance of the residues in the batch A004 compared to the batches A003 and A005.

Numeric remixing of the residues and third washes eliminates excessive U-Pb fractionation and isotopic fractionation of radiogenic ^{207}Pb and ^{206}Pb , and makes the residue analyses of all three batches consistent. The combined Pb-Pb isochron (Fig. 3) yields a radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ ratio (y-intercept) of 0.625000 ± 0.000092 , which corresponds to an age of 4567.18 ± 0.21 (± 0.50) Ma (age uncertainty in brackets includes uncertainty of the $^{238}\text{U}/^{235}\text{U}$ ratio). This is our preferred age for the CAI SJ101.

4. Discussion

4.1. Volatility-driven elemental and isotopic fractionation in the CAI SJ101

The CAI SJ101A has a Group II REE pattern and is therefore depleted in the ultra-refractory elements, including the REE between Gd and Er, and Lu (Ireland and Fegley 2000). Hence Group II inclusions have a characteristic Tm anomaly where Tm is at the same abundance level as the light REE). This pattern can be produced either by fractional condensation (Ireland and Fegley 2000), or by partial evaporation (Petaev and Wood 2005, Petaev and Jacobsen 2009) where the ultra-refractory component is isolated from the gas and removed prior to condensation of the less refractory elements.

Given that condensation and evaporation were operative in the accreting proto-planetary disk, U isotopic mass fractionation could have occurred during the formation of CAIs and chondrules. Evaporation favours light isotope enrichment in the gas and, hence, in any initial condensate from the early evaporated material. As evaporation proceeds, the residue becomes more refractory, and with preferential removal of the light isotopes, the isotopic composition of the residue becomes heavier and successive condensates originating from this residue will become heavier as well. Thus, the degree of evaporation, inferred from the REE pattern, gives an indication of the extent of isotopic mass fractionation to be expected.

However, in Group II inclusions the ultra-refractory component has been removed. Uranium is a very refractory element, therefore at least some of the U would also have been removed during the same event or events. The first condensate from a gas of solar composition, initially containing all elements and their isotopes in the gas phase, could show heavy isotope enrichment if condensation is the kinetic inverse of evaporation. This will lead to lighter isotopic species in the residual gas, and condensation of gas after the refractory elements are removed (including partial removal of uranium) could yield isotopically light uranium in the condensates. The same direction of isotopic mass fractionation should be expected if the Group II condensate is produced from evaporation. In this case, the ultra-refractory residue is always isotopically heavier than the condensate. It thus seems unavoidable that U will have light isotope enrichment if the Group II pattern is due to a loss of a super-refractory component.

4.2. Standardisation of $^{238}\text{U}/^{235}\text{U}$ measurements for U-Pb geochronology and cosmochronology.

Recent developments in “stable isotope” geochemistry of U have shown that the previously universally accepted $^{238}\text{U}/^{235}\text{U}=137.88$ is invalid in two ways. First, the ratio is variable in nature, most notably in CAIs (Brennecka et al. 2010a), but also in other extraterrestrial materials (Brennecka et al. 2010b and this study) as well as in terrestrial rocks (e.g. Stirling et al. 2007, Weyer et al. 2008), including those utilized as uranium isotopic standards (Stirling et al., 2007). Second, application of high-accuracy gravimetric standards and spikes (Richter et al. 2008) to U isotope analysis shows that the $^{238}\text{U}/^{235}\text{U}$ ratios in uranium ores, and in commonly used U standards prepared from ores, is typically lower than 137.88 (Richter et al. 2010, Condon et al. 2010).

The implications of U isotopic variability and a systematic shift in the accepted $^{238}\text{U}/^{235}\text{U}$ ratio away from the previously adopted value of 137.88 for U-Pb geochronology were discussed by Stirling et al. (2007), Brennecka et al. (2010a), and Condon et al. (2010), but further discussion of standardisation is warranted. Establishing a consistent geochronological framework requires a universally accepted, single reference point for U isotopic composition. The primary standard should be homogeneous, of high chemical purity so that it does not require further chemical preparation, suitable for various analytical techniques, available in a sufficiently large quantity to serve research and analytical communities for a long time, and its isotopic composition should be traceable to the International System of Units (SI). Several currently used materials may satisfy these requirements: “natural” U such as NBS SRM 960 and its derivatives (i.e. NBL CRM 112a, and NBL CRM 145 prepared by dissolving that material), artificial U isotopic mixtures with near natural isotopic composition, such as IRMM 184, or high purity ^{233}U - ^{236}U spikes such as IRMM 3636 (Richter et al. 2008). The advantages of SRM 960 as a primary U standard are its wide distribution in the community, and proximity to the U isotopic composition of rocks. The advantage of artificial, gravimetric IRMM standards is the ability to directly trace their composition to SI. The pros and contras of various choices need a broad discussion. After the primary standard and its $^{238}\text{U}/^{235}\text{U}$ reference values are chosen, the other standards and spikes should be precisely calibrated against it. The studies by Richter et al. (2010) and Condon et al. (2010) are important steps towards inter-calibration of U standards.

Some commonly used reference materials cannot be recommended as primary standards, although they can make useful secondary standards for certain analytical applications. Rocks (including the widely distributed Harwell Uraninite HU-1) and artificial multi-element standards

are not suitable as primary standards because their analysis by some methods requires chemical separation of U, and this introduces additional uncertainty. Also, the U isotopic composition in rocks and ores can be heterogeneous at a mineral grain scale. Furthermore, artificial U standards enriched in ^{235}U , such as IRMM 072, 073 and 074 series and the popular CRM U500, or standards depleted in ^{235}U , such as the NIST SRM 610 to 619 glasses, can cause undesirable memory effects in some analytical instruments, e.g. in MC-ICPMS with desolvating nebulisers, which can potentially compromise accuracy of $^{238}\text{U}/^{235}\text{U}$ determinations.

Accurate propagation of U standardisation errors in the total errors of U-Pb ages is as important as the choice of the standards. We believe that, if a single primary standard is universally accepted, and the ^{233}U - ^{236}U spike is calibrated directly against that primary standard, the error of calibration should be propagated in the total error, but the absolute error of the primary standard should not (with exception of special cases such as determination of decay constants, e.g. Schoene et al. 2006). If the spike is calibrated against a secondary standard, then both the spike calibration error and the standard inter-calibration error should be propagated into the total age error.

4.3. Elemental and isotopic fractionation in the U-Pb systems induced by acid leaching.

Pb-isotopic dating by stepwise leaching, or progressive dissolution, is a method initially developed for dating single mineral species and thus avoiding paragenetic complexity (Frei and Kamber 1995). A similar technique is becoming popular as a method for high-precision dating of meteorites (Connelly et al. 2008a,b, Connelly and Bizzarro 2009, Bouvier and Wadhwa 2010). This technique helps to remove non-radiogenic Pb and to increase the spread of the Pb-Pb isochron, thus improving precision of the age. Under favourable circumstances, it can help to separate non-radiogenic Pb components and to make Pb isotopic dates based on moderately radiogenic data less ambiguous (e.g., Connelly et al. 2008a). However, fractionation of radiogenic Pb isotopes induced by acid leaching, hypothesised by Amelin et al. 2009 and observed during the third washing step in this study, is a troubling effect that can produce inaccurate Pb isotopic dates even in highly radiogenic U-Pb systems. It requires further study and detailed monitoring of the effects of leaching steps on rocks and minerals by complete U-Pb

analysis (concordance tests) and chemical analysis of step leachates, and by observing changes in the sample mineralogy induced by leaching. It may also be possible to reduce leaching-induced Pb isotopic and U-Pb fractionation by annealing a meteorite and thereby creating a procedure similar to the “chemical abrasion” of zircons (Mattinson 2005), although preliminary tests by Amelin and Iizuka (2010) show that annealing can also make non-radiogenic Pb in chondrules more resistant to leaching.

4.4. Interval between formation of CAIs and chondrules.

The difference of 0.129 ± 0.046 in $^{238}\text{U}/^{235}\text{U}$ between the Allende CAI SJ101 and the combined whole rock and chondrule fractions of Allende requires an increase in the ^{207}Pb - ^{206}Pb age difference of 1.35 ± 0.49 Ma compared to the age interval calculated assuming identical $^{238}\text{U}/^{235}\text{U}$. Using the statistically distinct, measured $^{238}\text{U}/^{235}\text{U}$ values 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 Amelin and Krot (2007) 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 Connelly et al. (2008a) 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 $^{238}\text{U}/^{235}\text{U}$, is close to the CAI-chondrule time interval estimated using the ^{26}Al - ^{26}Mg (1.5-3.0 Ma, Villeneuve et al. 2009) and ^{182}Hf - ^{182}W (1.7 ± 0.7 Ma, Kleine et al. 2009) extinct nuclide chronometers, and thus appears to resolve the major inconsistency in the emerging pattern of early Solar System chronology (Burkhardt et al. 2008, Amelin et al. 2009, Nyquist et al. 2009).

4.5. U isotopic disparity between chondrites and terrestrial rocks

While the impact of the difference in $^{238}\text{U}/^{235}\text{U}$ between the CAI and the combined bulk meteorite and chondrule fractions of Allende on chronology is straightforward, the cause(s) of the difference between the U isotopic composition of bulk Allende and the three terrestrial mafic and ultramafic rocks is less clear. Considering the volume abundance of chondrules in Allende and

other CV chondrites of ~45% (Scott and Krot 2003), and the concentration of U in the chondrule fraction of 25 ppb (Table ES3), approximately twice that of average bulk rock concentration of 13.6 ppb (an average of the values reported by Chen and Tilton 1976, Tatsumoto et al. 1976, Arden and Cressey 1984, Stirling et al. 2005, 2006, and determined in this study, summarised in Table ES3), we infer that >80% of U in Allende resides in chondrules. This substantiates using combined bulk rock and chondrule average $^{238}\text{U}/^{235}\text{U}$ as a representative value for Allende chondrule age calculation. The meaning of the terrestrial value is less clear, because there is growing evidence that the fractionation of $^{238}\text{U}/^{235}\text{U}$ in terrestrial environments is not restricted to the direct influence of redox processes (Stirling et al. 2007, Weyer et al. 2008, Bopp et al. 2009). Isotopic variations of U due to previous involvement in redox processes before being incorporated in high-temperature magmatic systems is also possible. “Stable” isotope geochemistry of U is in its infancy, but it is already clear that $^{238}\text{U}/^{235}\text{U}$ fractionation is pervasive and probably caused by several mechanisms, such that no terrestrial rock of crustal or mantle origin can be taken as containing U with representative bulk Earth $^{238}\text{U}/^{235}\text{U}$ until the nature and extent of U isotopic variations are better understood.

Recent studies in isotope geochemistry (e.g. Ranen and Jacobsen 2006; Carlson et al. 2007, and Trinquier et al. 2007, 2009, and many other) have established the difference in isotopic composition of many elements between the Earth and chondrites, and isotopic heterogeneity among the chemical classes of chondrites. Our results and those of Brennecka et al. (2010b) show that U is no exception. Whether U isotopic composition is variable in mantle and crustal rocks that were not exposed to aqueous or hydrothermal environments is currently unknown. Our analyses of USGS standard rocks, similar data of Weyer et al. (2008) for some of the same standards, and observations for basalts reported in Stirling et al. (2005) have detected no such heterogeneity (although offsets in the $^{238}\text{U}/^{235}\text{U}$ composition between different datasets is possible), but more extensive studies are needed to evaluate the possible role of partial melting, and crystal growth and fractionation in U isotopic fractionation.

4.6. U-Pb chronology of CAIs in the case of variable $^{238}\text{U}/^{235}\text{U}$.

This is the first combined U-Pb and $^{238}\text{U}/^{235}\text{U}$ study of CAIs since Chen and Wasserburg (1981), and the first U-Pb chronological study of CAIs where U isotopic variations are detected and used to correct the age. Considering the magnitude of $^{235}\text{U}/^{238}\text{U}$ variations in Allende CAIs reported by Brennecka et al. (2010a) that would require adjustments on the $^{207}\text{Pb}/^{206}\text{Pb}$ age of up to 5 Ma, comparing the age of SJ101 to published Pb-isotopic ages of other CAIs would be premature.

In a recently published Pb-isotopic study of a CAI from CV chondrite NWA 2364, Bouvier and Wadhwa (2010) proposed to use the Th/U or Nd/U ratios as proxies to U isotopic variations on the basis of correlations between $^{238}\text{U}/^{235}\text{U}$ and $^{232}\text{Th}/^{238}\text{U}$ or $^{144}\text{Nd}/^{238}\text{U}$ ratios in CAIs reported by Brennecka et al. (2010a) that have been attributed to the decay of short-lived, extinct ^{247}Cm to its ^{235}U daughter nuclide. A special attractiveness of this approach is the possibility of retrospectively applying corrections to the published Pb isotopic ages of CAIs using Th/U model values calculated from radiogenic $^{208}\text{Pb}/^{206}\text{Pb}$, which closely match measured Th/U ratios in highly radiogenic U-Pb systems (Amelin et al. 2009). However, two conditions of using this approach must be satisfied: (1) the $^{238}\text{U}/^{235}\text{U}$ vs Nd/U or Th/U correlation holds for all CAIs, and (2) all $^{238}\text{U}/^{235}\text{U}$ variability can be attributed to ^{247}Cm decay within an accreting proto-planetary disk with a uniform initial $^{238}\text{U}/^{235}\text{U}$ composition. We explore these conditions by plotting the data for the CAI SJ101 on $^{238}\text{U}/^{235}\text{U}$ vs. $^{144}\text{Nd}/^{238}\text{U}$ and $^{235}\text{U}/^{238}\text{U}$ vs. $^{232}\text{Th}/^{238}\text{U}$ plots of Brennecka et al. 2010 (Figures 5 and 6, respectively). On both plots, the data point of SJ101 plots well below the trends of other CAIs, thus demonstrating that these correlations are not universal.

To further explore the effects of various age adjustments, we have plotted the isochron age of the CAI SJ101, calculated using five possible ways of correcting for U isotopic variability, in Fig. 7. The direction of adjustment implied by $^{235}\text{U}/^{238}\text{U}$ vs. $^{144}\text{Nd}/^{238}\text{U}$ correlation (#4) and $^{235}\text{U}/^{238}\text{U}$ vs. $^{232}\text{Th}/^{238}\text{U}$ correlation (#5) is opposite to the adjustment based on the measured $^{235}\text{U}/^{238}\text{U}$ ratio. The ages adjusted using different approaches (#3 vs. #4 and 5) diverge outside 95% error limits, despite magnification of the age errors due to imperfect coupling between $^{238}\text{U}/^{235}\text{U}$ and $^{144}\text{Nd}/^{238}\text{U}$ or $^{232}\text{Th}/^{238}\text{U}$, demonstrating that attempting the CAI age correction proposed by Bouvier and Wadhwa (2010) can produce inaccurate results. Clearly, the only reliable means of ensuring accurate $^{207}\text{Pb}/^{206}\text{Pb}$ ages is to measure the $^{238}\text{U}/^{235}\text{U}$ composition directly.

An additional factor that may contribute to the age variability among CAIs is the difference in the degree of metamorphism, aqueous alteration, shock metamorphism and terrestrial weathering between CV chondrites. The Pb-isotopic ages (calculated assuming $^{238}\text{U}/^{235}\text{U}=137.837$) for eight CAIs from four CV chondrites are plotted against $^{232}\text{Th}/^{238}\text{U}$ ratios in Fig. 8. The $^{232}\text{Th}/^{238}\text{U}$ ratios in the Efremovka CAIs are the lowest, in the Allende CAIs – the highest, and the CAIs from NWA 2364 and Vigarano have intermediate $^{232}\text{Th}/^{238}\text{U}$ values. The difference in $^{232}\text{Th}/^{238}\text{U}$ between the CAIs, and especially between groups of CAIs from different chondrites, is greater than the internal variations, supporting suggestion by Jacobsen et al. (2008) of the presence of heterogeneous chemical reservoirs, not related to high temperature evaporation, in the early solar nebula.

The ages of four CAIs from Allende and two CAIs from Efremovka are consistent, and give a weighted average value of 4566.76 ± 0.20 Ma, MSWD=1.8. The ages of two CAIs from NWA 2364 and Vigarano are about 1.6 Ma older. Neither $^{232}\text{Th}/^{238}\text{U}$ ratios nor ages correlate with the petrologic type of the CAI (compact type A, type B, or forsterite-bearing type B). The cause of the apparent age difference between six Efremovka and Allende CAIs of ca. 4566.8 Ma, and two NWA 2364 and Vigarano CAIs of ca. 4568.4 Ma is unclear. The CAIs from both age groups have well preserved ^{26}Al - ^{26}Mg systems (Amelin et al. 2002, Jacobsen et al. 2008, Bouvier and Wadhwa 2010) that yield initial $^{26}\text{Al}/^{27}\text{Al}$ close to the canonical value and suggest simultaneous formation. The possibility of post-accretional (e.g. related to alteration and/or metamorphism) disturbance of the U-Pb system in Allende and Efremovka appears unlikely, because such disturbance would have produced “aborted high- μ Pb” or “parentless radiogenic Pb” with anomalously high $^{207}\text{Pb}/^{206}\text{Pb}$ at a given $^{204}\text{Pb}/^{206}\text{Pb}$, such as found in lunar rocks, eucrites, and angrite Sahara 99555 (e.g. Tera et al. 1974, Galer and Lugmair 1996, Amelin 2008b). There is no evidence for such a Pb component in Allende and Efremovka CAIs. On the contrary, the Pb isotopic systematics of leachates of the CAI SJ101 point to primordial Pb as an initial Pb, as expected for an undisturbed U-Pb system. Pb isotope analyses were performed using different techniques: MC-ICPMS with Tl normalisation for the “older” NWA 2364 and Vigarano CAIs, and TIMS with double spike or external normalisation for “younger” Efremovka and Allende CAIs. However, considering the close agreement between standard results (Amelin 2008a, Bouvier and Wadhwa 2010, and this study), the difference in techniques is unlikely to have caused the observed age difference. The final possibility is that the age discrepancy is

caused by leaching-induced fractionation of radiogenic ^{207}Pb and ^{206}Pb , due to the difference in leaching procedures used in our analyses and in the studies by Bouvier and Wadhwa. The magnitude of leaching-induced fractionation that we observed in the CAI SJ101 exposed to hot concentrated HBr – 1.6 ± 0.9 Ma (Fig. 2) – is the same as the apparent age difference between the “old” and “young” groups of CAIs. A systematic study of leaching effects in the CAIs that currently appear in the “old” and “young” groups is required to determine whether the observed age difference is real, or an artifact of sample preparation.

As discussed in section 4.2, Richter et al. (2010) have recently determined an ‘absolute’ $^{238}\text{U}/^{235}\text{U} = 137.837 \pm 0.015$ (2σ) for the SRM 950a and 960 U isotopic standards using gravimetric principles. Bouvier and Wadhwa (2010) adopted this value in the calculation of Pb-isotope ages for CAIs from the CV3 chondrite NWA 2364. However, it is important to recognize that this $^{238}\text{U}/^{235}\text{U}$ value is almost 0.5 ‰ heavier than the average $^{238}\text{U}/^{235}\text{U}$ composition of chondritic meteorites and high-temperature terrestrial rocks (Stirling et al., 2007). Pb-isotope ages calculated for meteoritic samples assuming this “heavy” $^{238}\text{U}/^{235}\text{U}$ composition are likely to be too old compared with their true ages. This age offset is significant at the current levels of precision offered by modern Pb-Pb dating, again demonstrating the need to measure the $^{238}\text{U}/^{235}\text{U}$ composition of the sample directly.

4.7. Possible causes of $^{238}\text{U}/^{235}\text{U}$ variations in CAIs.

The $^{238}\text{U}/^{235}\text{U}$ ratio in meteorites is lowered if their parent bodies contained live ^{247}Cm , which decayed to ^{235}U (Arden 1977, Tatsumoto and Shimamura 1980, Chen and Wasserburg 1981, Stirling et al. 2005, 2006, Brennecka et al. 2010a). On the basis of observations on bulk samples, acid-etched leachates and mineral separates from a selection of meteorites, the upper limit for a Solar System initial $^{247}\text{Cm}/^{235}\text{U}$ of less than 8×10^{-5} was established (Stirling et al. 2005, 2006) using Nd/U as a proxy for Cm/U. However, low $^{238}\text{U}/^{235}\text{U}$ recently found in CAIs (Brennecka et al. 2010a) are attributed to the presence of significantly higher levels of ^{247}Cm in the early Solar System. Accepting that Nd is a suitable chemical proxy for Cm, and Cm and U were fractionated while ^{247}Cm was still “live” in the samples analysed (Boynton 1978, Stirling et al. 2005; Stirling et al., 2006), we can assess whether ^{247}Cm is likely to have contributed to the observed difference in $^{238}\text{U}/^{235}\text{U}$ between the CAI SJ101 and bulk Allende by comparing their

$^{144}\text{Nd}/^{238}\text{U}$ ratios following the same approach. 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 a $^{144}\text{Nd}/^{238}\text{U}$ value of 58.7. This is approximately twice as high as the bulk Allende values of 25-32 (Stirling et al. 2005, 2006) and would require CAI SJ101 to have a higher relative abundance of ^{235}U , and thereby a lower $^{238}\text{U}/^{235}\text{U}$, than the bulk sample to be consistent with the former presence of “live” ^{247}Cm . This is contrary to the reported observations. The observed difference in $^{238}\text{U}/^{235}\text{U}$ is, therefore, caused by some other mechanism, possibly isotope fractionation, a redox processes, or a nucleosynthetic isotope anomaly, rather than ^{247}Cm decay. The elevated Nd/U ratio is consistent with the Group II rare earth element pattern (Ireland and Fegley 2000), reflecting higher volatility of Nd relative to U (Lodders 2003).

The population of CAIs analysed by Brennecka et al. (2010a) contains four inclusions with very high $^{232}\text{Th}/^{238}\text{U} > 20$ and $^{144}\text{Nd}/^{238}\text{U} > 100$. These inclusions also contain the largest excesses of ^{235}U that may be difficult to explain by isotope fractionation caused by a redox process, or by evaporation and/or condensation, particularly given their correlation with Nd/U and Th/U. The U concentration in two of these inclusions (calculated from sample weights and total U contents reported by Brennecka et al. 2009) is 17-24 ppb – several times lower than in the CAIs with low Th/U and Nd/U ratios (the U concentrations in the other two inclusions were not reported). Correlation between U content and Th/U, Nd/U and $^{235}\text{U}/^{238}\text{U}$ ratios may be a result of two-component mixing with a material with very high Nd/U and Th/U and low U content. A plausible endmember is represented by an Allende FUN CAI C-1, which contains ca. 2 ppb U (Chen and Wasserburg 1981) and flat REE distribution with ca. 26 times enrichment relative to CI chondrites (Hutcheon et al. 1989). This yields $^{144}\text{Nd}/^{238}\text{U}$ of ~2300. The compositions of two high-Nd/U CAIs for which the U concentrations were reported (CAIs 166 and 167 of Brennecka et al. 2009) are consistent with mixing of 80-90% (by mass) of material similar to the CAI C-1 with 10-20% of “normal” low-Nd/U CAI material. If the high-Nd/U endmember contains isotopic anomalies similar to those measured in the CAI C-1, then it would dominate the isotopic systematics of the mixtures. Furthermore, if the high-Nd/U endmember plots on the $^{235}\text{U}/^{238}\text{U}$ vs. Nd/U correlation, then it would contain a 1.94% excess of ^{235}U , and would require a correction of ~28 Ma to the measured $^{207}\text{Pb}/^{206}\text{Pb}$ age. The possibility that the $^{235}\text{U}/^{238}\text{U}$ vs. Th/U and Nd/U correlations are caused by mixing with a C-1-like material emphasizes the importance of a comprehensive characterisation of CAIs analysed for their isotopic systematics.

5. Conclusions

Recently discovered large $^{238}\text{U}/^{235}\text{U}$ variations in Ca-Al-rich refractory inclusions make precise U isotope determinations a mandatory part of U-Pb geochronological studies of these materials. The date of the Allende CAI SJ101 of 4567.18 ± 0.50 Ma, calculated using the measured $^{238}\text{U}/^{235}\text{U} = 137.876 \pm 0.043$, is a first step towards establishing a reliable Pb-isotope chronology of the early Solar System that takes into account U isotope variability. Our data support the growing understanding that $^{238}\text{U}/^{235}\text{U}$ variations in planetary materials are pervasive, caused by more than one mechanism (^{247}Cm decay, “stable” U isotope fractionation, and possibly heterogeneity in the initial U isotopic composition in the accreting proto-planetary disk), 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 $^{238,235}\text{U}$ - $^{206,207}\text{Pb}$ isotopic chronometer must include precise determination of the $^{238}\text{U}/^{235}\text{U}$ ratio. Our data show that using Nd/U or Th/U ratios as a substitute for U isotopic measurements can produce an inaccurate age.

Establishing a precise and reliable age of CAIs and, by inference, the timing of beginning of accretion in the Solar System, would require analysis of multiple CAIs from several CV chondrites with a combination of U-Pb, U-isotopic, and ^{26}Al - ^{26}Mg systems, resolving observed age disparities, establishing sample handling procedures free from fractionation artifacts, and detailed mineralogical, geochemical and isotopic characterisation of CAIs for such studies. 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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Figure captions

Fig. 1. Uranium isotopic compositions of USGS standard rocks BCR-2 (basalt, n=5), BHVO-2 (basalt, n=2) and DTS-2b (dunite, n=4), fragments of the Allende meteorite (n=5), an aliquot of an Allende chondrule population (n=1), and Allende CAI SJ101 (n=1). The weighted average values, with 95% confidence intervals, are shown with shaded areas: 137.821 ± 0.014 (MSWD=0.32) for USGS standard rocks, and 137.747 ± 0.017 (MSWD=1.07) for Allende whole rock fragments and chondrules.

Fig. 2. Pb-isotopic data for residues and third washes of the CAI SJ101. Residues of the batch A003 (fractions 1 and 1+) and A005 (fractions 7, 8 and 9) are shown with grey ellipses; residues of the batch A004 (fractions 2, 3, 4 and 5) – white ellipses with thicker outline, third (HBr) washes of the batch A004 – striped ellipses.

Fig. 3. Pb-isotopic data for the Allende CAI SJ101. The regression includes residues after acid washing of the fractions 1, 1+, 7, 8, 9, and numerically recombined residues and third washes of the fractions 3, 4 and 5. Age uncertainty in brackets includes uncertainty of the $^{238}\text{U}/^{235}\text{U}$ ratio.

Fig. 4. The difference in Pb isotopic ages between CAI SJ101 (black rectangle) and Allende chondrules dated by Amelin and Krot 2007 (striped rectangle), and by Connelly et al. 2008 (grey rectangle). The ages in the left section are calculated assuming uniform $^{238}\text{U}/^{235}\text{U}=137.837$; the ages in the right section are based on the same Pb isotope data but calculated using $^{238}\text{U}/^{235}\text{U}$ measured in this study: 137.876 ± 0.043 in the CAI and 137.747 ± 0.017 in chondrules and bulk meteorite. The errors of the ages plotted in the right section include uncertainty of the $^{238}\text{U}/^{235}\text{U}$ ratios.

Fig. 5. $^{235}\text{U}/^{238}\text{U}$ vs. $^{144}\text{Nd}/^{238}\text{U}$ for the CAIs analysed by Brennecka et al. 2010a (open circles), and SJ101 (black circle). The grey squares denote whole rock Allende analyses (Brennecka et al. 2010a, Stirling et al. 2005, 2006, and this study). The $^{144}\text{Nd}/^{238}\text{U}$ ratio in the CAI SJ101 is 58.7 (with estimated error of 5%), calculated from Nd and U concentrations of 9.25 ppm and 62.37 ppb, respectively, measured in a representative whole rock powder sample. All U isotope

compositions are reported relative to $^{238}\text{U}/^{235}\text{U}=137.837$ in SRM 960 and SRM 950a (Richter et al. 2010). The regression and 95% error envelopes (dashed curves) are calculated using only the CAI data of Brennecka et al. (2010a) and the Model 1 of Isoplot (Ludwig 2003).

Fig. 6. $^{235}\text{U}/^{238}\text{U}$ vs. $^{232}\text{Th}/^{238}\text{U}$ for the CAIs analysed by Brennecka et al. 2010a (open circles), and SJ101 (black circle). The grey square denotes a whole rock Allende analysis by Brennecka et al. (2010a). The $^{232}\text{Th}/^{238}\text{U}$ ratio in the CAI SJ101 is 5.4 ± 0.4 , an average value calculated from radiogenic $^{208}\text{Pb}/^{206}\text{Pb}$ ratios in all fractions analysed for U-Pb. All U isotope compositions are reported relative to $^{238}\text{U}/^{235}\text{U}=137.837$ in SRM 960 and SRM 950a (Richter et al. 2010). The regression and 95% error envelopes (dashed curves) are calculated using only the CAI data of Brennecka et al. (2010a) and the Model 1 of Isoplot (Ludwig 2003).

Fig. 7. Age of the CAI SJ101 based on the isochron shown on Fig. 3, calculated using five possible ways of correcting for U isotopic variability: adjusted to old (#1) and new (#2) assumed $^{238}\text{U}/^{235}\text{U}$ ratios, adjusted to measured $^{238}\text{U}/^{235}\text{U}$ ratio (#3), corrected using $^{235}\text{U}/^{238}\text{U}$ vs. $^{144}\text{Nd}/^{238}\text{U}$ correlation shown in Fig. 5 (#4), and corrected using $^{235}\text{U}/^{238}\text{U}$ vs. $^{232}\text{Th}/^{238}\text{U}$ correlation shown in Fig. 6 (#5). The values 3, 4 and 5 include uncertainties of respective corrections.

Fig. 8. Pb-Pb ages of CAIs from CV chondrites, calculated assuming $^{238}\text{U}/^{235}\text{U}=137.837$, and plotted against $^{232}\text{Th}/^{238}\text{U}$ ratios. Meteorites: circles – Allende, squares – Efremovka, diamond – NWA 2364, triangle – Vigarano. The data from Jacobsen et al. (2008), Connelly et al. (2008a), Amelin et al. (2002, 2009), Bouvier and Wadhwa (2010), Bouvier et al. (2010), and this study. The labels of compact type A CAIs are underlined, *type B – shown in italic*, and **forsterite-bearing type B CAIs – in bold**.

Electronic supplementary files

ES1. Detailed description of U-Pb analytical procedures, U-Pb data, uranium $^{238}\text{U}/^{235}\text{U}$ analytical procedures, and uranium $^{238}\text{U}/^{235}\text{U}$ standard measurements. The text contains 11 figures denoted S1-S11.

ES2. Pb isotopic data for ca. 300 pg loads of the NIST standard SRM-981, analysed with ^{202}Pb - ^{205}Pb spike.

ES3. Uranium isotopic data. The table is presented in two versions: first, containing formulas to facilitate re-calculations, and second, with the contents of the cells containing formulas saved as calculated values.

ES4. U-Pb data. The table is presented in two versions: first, containing formulas to facilitate re-calculations, and second, with the contents of the cells containing formulas saved as calculated values.

Research highlights

- Pb-isotopic age of an Allende CAI of 4567.18 ± 0.50 Ma
- Calculated using measured $^{238}\text{U}/^{235}\text{U} = 137.876 \pm 0.043$
- The difference in $^{238}\text{U}/^{235}\text{U}$ ratio increases CAI-chondrule age difference by 1.4 Ma

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

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