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

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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 $^{238}U/^{235}U$ 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 $^{238}U/^{235}U = 137.876 \pm 0.043$ (2σ), reported relative to $^{238}U/^{235}U = 137.837$ of the CRM 145 standard. Our best current estimate of the average terrestrial value is: $^{238}U/^{235}U = 137.821 \pm 0.014$.The error in the age includes uncertainties in the Pb–Pb isochron intercept and in the $^{238}U/^{235}U$ ratio. Allende bulk rock and chondrules have $^{238}U/^{235}U = 137.747 \pm 0.017$ (2σ), distinctly lower than the CAI. The difference in the $^{238}U/^{235}U$ 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 Ma, 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 standardisation of $^{238}U/^{235}U$ measurements for U–Pb geochronology and cosmochronology, elemental and isotopic fractionation induced by intensive acid leaching, ages of CAIs in the context of $^{238}U/^{235}U$ variability, and possible causes of U isotopic variations in CAIs and meteorites.

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 and Krot, 2007; Amelin et al., 2002; Bizzarro et al., 2004; Bouvier and Wadhwa, 2009; Bouvier et al., 2007; Burkhardt et al., 2008; Connelly et al., 2008a; Jacobsen et al., 2008; Krot et al., 2009; Nyquist et al., 2009; Thrane et al., 2006; Villeneuve et al., 2009) using extinct ^{26}Al–^{26}Mg and ^{182}Hf–^{182}W, and extant $^{238,235}U$–$^{206,207}Pb$ 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 (Amelin et al., 2009; Burkhardt et al., 2008; Davis, 2009; Kleine et al., 2009; Nyquist et al., 2009).

Among the causes of possible inaccuracy in $^{207}Pb/^{206}Pb$ ages of meteorites and their components are variations in the $^{238}U/^{235}U$ 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 Ma, 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 $^{238}U/^{235}U = 137.88$ was adopted

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for use in all geochronological studies (Steiger and Jäger, 1977), largely based on absolute $^{238}U/^{235}U$ 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 (Bopp et al., 2009; Stirling et al., 2007; Weyer et al., 2008), particularly in surface samples formed in low-temperature environments, and in some CAIs from carbonaceous chondrites (Brennecka et al., 2010a). The magnitude of $^{235}U/^{238}U$ variations in CAIs reported in the latter study is such that it would infer adjustments to the $^{207}Pb/^{206}Pb$ 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 $^{238}U/^{235}U$ and $^{238,235}U$–$^{206,207}Pb$ 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, ~2.5 × 1.5 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 ($>1\times10^{-12}$ 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 normalisation against $^{236}U/^{233}U$). The $^{236}U/^{233}U$ ratio of the mixed spike tracer was calibrated against the U metal standard CRM 145, assuming CRM 145 has a $^{238}U/^{235}U$ value of 137.837 ± 0.015 (Richter et al., 2010). Repeat $^{238}U/^{235}U$ 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 pg 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 0.5 M HNO_3 with ultrasonic agitation (first wash), and in hot 7 M HNO_3 and 7 M HCl (second wash). Batch A004 was additionally leached in hot 9 M HBr for 14 h (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 Figure 1, and are described in detail in Supplementary Material ES1. A terrestrial reference value of $^{238}U/^{235}U = 137.821\pm0.014$ (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 $^{238}U/^{235}U = 137.876\pm0.043$ 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 $^{238}U/^{235}U = 137.751\pm0.021$ (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 $\varepsilon^{235}U$ notation into absolute $^{238}U/^{235}U$ values). The

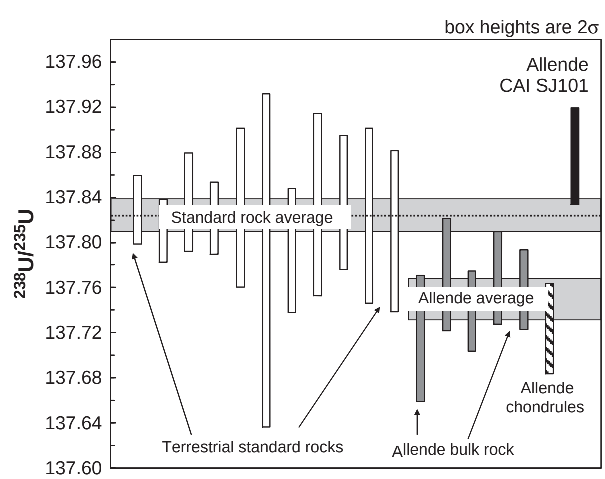

Fig. 1. Uranium isotopic compositions of USGS standard rocks BCR-2 (basalt, n = 5), BHVO-2 (basalt, n = 2) and DTS-2b (dunite, n = 4), fragments of the Allende meteorite (n = 5), an aliquot of an Allende chondrule population (n = 1), and Allende CAI SJ101 (n = 1). The weighted average values, with 95% 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.