238U/235U Variations in Meteorites: Extant 247Cm and Implications for Pb-Pb Dating
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$^{238}U/^{235}U$ Variations in Meteorites: Extant ^{247}Cm and Implications for Pb-Pb Dating

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The $^{238}U/^{235}U$ isotope ratio has long been considered invariant in meteoritic materials (equal to 137.88). This assumption is a cornerstone of the high-precision lead-lead dates that define the absolute age of the solar system. Calcium-aluminum–rich inclusions (CAIs) of the Allende meteorite display variable $^{238}U/^{235}U$ ratios, ranging between 137.409 ± 0.039 and 137.885 ± 0.009. This range implies substantial uncertainties in the ages that were previously determined by lead-lead dating of CAIs, which may be overestimated by several million years. The correlation of uranium isotope ratios with proxies for curium/uranium (that is, thorium/uranium and neodymium/uranium) provides strong evidence that the observed variations of $^{238}U/^{235}U$ in CAIs were produced by the decay of extant curium-247 to uranium-235 in the early solar system, with an initial $^{247}Cm/^{235}U$ ratio of approximately 1.1×10^{-4} to 2.4×10^{-4}.

Meteorites can provide a wealth of information about the formation and evolution of the solar system. In chondrite meteorites, calcium-aluminum–rich inclusions (CAIs) represent the first solids to condense from the cooling protoplanetary disk during the birth of the solar system (*1*); therefore, the ages of CAIs are generally considered to date the solar system's origin (*2*–*4*). High-precision Pb-Pb dating studies, which rely on a known ratio of parent U isotopes, assume that the $^{238}U/^{235}U$ ratio is invariant in meteoritic material (equal to 137.88) (*5*). Uranium isotope variations in meteorites may be produced by many mechanisms, including the decay of extant ^{247}Cm to ^{235}U, nucleosynthetic anomalies in U isotopes, or fractionation of U isotopes during chemical reactions, as recently observed on Earth (*6*, *7*). Any or all of these mechanisms may play some role in $^{238}U/^{235}U$ variability in early solar system materials; however, the existence and effect of ^{247}Cm on the $^{238}U/^{235}U$ ratio can be studied using geochemical proxies for Cm.

^{247}Cm is only created in certain types of supernovae during *r*-process nucleosynthesis. It decays to ^{235}U with a half-life of 15.6 million years (My) (*8*–*13*). If ^{247}Cm was present during the formation of the solar system, it would be detected by variations of $^{238}U/^{235}U$ in ancient meteoritic materials in which the original solar system Cm/U ratio may have been substantially fractionated by processes associated with the formation of the meteoritic materials. The CAIs in chondritic meteorites are likely to be such materials, because many of them experienced elemental fractionation during condensation and evaporation processes that were involved in their formation and because Cm is more refractory than U (*14*).

Quantification of the abundance of extant ^{247}Cm has the potential to provide new constraints on the origin of short-lived radionuclides in the early solar system. If the ^{247}Cm in the early solar system was predominantly inherited from galactic chemical evolution (*13*), then it should be possible for us to determine the time interval of free decay (Δ) between the last *r*-process nucleosynthetic event and the formation of the solar system (*5*, *11*, *15*, *16*). Supposed claims of large variations in the $^{238}U/^{235}U$ ratio that were caused by the decay of ^{247}Cm (*8*, *9*) were refuted in subsequent studies (*5*, *10*, *11*, *17*). Here we present high-precision $^{238}U/^{235}U$ ratios obtained from 13 CAIs of the Allende meteorite to quantify the amount of ^{247}Cm present in the early solar system and to determine the extent of potential offsets in the calculated Pb-Pb ages of early solar system materials (*18*).

The $^{238}U/^{235}U$ ratios of the two bulk meteorites (Allende and Murchison) are 137.818 ± 0.012 and 137.862 ± 0.042, respectively (Fig. 1). The 13 CAIs show a large range of U isotope compositions, with $^{238}U/^{235}U$ ratios varying from 137.409 ± 0.039 to 137.885 ± 0.009. All but two CAIs differ outside uncertainties from the standard value, and five CAIs have significantly lower $^{238}U/^{235}U$ values than that of bulk Allende.

If ^{247}Cm decay is the primary mechanism for $^{238}U/^{235}U$ variability, then materials with a high initial Cm/U value would contain a higher relative amount of ^{235}U than those with lower initial Cm/U values. However, because Cm has no long-lived stable isotope, the initial Cm/U ratio of a sample cannot be directly determined. Because Th and Nd have similar geochemical behavior to Cm, Th/U and Nd/U ratios can serve as proxies for the initial Cm/U ratio in the sample (*9*, *11*). Our sample set spans a large range of Th/U and Nd/U, and both these ratios correlate with the U isotopic composition (Fig. 2).

Because of the higher volatility of U, thermodynamic calculations suggest that substantial fractionation of Cm (and other geochemically similar elements such as Th and Nd) from U is possible in the early solar nebula (*19*). Large variations in the Th/U and Nd/U ratios seen in our CAI data set (table S1) support this claim. A special group of CAIs, called group II CAIs, are distinguished by a unique abundance pattern of the rare earth elements (REEs). Group II CAIs are highly depleted in the most refractory (that is, heavy REEs, except Tm and Yb) and the most volatile (that is, Eu and Yb) REEs, yet the moderately refractory light REEs (including Nd) are only present in chondritic relative abundances (*20*). This REE pattern, which is characteristic of

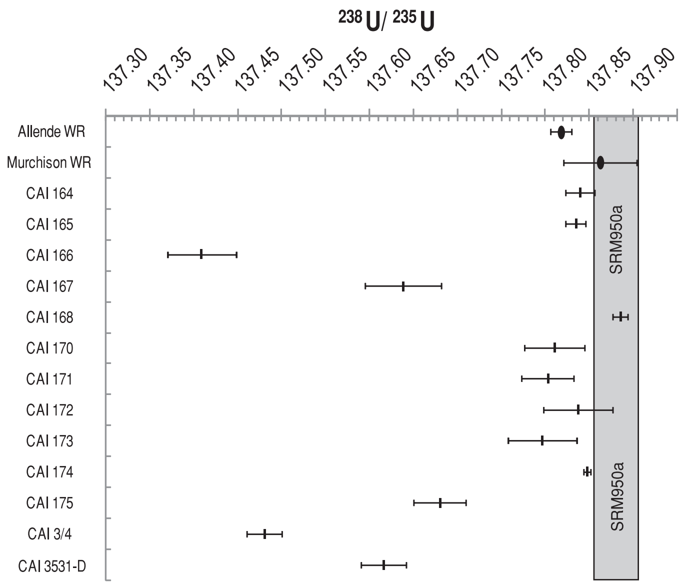

Fig. 1. $^{238}U/^{235}U$ isotope values for the samples of this study. The box represents the measured value and analytical precision of replicate analyses of 20– to 100–parts per billion solutions of the SRM950a standard. Error bars are calculated as 2 times the standard deviation (2SD) of multiple runs of each sample, when possible. In samples with extremely limited uranium, for which fewer than three runs were possible, the reported errors are conservatively represented by the long-term reproducibilities (2SD) based on multiple runs of SRM950a measured over the course of this study at the same concentration as the sample.

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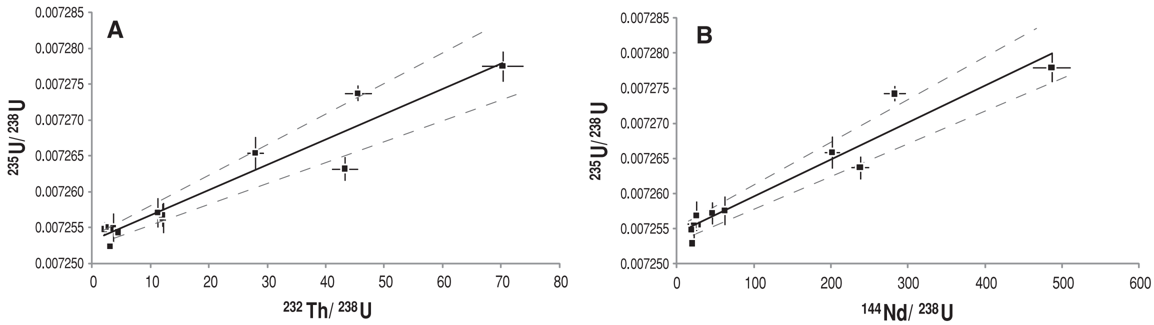

Fig. 2. (**A**) $^{232}Th/^{238}U$ and (**B**) $^{144}Nd/^{238}U$ ratios plotted versus $^{235}U/^{238}U$ ratios, the reciprocal values of our measured $^{238}U/^{235}U$ ratios. The gray dashed lines represent the 2SD errors on the best-fit line (solid black). Errors on the *y*-axis data are ±2SD; *x*-axis error bars are ±5% of the determined value of the elemental ratio.

group II CAIs, suggests a complex condensation history involving fractional condensation (*21*, *22*). The four CAIs of this study that have the highest Nd/U and Th/U ratios (as well as the lowest $^{238}U/^{235}U$ ratios) are all classified as group II CAIs by their REE patterns (Fig. 3). Because of the lower condensation temperature of U relative to Nd and Th (*23*), the fractional condensation history that resulted in the characteristic group II REE pattern in these objects is likely to have produced the relatively high Nd/U and Th/U ratios.

The correlation of both Th/U and Nd/U with U isotope ratios in the CAIs indicates that the $^{238}U/^{235}U$ variations do not arise from nucleosynthetic anomalies or U isotope fractionation, neither of which easily give rise to such a trend, and instead provide evidence for the presence of extant ^{247}Cm in the early solar system. Under this interpretation, deviations from the best-fit lines in Fig. 2 could be caused by heterogeneity of $^{238}U/^{235}U$ in the solar nebula, Th and Nd acting as imperfect proxies for Cm, or $^{238}U/^{235}U$ fractionation following Allende CAI formation, possibly from variable redox during secondary alteration processes (*7*).

In contrast to our findings, a recent study did not detect deviations in the $^{238}U/^{235}U$ ratio among a variety of bulk meteorite samples, including Allende and Murchison (*11*). Given the reported precision of the study's U isotope analysis, the $^{144}Nd/^{238}U$ ratios should have been sufficient to reveal detectable variations in $^{238}U/^{235}U$ from ^{247}Cm decay. Although the $^{238}U/^{235}U$ value of bulk Murchison samples agrees within error with our observed values, those for bulk Allende differ well outside of reported errors. The reason for this disagreement is unclear at this time.

The initial $^{247}Cm/^{235}U$ ratio in the early solar system can be estimated by using the slopes of the best-fit lines in Fig. 2 (*11*). Using Th and Nd as proxies for Cm, we estimate the initial solar system $^{247}Cm/^{235}U$ ratio to be $2.4 \times 10^{-4} \pm 0.6 \times 10^{-4}$ and $1.1 \times 10^{-4} \pm 0.2 \times 10^{-4}$, respectively. The difference between the estimates may be due to slight differences in the geochemical behavior of Th and Nd or possibly because of uncertainties in the assumed solar system Nd/U or Th/U ratios. Nevertheless, these values are, on average, higher than the upper limit derived previously using analyses of the U isotope compositions of bulk chondritic meteorites (*11*). Our estimates are, however, in agreement with the upper limit of ~4×10^{-3} that was determined previously based on analyses of CAIs (*12*). If ^{247}Cm is inherited from galactic chemical evolution, the range of initial solar system $^{247}Cm/^{235}U$ ratios estimated here translates to Δ ~ 110 to 140 My. This value is similar to, but more precise than, previous estimates of Δ based on the inferred initial solar system abundances of other *r*-process–only radionuclides such as ^{244}Pu and ^{129}I, but does not match the significantly shorter estimate of Δ (~30 My) derived from the initial abundance of ^{182}Hf (*16*). However, because ^{182}Hf was overabundant in the early solar system compared with its expected abundance from galactic chemical evolution, it may have been injected into the presolar molecular cloud or the solar nebula by a nearby supernova event [for example, (*13*)].

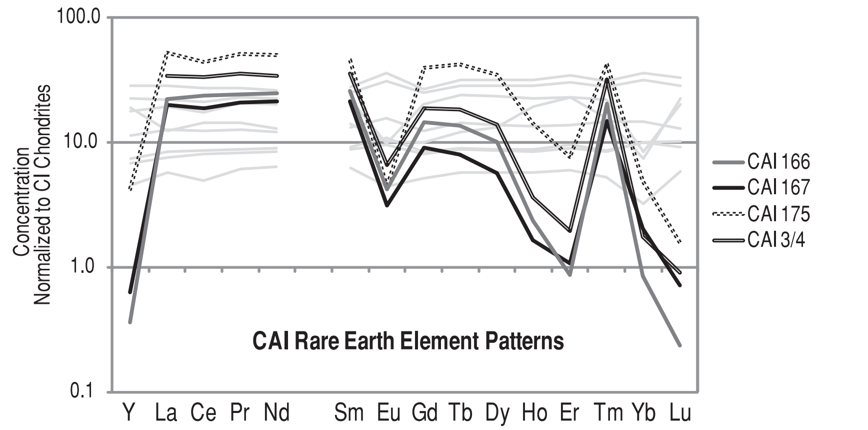

Fig. 3. REE patterns of four group II CAIs analyzed in this study, normalized to CI chondrites. All other CAI samples studied here (except 3531-D, for which the REE abundances were not measured) display flat REE patterns, indicating chondritic relative abundances of these elements (light gray lines).

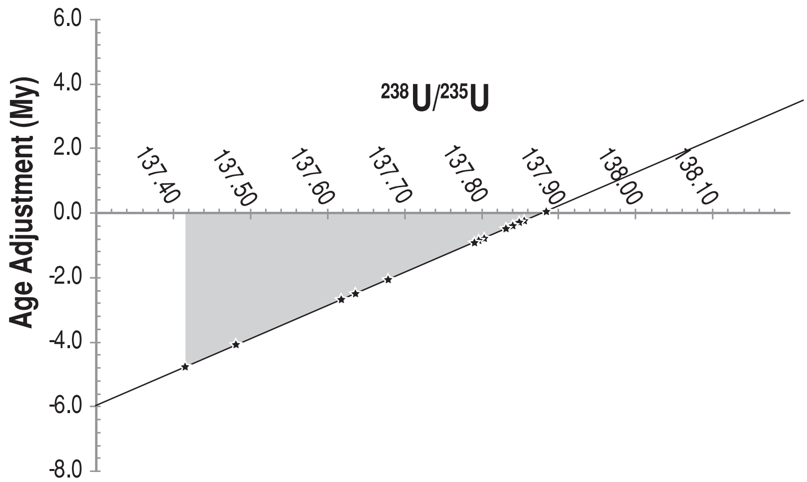

Fig. 4. Age adjustment required for samples found not to have a $^{238}U/^{235}U$ value of 137.88, as assumed in the Pb-Pb age equation (Eq. 1). The shaded region represents the range of U isotope compositions reported in this study, and the asterisks represent the specific $^{238}U/^{235}U$ ratios measured in these samples.

Our findings also have implications for precise dating of early events in the history of the solar system. The Pb-Pb age equation (Eq. 1) has been used for decades to calculate the absolute ages of both meteoritic and terrestrial materials (*24*). This equation assumes that $^{238}U/^{235}U$ is invariant at any given time, and that the present-day value is 137.88.

$$\frac{^{206}Pb^*}{^{206}Pb^*} = \frac{^{235}Ue^{\lambda_{235}t} - 1}{^{238}Ue^{\lambda_{238}t} - 1} = \frac{1}{137.88}\frac{e^{\lambda_{235}t} - 1}{e^{\lambda_{238}t} - 1} \quad (1)$$

Here, λ is the decay constant for the specific isotope and t is the age. Any deviation from this assumed $^{238}U/^{235}U$ would cause miscalculation in the determined Pb-Pb age of a sample. A difference of up to 3.5 per mil (‰) implies that a correction of up to –5 My would be required if the Pb-Pb ages of these CAIs were obtained using the previously assumed $^{238}U/^{235}U$ value (Fig. 4).

Because $^{238}U/^{235}U$ variations in solar system materials are not restricted to CAIs, this requirement may extend to high-precision Pb-Pb dating of other materials as well. It is possible, however, that the $^{238}U/^{235}U$ values of bulk chondrites are controlled to a substantial degree by CAIs, which may be heterogeneously distributed at the scale at which these analyses were made.

The Pb-Pb dating technique is the only absolute dating technique able to resolve age differences of <1 My in materials formed in the early solar system. Whereas the full range of $^{238}U/^{235}U$ ratios reported here would result in an overestimation of the ages of these CAIs by up to 5 My, the largest excesses (>3.5‰) in ^{235}U occur in the group II CAIs that appear to have experienced the largest Cm/U fractionation. For non–group II CAIs, the age overestimation is ≤1 My. The apparent discrepancies between absolute Pb-Pb ages and relative (for example, ^{26}Al-^{26}Mg, ^{53}Mn-^{53}Cr, and ^{182}Hf-^{182}W) ages (*2*, *4*, *25*, *26*) may therefore place limits on the uncertainty of the age of the solar system.

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Supporting Online Material
www.sciencemag.org/cgi/content/full/science.1180871/DC1
Materials and Methods
Fig. S1
Tables S1 and S2
References

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Contribution of Semi-Arid Forests to the Climate System

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Forests both take up CO_2 and enhance absorption of solar radiation, with contrasting effects on global temperature. Based on a 9-year study in the forests' dry timberline, we show that substantial carbon sequestration (cooling effect) is maintained in the large dry transition zone (precipitation from 200 to 600 millimeters) by shifts in peak photosynthetic activities from summer to early spring, and this is counteracted by longwave radiation (*L*) suppression (warming effect), doubling the forestation shortwave (*S*) albedo effect. Several decades of carbon accumulation are required to balance the twofold *S* + *L* effect. Desertification over the past several decades, however, contributed negative forcing at Earth's surface equivalent to ~20% of the global anthropogenic CO_2 effect over the same period, moderating warming trends.

The need to generate measurement-based estimates of biosphere-atmosphere carbon and energy exchange on land (*1*, *2*) led to global observational efforts to measure the carbon, water, and radiation fluxes at the canopy scale (www.fluxnet.ornl.gov). Obtaining primary data from semi-arid regions is important principally because of their size [2.4 billion ha or ~17.7% of total land surface area (*3*)] coupled with their low clouds–high solar radiation conditions: 18 to 21 and 10 to 13 MJ m^{-2} day^{-1} in semi-arid and temperate regions, respectively (*4*). These regions have potentially large impacts on local climate (*5*–*7*) and the global radiation budget and represent climatic conditions predicted for large areas of currently wetter regions (*8*). We used the concept of "radiative forcing" as a metric for comparing changes in surface energy balance with carbon uptake and storage associated with semi-arid forestation.

We used a field research site with continuous flux measurements of CO_2, water vapor, and energy established in 2000 in a 2800-ha pine forest (Yatir) in southern Israel, using methodology established in the Euroflux network (*9*). The forest represents a low-stature (10 m), low-density [leaf area index (LAI) ~ 1.3] woody vegetation ecosystem at the dry timberline (285 mm mean precipitation). The forest maintains relatively high productivity, with a mean annual net ecosystem CO_2 exchange (*NEE*) of 2.3 ton C ha^{-1} for the study period (*10*), compared with ~2.0 ton C ha^{-1} in European pine forests and a Fluxnet mean of ~2.5 ton C ha^{-1} (Table 1). This reflects moderate mean annual gross primary productivity (*GPP*) coupled with low mean annual

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