PLANETARY SCIENCE RESEARCH PSRD Discoveries

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A Complication in Determining the Precise Age of the Solar System

--- The presence of short-lived isotope Curium-247 in the early Solar System complicates the job of dating the earliest events in the solar nebula.

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Primitive components in meteorites contain a detailed record of the conditions and processes in the solar nebula, the cloud of dust and gas surrounding the infant Sun. Determining accurately when the first materials formed requires the lead-lead (Pb-Pb) dating method, a method based on the decay of uranium (U) isotopes to Pb isotopes. The initial ratio of U-238 to U-235 is critical to determining the ages correctly, and many studies have concluded that the ratio is constant for any given age. However, my colleagues at Arizona State University, Institut für Geowissenschaften, Goethe-Universität (Frankfurt, Germany), and the Senckenberg Forschungsinstitut und Naturmuseum (also in Frankfurt) and I have found that some calcium-aluminum-rich inclusions (CAIs) in chondritic meteorites deviate from the conventional value for the U-238/U-235 ratio. This could lead to inaccuracies of up to 5 million years in the age of these objects, if no correction is made. Variations in the concentrations of thorium and neodymium with the U-238/U-235 ratio suggest that the ratio may have been lowered by the decay of curium-247, which decays to U-235 with a half-life of 15.6 million years. Curium-247 is created in certain types of energetic supernovae, so its presence suggests that a supernova added material to the pre-solar interstellar cloud between 110 and 140 million years before the Solar System began to form.

Reference:

- Brennecka, G. A., Weyer, S., Wadhwa, M., Janney, P.E., Zipfel, J., and Anbar, A.D. (2010) $^{238}U/^{235}U$ Variations in Meteorites: Extant ^{247}Cm and Implications for Pb-Pb Dating. *Science*, v. 327(5964), p. 449-451.

PSRDpresents: A Complication in Determining the Precise Age of the Solar System --Short Slide Summary (with accompanying notes).

Meteorites and the Uranium Clock

Meteorites provide a wealth of information about the formation and evolution of the Solar System. Found within a certain type of meteorite, called chondrites, calcium-aluminum-rich inclusions (CAIs) are present. These ultra-refractory materials represent the first solids to condense during the birth of the Solar System and, therefore, the ages of CAIs date the origin of the Solar System. Obtaining an absolute age of these types of materials requires the use of the Pb-Pb dating method, a method based on the decay of different isotopes of uranium (U) to stable daughter isotopes of lead (Pb). Uranium-238 decays to lead-206 (^{206}Pb) with a half-life of ~4.5 billion years, and ^{235}U decays to ^{207}Pb with a half-life of ~700 million years. Cosmochemists use the ratio of $^{206}Pb/^{207}Pb$ as a "clock" to date how old a material is, and have used this chronometer for decades to date rocks on Earth, as well as meteorites. (See, for example, **PSRD** article: Dating the Earliest Solids in our Solar System.) However, the method relies on a known ratio of parent U isotopes, and up until this point, we have assumed that the modern $^{238}U/^{235}U$ ratio (137.88) is invariant in meteoritic material. Modern techniques and mass spectrometers now allow us to measure slight variations in isotope systems long thought not to fractionate, and our research suggests that the assumption of an invariant $^{238}U/^{235}U$ ratio is not valid. Our paper demonstrates deviations from the standard ratio, explores the reasons for the variation in the $^{238}U/^{235}U$ ratio in CAIs, and discusses the implications that a variable $^{238}U/^{235}U$ ratio has on the Pb-Pb dating method and the age of the Solar System.

The Curious Curium-247 Complication

Uranium isotope variations in meteorites may be produced by many mechanisms, ranging from anomalies produced during synthesis of U isotopes in exploding stars, fractionation of U isotopes during chemical reactions (as recently observed on Earth), or from the decay of the short-lived isotope ^{247}Cm to ^{235}U. While any or all of these mechanisms may play some role in $^{238}U/^{235}U$ variability in early Solar System materials, the existence and effect of ^{247}Cm on the $^{238}U/^{235}U$ ratio can be studied using geochemical proxies for Cm.

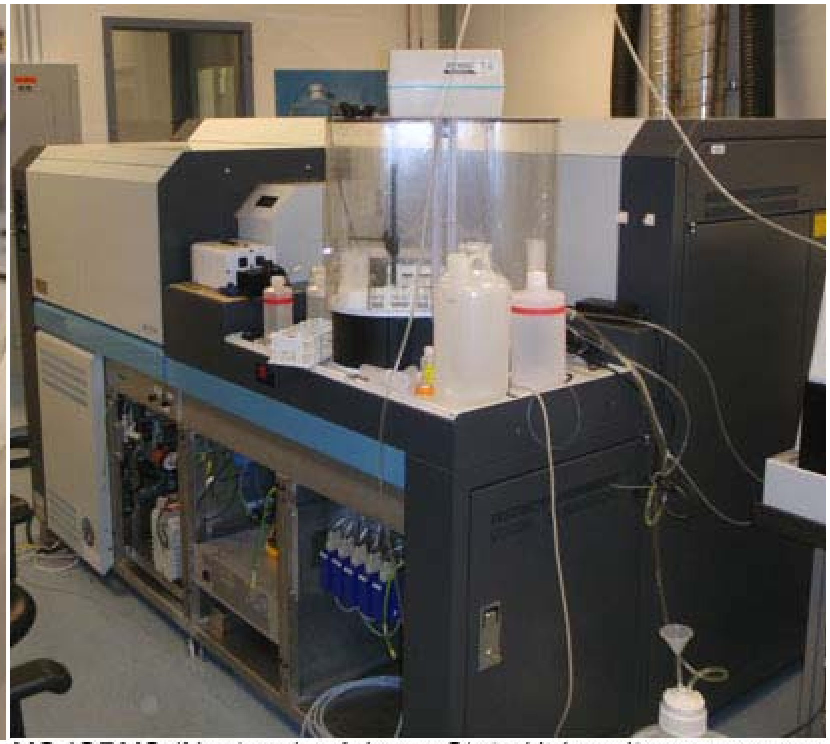
Curium-247 is created exclusively in certain types of supernovae during something called "*r*-process nucleosynthesis." It decays to ^{235}U with a half-life of 15.6 million years, so has been long extinct in meteoritic material. If ^{247}Cm was present during the formation of the Solar System, it would be detected by apparent excesses in ^{235}U found in ancient meteoritic materials. The largest ^{235}U excesses would occur in materials in which the original Solar System Cm/U ratio was significantly fractionated by processes associated with their formation. The CAIs in chondritic meteorites are likely to be such materials, as many of them experienced elemental fractionation during condensation/evaporation processes involved in their formation.

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. By determining the original amount of ^{247}Cm in the Solar System, and comparing to isotope production models, it should be possible to determine the approximate time interval between the last *r*-process nucleosynthetic event (supernovae) and the formation of the Solar System. We made high-precision $^{238}U/^{235}U$ ratio measurements on 13 CAIs from 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.

High-Precision Measurements

We separated the 13 CAIs from different sections of the CV3 Allende meteorite. We crushed the samples and dissolved them utilizing HNO_3, HF, and $HClO_4$ acids, and reserved approximately 5% of each sample for trace element measurements (i.e., REE patterns, Th/U and Nd/U ratios). Uranium isotope measurements were performed both at Arizona State University and the University of Frankfurt (Germany) using multi-collector inductively coupled plasma mass spectrometers (MC-ICPMS).

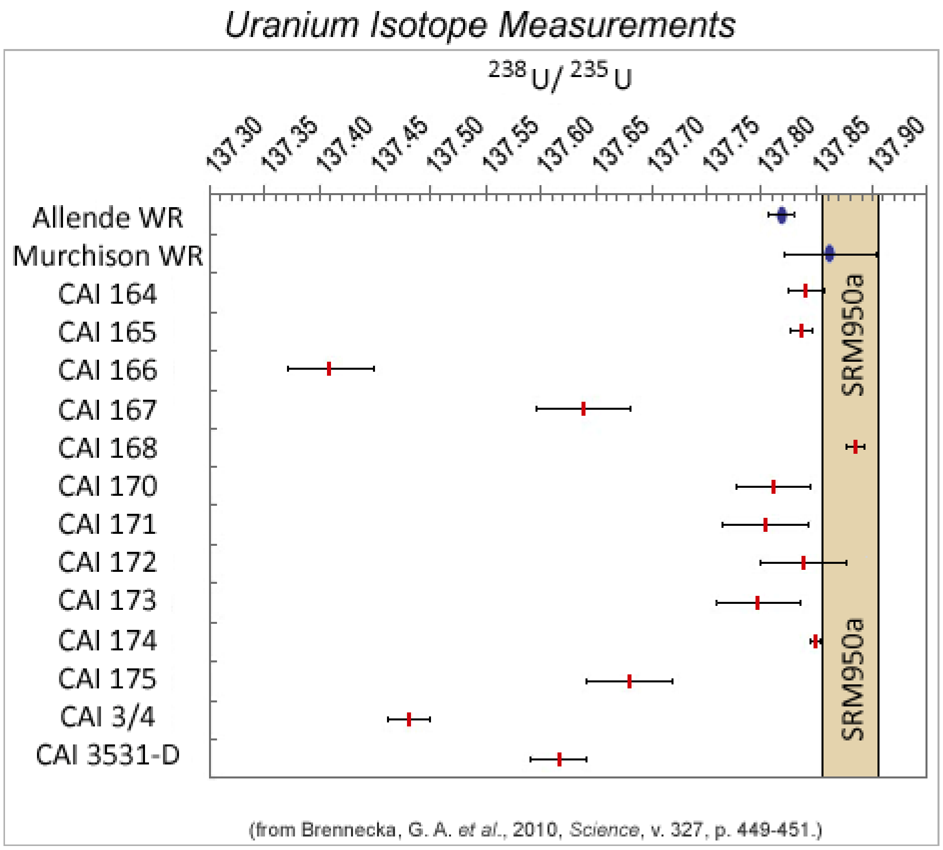
(Photo by Celeste Riley, ASU.)



MC-ICPMS (Neptune) at Arizona State University (Photo by Greg Br

This research used samples of calcium-aluminum-rich inclusions (CAIs) from the Allende meteorite, which I am holding in m
the ASU laboratory. Photo on the right shows the multi-collector inductively coupled plasma mass spectrometer (MC-ICPM

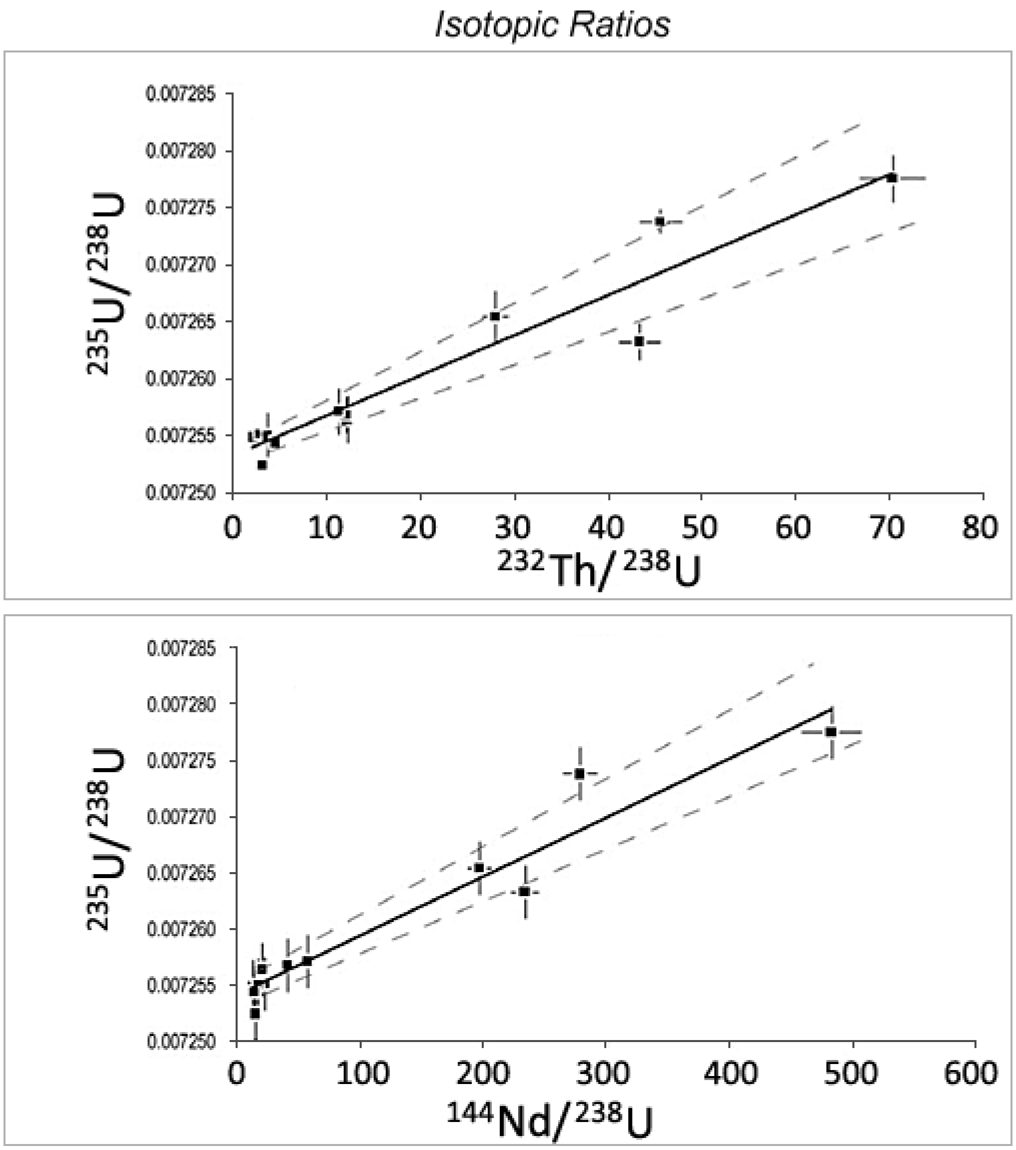
These state-of-the-art instruments allow for extremely precise measurement of isotope ratios by measuring multiple isotopes signals at the same time. This collaboration between two labs was important because in many cases during this study, we measured samples and standards independently at the two labs to ensure data accuracy and reproducibility. 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 (see the graph below). 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 of 137.88 and five CAIs have significantly lower $^{238}U/^{235}U$ values than that of the bulk Allende meteorite. These differences seem small, but they are highly significant!



$^{238}U/^{235}U$ isotope values for the samples of this study. The box represents the measured value and analytical precision of replicate analyses of 20-100 ppb solutions of a standard named SRM950a. Error bars are calculated as twice the standard deviation (2SD) of multiple runs of each sample, when possible.

Evidence that ^{247}Cm Causes the Low $^{238}U/^{235}U$ Ratios

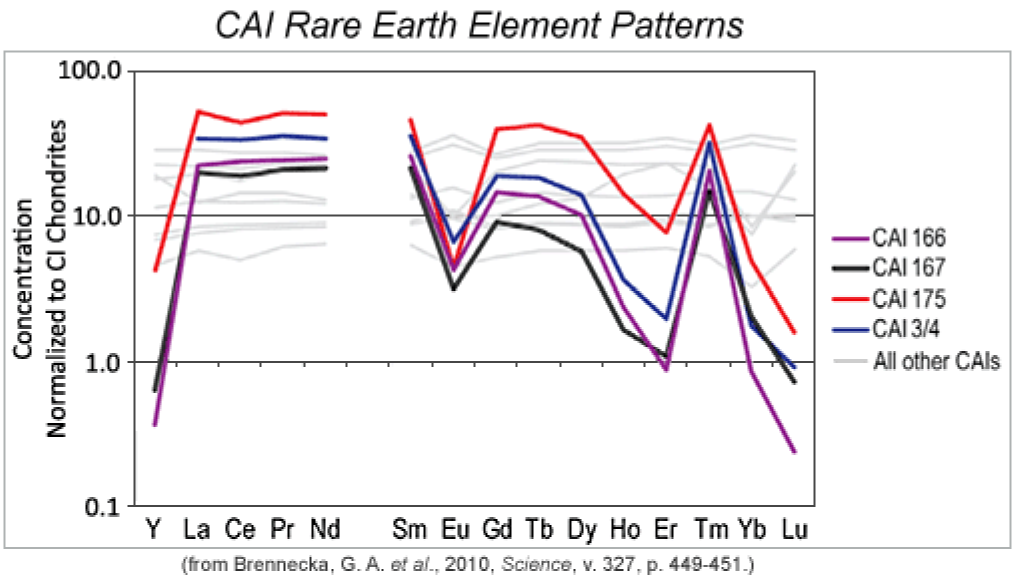
If ^{247}Cm decay is the primary mechanism for $^{238}U/^{235}U$ variability, then materials with high initial Cm/U would contain a higher relative amount of ^{235}U than those with lower initial Cm/U. However, as Cm has no long-lived stable isotope, the initial Cm/U ratio of a sample cannot be directly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



(from Brennecka, G. A. *et al*., 2010, *Science*, v. 327, p. 449-451.)

^{232}Th/^{238}U and ^{144}Nd/^{238}U ratios plotted versus ^{235}U/^{238}U ratios. (We plotted the inverse values of our measured ^{238}U/^{235}U ratios. We did that because geochronological plots usually have the daughter isotope in the numerator of the y-axis, making the line slope up to the right.) The grey 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. The correlation of increasing ^{235}U/^{238}U with increasing Th/U and Nd/U, which we think are proportional to Cm/U, is consistent with excess formation of ^{235}U by decay of ^{247}Cm.

Due to the higher volatility of uranium, substantial fractionation of Cm (and other geochemically similar elements such as Th and Nd) from U is possible in the early solar nebula. A special group of CAIs, called "Group II" CAIs, are distinguished by a unique abundance pattern of the rare earth elements (REEs); they are highly depleted in the most refractory and the most volatile REEs, yet the moderately refractory light REE are present only in chondritic relative abundances. This REE pattern characteristic of Group II CAIs suggests a complex condensation history involving fractional condensation. 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. Because U has a lower condensation temperature than do Nd and Th, the fractional condensation history that resulted in the characteristic Group II REE pattern in these objects is likely to have produced the elevated Nd/U and Th/U ratios.

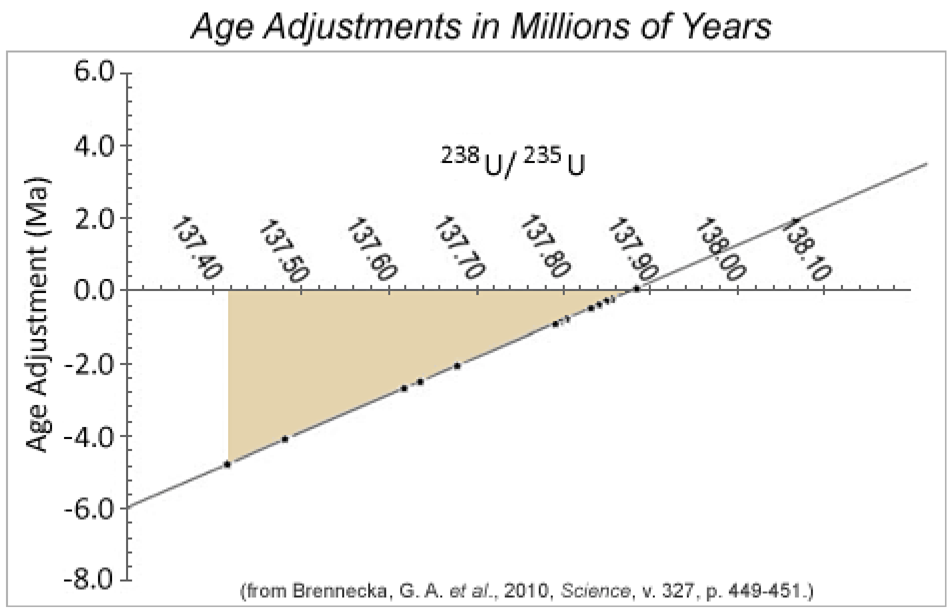


REE patterns of four Group II CAIs analyzed in this study, normalized to CI chondrites. All other CAI samples studied here (except 3531-D, for which the REE abundances were not measured) display flat REE patterns indicating chondritic relative abundances of these elements (light-grey lines).

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 provides evidence for the presence of extant ^{247}Cm in the early Solar System. The initial $^{247}Cm/^{235}U$ ratio in the early Solar System is estimated by using the slopes of the best-fit lines on the $^{235}U/^{238}U$ vs Th/U and Nd/U diagram. Using Th and Nd as proxies for Cm, we estimate the initial Solar System $^{247}Cm/^{235}U$ ratio to be $2.4 \pm 0.6 \times 10^{-4}$ and $1.1 \pm 0.2 \times 10^{-4}$, respectively. The difference between the estimates may be caused by slight differences in the geochemical behavior of Th and Nd, or possibly by uncertainties in the assumed Solar System Nd/U or Th/U ratios. If ^{247}Cm is inherited from galactic chemical evolution, the range of initial Solar System $^{247}Cm/^{235}U$ ratios estimated here translates to a time interval between the last *r*-process supernovae and the formation of the Solar System of approximately 110 to 140 million years.

Correcting Ages

Our findings of variable $^{238}U/^{235}U$ in meteoritic materials also have implications for precise dating of early events in the history of the Solar System. Geochronologists have used a standard Pb-Pb age equation for decades to calculate the absolute ages of both meteoritic and terrestrial materials. This equation assumes that $^{238}U/^{235}U$ is invariant at any given time, and that the present-day value is 137.88. Therefore, any deviation from this assumption would cause miscalculation in the determined Pb-Pb age of a sample. The differences seen in these samples would require correction of up to -5 million years if the Pb-Pb ages of these CAIs were obtained using the previously assumed $^{238}U/^{235}U$ value.



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. The shaded region represents the range of U isotope compositions reported in this study, and the dots represent the specific $^{238}U/^{235}U$ ratios measured in these samples.

From the correlations of Th/U and Nd/U with $^{238}U/^{235}U$ ratios in Allende CAIs, we infer that ^{247}Cm was present in the early Solar System and that the initial $^{247}Cm/^{235}U$ ratio was ~1-2 x 10^{-4}. This value constrains the time interval between the last *r*-process nucleosynthetic event and the formation of the Solar System to approximately 110-140 million years. It is also clear from these samples that the $^{238}U/^{235}U$ ratio can no longer be assumed to be invariant in Solar System materials. The Pb-Pb dating technique is the only absolute dating technique able to resolve age differences of less than one million years in materials formed in the early Solar System and in order to produce a truly robust Pb-Pb age, it is essential to measure precisely and accurately the $^{238}U/^{235}U$ ratio in the dated material. At least for the oldest materials in the Solar System the good old days of measuring only lead isotopes are gone. The Pb-Pb dating method will still work fine, but cosmochemists will have to measure uranium isotopes, too.

Additional Resources

LINKS OPEN IN A NEW WINDOW.

- **PSRDpresents:** A Complication in Determining the Precise Age of the Solar System --Short Slide Summary (with accompanying notes).

- Brennecka, G. A., Weyer, S., Wadhwa, M., Janney, P.E., Zipfel, J., and Anbar, A.D. (2010) $^{238}U/^{235}U$ Variations in Meteorites: Extant ^{247}Cm and Implications for Pb-Pb Dating. *Science*, v. 327(5964), p. 449-451.
- Krot, A. N. (September, 2002) Dating the Earliest Solids in our Solar System. *Planetary Science Research Discoveries*. http://www.psrd.hawaii.edu/Sept02/iostopicAges.html.
- Press Release: (December 31, 2009) ASU Researchers Recalculate Age of Solar System. Arizona State University News.

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