Origin of Nucleosynthetic Isotope Heterogeneity in the Solar Protoplanetary Disk

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Origin of Nucleosynthetic Isotope Heterogeneity in the Solar Protoplanetary Disk

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Stable-isotope variations exist among inner solar system solids, planets, and asteroids, but their importance is not understood. We report correlated, mass-independent variations of titanium-46 and titanium-50 in bulk analyses of these materials. Because titanium-46 and titanium-50 have different nucleosynthetic origins, this correlation suggests that the presolar dust inherited from the protosolar molecular cloud was well mixed when the oldest solar system solids formed, but requires a subsequent process imparting isotopic variability at the planetary scale. We infer that thermal processing of molecular cloud material, probably associated with volatile-element depletions in the inner solar system, resulted in selective destruction of thermally unstable, isotopically anomalous presolar components, producing residual isotopic heterogeneity. This implies that terrestrial planets accreted from thermally processed solids with nonsolar isotopic compositions.

The presence of isotope anomalies (*1*) of nucleosynthetic origin in meteorites is commonly interpreted as reflecting large-scale isotope heterogeneity resulting from inefficient mixing of stellar-derived dust and gas following collapse of the protosolar molecular cloud core (*2–4*). Late-forming planetary bodies like Earth and Mars record the lowest levels of isotope heterogeneity compared to that of the solar system's oldest dated solids, calcium-aluminum–rich inclusions (CAIs), possibly reflecting progressive isotope homogenization of the protoplanetary disk or, alternatively, sampling of disk material at a much broader scale. However, this is apparently at odds with the observation that ^{26}Al—a short-lived nuclide injected into the nascent solar system from a nearby star (*5*)—was evenly distributed in the accretion regions of the terrestrial planets and chondrite meteorites (*6*) at levels comparable to that observed in CAIs (*7–10*).

Establishing how and when presolar components were homogenized within the solar protoplanetary disk is uncertain, but central to test models of solar system formation. Titanium is a refractory iron-group element comprising five isotopes (^{46}Ti, ^{47}Ti, ^{48}Ti, ^{49}Ti and ^{50}Ti) synthesized by distinct processes during hydrostatic and explosive nucleosynthesis in stars (*11*). Therefore, we used titanium isotopes to understand the origin and degree of isotope heterogeneity in the inner solar system and track the isotopic evolution of solids that formed the terrestrial planets. Previous studies have identified nonterrestrial, and hence anomalous, titanium isotope compositions in bulk carbonaceous chondrites and in chondritic components such as CAIs and isolated hibonites ($CaAl_{12}O_{19}$), as well as in presolar grains (*2*, *12–17*). Whereas titanium isotope anomalies in solar system materials are typically expressed as variations in the neutron-rich ^{50}Ti nuclide, presolar grains display a wider spectrum of anomalous compositions affecting most titanium isotopes.

We obtained high-precision titanium isotope measurements of early solar system materials, by multicollection inductively coupled plasma mass spectrometry in two laboratories [Bristol and Copenhagen (*18*)] (Fig. 1). Apart from enstatite chondrites, enstatite achondrites, and lunar meteorites, all solar system objects show significant correlated variations in ε^{46}Ti and ε^{50}Ti compared to terrestrial values, defining a single line with slope 5.48 ± 0.27 and intercept −0.04 ± 0.20. Whole-rock carbonaceous chondrites record variable excesses in ε^{46}Ti and ε^{50}Ti, whereas ordinary chondrites are characterized by uniform deficits in these isotopes with respect to Earth. With the exception of the NWA 2976 basalt, which has a titanium isotope composition similar to that of carbonaceous chondrites, all samples originating from differentiated asteroids (eucrites, diogenites, angrites, mesosiderites, pallasites, and ureilites) and Mars exhibit deficits in ε^{46}Ti and ε^{50}Ti. One chondrule extracted from the Dar al Gani 313 ordinary chondrite has a titanium isotope composition similar to the average defined by whole-rock ordinary chondrites. In contrast, chondrules from the Allende carbonaceous chondrite show variable correlated titanium isotope compositions, with both excesses and deficits in ε^{46}Ti and ε^{50}Ti. Four coarse-grained igneous CAIs, compact Type A and Type B, and one amoeboid olivine aggregate (AOA) from the Allende and Efremovka CV carbonaceous chondrites display relatively uniform excesses in ε^{46}Ti and ε^{50}Ti of 1.7 ± 0.3 and 9.4 ± 0.9 ε units, respectively.

The chemical dissolution procedures that we used are not expected to dissolve refractory phases such as SiC or hibonite grains present in fine-grained matrices of chondritic meteorites. This raises the possibility that the titanium isotope heterogeneity among chondrites reflects incomplete dissolution of these potentially isotopically anomalous phases or of other unidentified presolar grains. However, mass balance

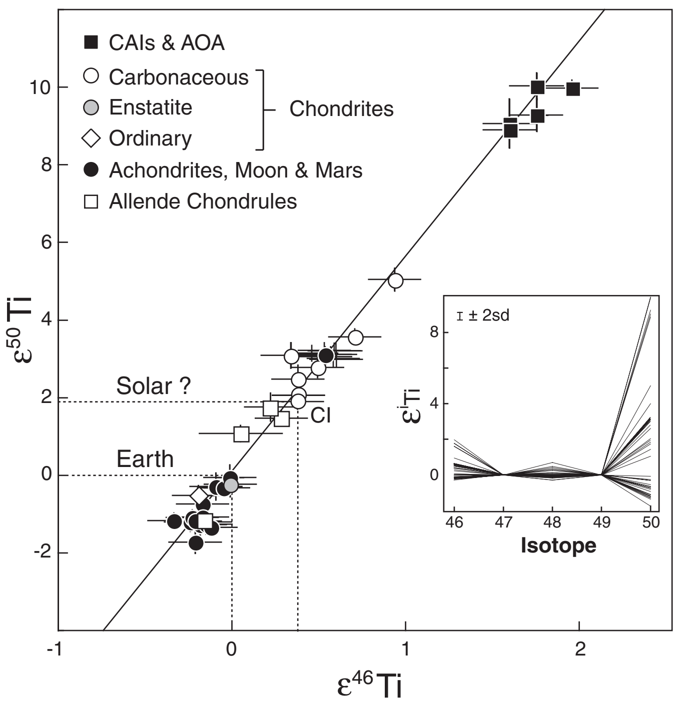

Fig. 1. ε^{46}Ti-ε^{50}Ti variation diagram for inner solar system planetary materials. Data are reported in the ε notation (deviations in parts per 10,000 from the terrestrial $^{50}Ti/^{47}Ti$ and $^{46}Ti/^{47}Ti$ ratios) and internally normalized to $^{49}Ti/^{47}Ti$ = 0.749766 (*12*). This normalization approach assumes that the $^{49}Ti/^{47}Ti$ ratios of samples we analyzed are terrestrial. Error bars represent the external reproducibility or the internal precision, whichever is larger. (**Inset**) ε^{46}Ti, ε^{48}Ti, and ε^{50}Ti variations for the same samples, with the external reproducibility indicated.

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calculations indicate that incomplete dissolution of SiC or hibonite grains will only lead to a shift in the bulk ^{50}Ti composition of <0.3 ε unit (SOM Text 1), which is inconsistent with the range of ε^{50}Ti values observed among chondrites (Fig. 1). Apart from CAIs and AOA, all meteorites display the terrestrial ^{48}Ti/^{47}Ti ratio when the ^{49}Ti/^{47}Ti ratio is used to correct for instrumental mass fractionation (Fig. 1, inset) and, hence, using a different pair of isotopes (^{48}Ti/^{47}Ti or ^{49}Ti/^{48}Ti) to correct for instrumental mass fractionation yields identically correlated anomalies in ^{46}Ti and ^{50}Ti. Therefore, the most straightforward interpretation of these data is that Ti isotope anomalies are restricted to ^{46}Ti and ^{50}Ti, whereas the ^{47}Ti, ^{48}Ti and ^{49}Ti abundances of most samples that we analyzed are terrestrial within the resolution of our analyses (SOM Text 2).

The ^{50}Ti anomalies that we found for inner solar system materials are comparable to ^{54}Cr compositions for the same meteorites and components (Fig. 2). We attribute the lack of correlation between the ^{54}Cr and ^{50}Ti anomalies in carbonaceous chondrites to the presence of variable amounts of CAIs in these meteorites. CAIs are elementally enriched in titanium and depleted in chromium compared to solar system abundances (*19*) such that addition of small quantities [<10 weight percent (wt%)] of this material to a CAI-free chondrite matrix will almost exclusively modify its bulk titanium isotope composition (Fig. 2). In contrast, the well-correlated abundances of ^{54}Cr and ^{50}Ti in samples from terrestrial planets and most differentiated asteroids, as well as from ordinary and enstatite chondrites, imply that their accretion regions were essentially free of CAIs. Therefore, the ^{46}Ti-^{50}Ti covariation recorded by inner solar system planets and asteroids cannot uniquely reflect admixing of variable amounts of CAIs in their precursor material.

To understand the scale of this heterogeneity, we have subjected the CI chondrite Orgueil to a stepwise-leaching procedure aimed at providing a crude chemical separation of the various mineralogical components (*3*, *20*). Composed of matrix material with the highest abundances of presolar grains, CI chondrites are generally considered to represent the least chemically fractionated and least thermally processed meteorites (*21*). Analysis of the different leach fractions show that none has a terrestrial titanium isotope composition (Fig. 3) and that the bulk of the titanium (>99.5%) resides in acid-soluble nonrefractory silicate minerals. Most fractions plot off the ^{46}Ti-^{50}Ti correlation line defined by the inner solar system solids (Fig. 3), implying the existence of multiple titanium nucleosynthetic components in Orgueil silicates. The largest excess of ^{50}Ti was identified in fractions where significant excesses ^{54}Cr have been previously reported (*3*, *20*), thereby suggesting a common carrier for ^{50}Ti and ^{54}Cr. In contrast, the positively anomalous ^{46}Ti apparently resides in a distinct mineralogical component and, hence, in a different carrier. Given that the magnitude of the titanium isotope heterogeneity we report for chondrites cannot be explained by addition or removal of typical presolar grain assemblages retrieved from the matrices of carbonaceous chondrites, it must represent the existence of additional—as yet unidentified—presolar carriers of anomalous titanium inherited from the protosolar molecular cloud. We infer that the titanium isotope heterogeneity defined by the various fractions of Orgueil reflects admixing of multiple generations of presolar silicates, possibly of distinct stellar origins, given that the nucleosynthesis of ^{46}Ti and that of ^{50}Ti are believed to be decoupled (*11*). Silicates are the most abundant presolar phases in carbonaceous chondrites, but are typically difficult to identify with conventional techniques given their minute size and fragile nature. However, we note that addition or removal of ~500 parts per million (ppm) of presolar silicates with chondritic titanium concentrations and ^{50}Ti enrichments similar to that present in other presolar components (e.g., SiC) to a terrestrial composition is sufficient to produce the ^{50}Ti variability observed in planetary materials.

It is unlikely that the ^{46}Ti-^{50}Ti correlation line defined by solar system objects results from simple heterogeneous distribution of presolar silicates within the inner protoplanetary disk, given that the anomalous ^{46}Ti and ^{50}Ti reside in different carriers. Instead, it suggests that the presolar dust inherited from the protosolar molecular cloud was initially homogeneously distributed within the inner protoplanetary disk, but requires the existence of a secondary process imparting selective loss of presolar silicates before the formation of solar system solids and accretion of planetary bodies. The magnitude of the ^{54}Cr excesses in carbonaceous chondrites—and by extension that of the ^{46}Ti and ^{50}Ti excesses—correlates with a degree of depletion in moderately volatile elements of the host meteorite matrices (Fig. 4). The chemical fractionations of moderately volatile elements in carbonaceous chondrite matrices and the survival of their presolar grain assemblages are believed to reflect the degree of thermal processing experienced by the matrix before parent body accretion (*21*–*23*). Therefore, we propose that the thermal event(s) responsible for moderately volatile element fractionation in the inner solar system also resulted in the preferential loss by sublimation of thermally unstable presolar silicates containing ^{46}Ti and ^{50}Ti excesses. However, the ^{46}Ti-^{50}Ti correlation observed in Fig. 1 requires that the ^{46}Ti and ^{50}Ti carriers were removed in approximately the same proportion and, hence, have similar thermal properties, which is not unexpected if they are both nonrefractory silicates. Thus, nucleosynthetic anomalies in meteorites may reflect the degree of thermal pro-

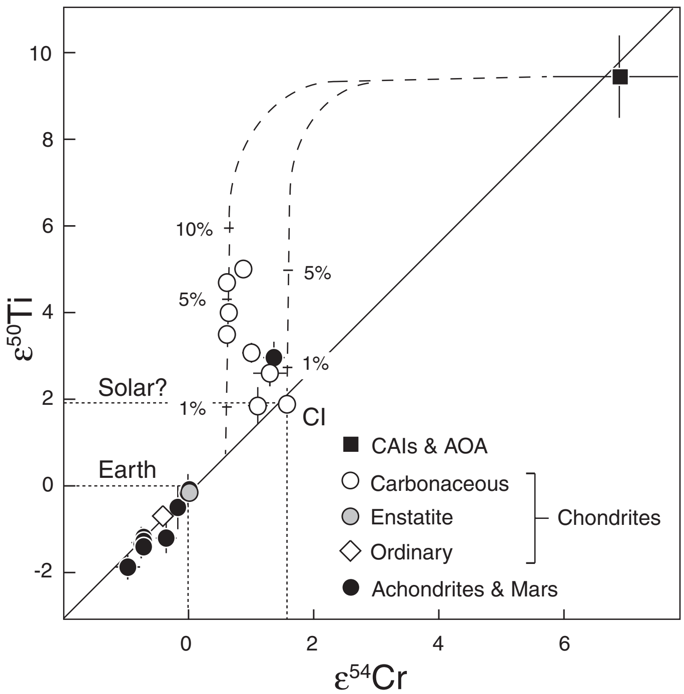

Fig. 2. ε^{54}Cr-ε^{50}Ti variation diagram of inner solar system planets, asteroids, and chondrite components. CAIs, the CI chondrite Orgueil, martian meteorites, and ordinary and enstatite chondrites, as well as most differentiated meteorites, define a correlation line with slope and intercept of 1.4 ± 0.1 and −0.2 ± 0.1, respectively (mean square weighted deviation = 1.3). Bulk CO, CV, CR, and CK carbonaceous chondrites plot above this line, and we attribute this feature to the presence of CAIs in these objects. The dashed lines are mixing curves between CAIs and CAI-free compositions defined by the correlation line, with percent mixing indicated. For the CAI reservoir, we used chromium and titanium concentrations of 200 and 5400 ppm, respectively, and ε^{54}Cr and ε^{50}Ti compositions from (*24*) and as defined here, respectively. We adopted Orgueil as a proxy for the CAI-free chondritic reservoir, using titanium and chromium concentrations from (*19*) and ε^{54}Cr and ε^{50}Ti compositions from (*3*) and as defined here. These models show that a decoupling in ε^{54}Cr and ε^{50}Ti can be explained by addition of small quantities of CAI material (<10 wt %). Error bars represent the external reproducibility or the internal precision, whichever is larger.

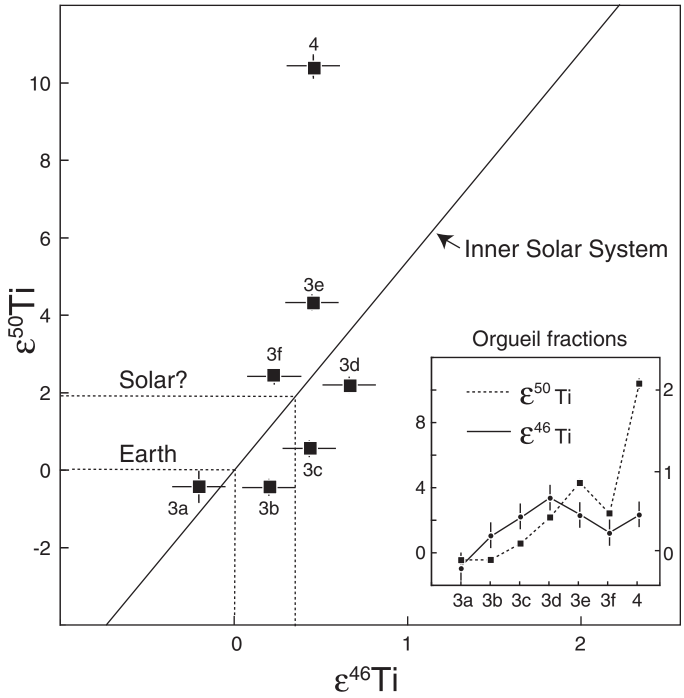

Fig. 3. ε^{46}Ti-ε^{50}Ti variation diagram for fractions of the Orgueil CI chondrite defined by stepwise leaching. Apart from fraction 3a, all fractions plot off the correlation line defined by inner solar system planets, asteroids, and solids (Fig. 1). **(Inset)** ε^{46}Ti and ε^{50}Ti values plotted as a function of leaching step numbers (table S2). The ε^{46}Ti and ε^{50}Ti scales are different and positioned to the right and left, respectively. Using a different pair of isotopes (^{48}Ti/^{47}Ti or ^{48}Ti/^{49}Ti) to correct for instrumental mass fractionation would not change our conclusion that the anomalous ^{46}Ti and ^{50}Ti reside in different presolar carriers. Error bars represent the external reproducibility or the internal precision, whichever is larger.

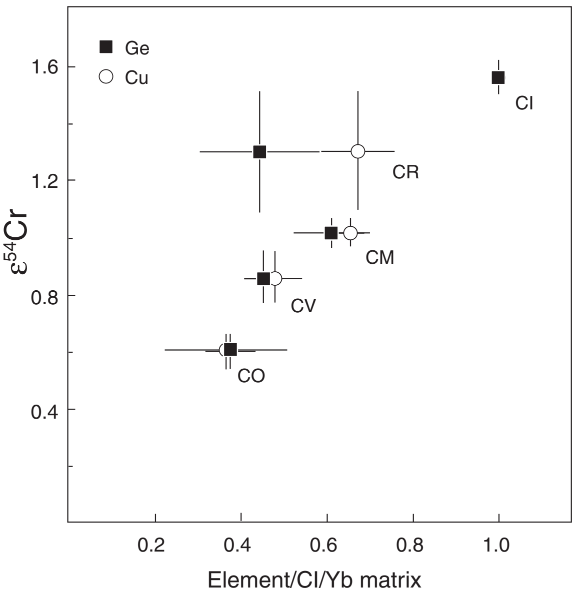

Fig. 4. ^{54}Cr versus Cu and Ge concentrations (ratioed to CI chondrites and ytterbium) in carbonaceous chondrite matrices. Data are from (*3*, *22*). We plot the ^{54}Cr in this diagram because the ^{46}Ti and ^{50}Ti compositions of carbonaceous chondrites are variably affected by the presence of CAIs in these meteorites. Error bars represent the external reproducibility or the internal precision, whichever is larger.

cessing experienced by their precursor material, and not initial disk heterogeneity. Our study demonstrates that Earth and the bulk of the inner solar system's rocky mass did not form from a CI-like precursor but, instead, from appreciably thermally processed material.

The average chemical composition of the protosolar molecular cloud material—and hence that of the Sun—is best approximated by CI chondrites for a refractory element such as titanium. Therefore, mass balance arguments require the existence of a complementary reservoir enriched in ^{46}Ti and ^{50}Ti to account for the widespread depletions observed among the inner solar system bodies. CAIs are the only objects with consistently elevated abundances in ^{46}Ti and ^{50}Ti compared to CI chondrites (Figs. 1 and 2). A possibility is that CAIs represent samples of the complementary gaseous reservoir enriched in ^{46}Ti and ^{50}Ti by thermal processing of pristine molecular cloud material. If correct, this implies that substantive thermal processing and dust-gas fractionation of the inner solar system solids, possibly including moderately volatile-element depletion, occurred before the formation of most CAIs.

References and Notes

1. Isotope anomalies are deviations in the stable-isotope composition of an element compared to that of the Earth.
2. J.-L. Birck, *Rev. Mineral. Geochem.* **55**, 25 (2004).
3. A. Trinquier, J.-L. Birck, C. J. Allègre, *Astrophys. J.* **655**, 1179 (2007).
4. R. Andreasen, M. Sharma, *Astrophys. J.* **655**, 874 (2007).
5. J. N. Goswami, K. K. Marhas, M. Chaussidon, M. Gounelle, B. S. Meyer, in *Chondrites and the Protoplanetary Disk*, A. N. Krot, E. R. D. Scott, B. Reipurth, Eds. (Astrophysical Society of the Pacific, San Francisco, CA, 2005), pp. 485–514.
6. Chondrite meteorites are undifferentiated stony meteorites composed of CAIs, Fe-Mg-silicates spherules called chondrules, and a fine-grained volatile-rich matrix.
7. G. J. MacPherson, A. M. Davis, E. K. Zinner, *Meteoritics* **30**, 365 (1995).
8. M. Bizzarro, J. A. Baker, H. Haack, *Nature* **431**, 275 (2004).
9. K. Thrane, M. Bizzarro, J. A. Baker, *Astrophys. J.* **646**, L159 (2006).
10. J. N. Connelly, Y. Amelin, A. N. Krot, M. Bizzarro, *Astrophys. J.* **675**, L121 (2008).
11. D. D. Clayton, *Handbook of Isotopes in the Cosmos: Hydrogen to Gallium* (Cambridge Univ. Press, Cambridge, UK, 2003).
12. F. R. Niederer, D. A. Papanastassiou, G. J. Wasserburg, *Geochim. Cosmochim. Acta* **45**, 1017 (1981).
13. S. Niemeyer, G. W. Lugmair, *Earth Planet. Sci. Lett.* **53**, 211 (1981).
14. F. R. Niederer, D. A. Papanastassiou, G. J. Wasserburg, *Geochim. Cosmochim. Acta* **49**, 835 (1985).
15. I. Leya, M. Schönbächler, U. Wiechert, U. Krähenbühl, A. N. Halliday, *Earth Planet. Sci. Lett.* **266**, 233 (2008).
16. T. R. Ireland, *Geochim. Cosmochim. Acta* **52**, 2827 (1988).
17. E. Zinner *et al.*, *Geochim. Cosmochim. Acta* **71**, 4786 (2007).
18. Materials and methods are available as supporting online material (SOM) at *Science* Online.
19. H. Palme, A. Jones, in *Treatise on Geochemistry*, H. D. Holland, K. K. Turekian, Eds., Vol. 1, *Meteorites, Comets and Planets*, A. M. Davis, Ed. (Elsevier-Pergamon, Oxford, 2003), pp. 41–61.
20. M. Rotaru, J.-L. Birck, C. J. Allègre, *Nature* **358**, 465 (1992).
21. G. R. Huss, A. P. Meshik, J. B. Smith, C. M. Hohenberg, *Geochim. Cosmochim. Acta* **67**, 4823 (2003).
22. P. A. Bland *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **102**, 13755 (2005).
23. A. Trinquier, J.-L. Birck, C. J. Allègre, C. Göpel, D. Ulfbeck, *Geochim. Cosmochim. Acta* **72**, 5146 (2008).
24. O. Bogdanovski, D. A. Papanastassiou, G. J. Wasserburg, *Lunar Planet. Sci.* **33**, 1802 (2002).

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Methods
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Figs. S1 and S2
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References

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