Comment on “Neodymium-142 Evidence for Hadean Mafic Crust”

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O’Neil et al. (Reports, 26 September 2008, p. 1828) presented neodymium-142 data for rocks from northern Quebec, Canada, and suggested that these rocks may represent the oldest preserved crustal section on Earth. We argue that the age of the rocks is based on a spurious correlation between rocks that are probably not co-genetic and negative 142Nd anomalies that may be the result of an analytical artifact.

O’Neil et al. (1) presented high-precision Nd isotope data for a suite of rocks from the Nuvvuagittuq greenstone belt in Canada and suggested that these rocks formed 4.29 ± 0.3 million years ago (Ma). They sampled an enriched reservoir that must have formed shortly after the formation of Earth 4.567 Ma. These inferences hinge on the interpretation of the observed positive correlation between the 144Sm/142Nd and 142Nd/144Nd ratios for faunal-amphibolites and gabbros, which suggests that the rocks sample a reservoir formed when short-lived 146Sm (half life = 103 million years) was abundant on Earth. O’Neil et al. (1) calculated the statistically significant age by assuming that the two types of rocks are co-genetic and that the positive correlation represents an isochron. That the faunal-amphibolites display negative 142Nd anomalies with respect to the upper mantle supports the notion that these rocks sample material formed shortly after Earth’s formation.

We contend that the faunal-amphibolites and gabbros are not co-genetic and that the observed negative 142Nd anomalies are an analytical artifact. The faunal-amphibolites yield average depleted-mantle model ages [4.290 ± 0.340 million years ago (Ma)] that appear distinct from the gabbros (3.580 ± 0.580 Ma) (Table S2 in (1)). Thus, these two rock types, although spatially associated, are not co-genetic, and combining their data results in an age that is likely meaningless [see (2) for discussion]. Moreover, the faunal-amphibolites do not yield a precise isochron, and forcing the isochron through the modern upper-mantle value yields a model-dependent age and not a true age of formation of the faunal-amphibolites or the incompatible element-rich material they sample. A more serious issue, however, is the extent to which the observed deficits in 142Nd are artifacts of thermal ionization mass spectrometry (TIMS) analyses. The most relevant observation is that the Nuvvuagittuq samples that display negative 142Nd anomalies also display negative 148Nd and 150Nd anomalies, whereas the ones that show no 142Nd anomalies also show no anomalies in 148Nd and 150Nd. Indeed, the strong correlations between the 142Nd anomalies and the 148Nd and 150Nd anomalies suggest a causal mechanism operating during mass spectrometry (Fig. 1).

During thermal ionization, isotope ratios are primarily affected by mass-dependent isotope fractionation akin to Rayleigh distillation, which leads to increasingly heavy/light isotope ratios as the sample on the filament becomes increasingly depleted during analysis (3). In the case of Nd isotope measurements, mass fractionation effects are corrected by using an exponential fractionation law (4) that relates the measured 146Nd/144Nd ratio to the “true” 146Nd/144Nd ratio (= 0.72159) and estimates a “fractionation factor” that is used to calculate true values for other measured isotope ratios (142Nd/144Nd, 148Nd/144Nd, and so on). However, imperfect assessment of the fractionation factor, resulting from incomplete homogenization of the sample during analysis, affects the accuracy of high-precision Nd isotope measurements (5, 6). This occurs as sluggish diffusion within the evaporating sample leads to the creation of variably depleted domains. Because of the nonlinear nature of thermal ionization, mixing of ions derived from these domains yields 146Nd/144Nd ratios that are different from those derived from a single domain. Modeling indicates that when 146Nd/144Nd is used for fractionation correction, increasing levels of mixing between different domains will lead to increases in 142Nd/144Nd with collateral increases in 148Nd/144Nd and 150Nd/144Nd (e.g., (6)). It follows that if a comparison is made between Nd isotope ratios obtained for standards and samples, with the latter mixing less, on average, than the former, the samples will show collateral negative anomalies in 142Nd, 148Nd, and 150Nd (Figs. 1 and 2).

As diffusion-ionization is matrix-dependent, mixing effects are not expected to be present in all samples. For example, no anomalies in 148Nd and 150Nd accompany the 142Nd anomalies reported for the Allende carbonaceous chondrite (7, 8) or the 3.8 billion years ago (Ga) metamaterials from Isua, Greenland (9) (Fig. 1). In contrast, averages of the five different Nuvvuagittuq lithologies measured by O’Neil et al. (1) (excluding spike-contaminated samples) fall on domain-mixing lines in both 142Nd−148Nd and 142Nd−150Nd space (Fig. 1). It is intriguing that Nd isotope data from a Deccan Traps sample that initially showed a negative 142Nd anomaly (10) also fall in the cluster of Nuvvuagittuq lithologies. Subsequent analyses of this sample proved it to be normal with respect to 142Nd and stable Nd isotopes (11).

O’Neil et al. (1) interleaved measurements of their rock samples with those of the La Jolla Nd standard. Their preferred explanation for why some of the rock samples display negative 148Nd and 150Nd is that La Jolla itself is fractionated. To support this, they presented stable Nd isotope MC-ICP-MS (multicollector–inductively coupled plasma mass spectrometry) data for La Jolla with respect to another Nd standard (JNdi-1), which they demonstrated to have a normal Nd isotope composition (table S5 in (1)). They showed that La Jolla is enriched in light Nd with respect to JNdi-1 by 0.112‰ per atomic mass unit. This would indicate that the true 146Nd/144Nd ratio of La Jolla is 0.72174, which when the exponential law and 146Nd/144Nd = 0.7219 are used, results in small negative anomalies in 142Nd [-2.8 ± 0.8 parts per million (ppm)], 148Nd (-1.6 ± 0.8 ppm), and 150Nd (-9.1 ± 2.2 ppm) (table S5 and S6 in (1)) for La Jolla that cannot be resolved from the values of JNdi-1. This is consistent with the comprehensive TIMS study by Boyet and Carlson (7), who found that La Jolla and JNdi-1 are identical within error (Fig. 1). Using results from Carlson et al. (12), O’Neil et al. (1) concluded that whereas La Jolla is normal in 142Nd, it is enriched in 148Nd by 9 ppm and in 150Nd by 30 ppm with respect to JNdi-1. However, this inference is inconsistent with the expected depletions in 142Nd, 148Nd, and 150Nd. No process is known to generate the isotopic values for La Jolla seen in (12), and we can only speculate that they result from the much smaller number of analyses in (12) compared with those of (7).

So far, all terrestrial samples with reported negative 142Nd anomalies also exhibit pronounced associated negative anomalies in 148Nd and 150Nd, which suggests that their anomalous Nd isotopic compositions are likely a consequence of mixing of variably depleted domains (Fig. 2). Therefore, we contend that these samples do not hold any additional information about the earliest history of Earth’s mantle.

References

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that La Jolla could be enriched in $^{148}\text{Nd}$ and $^{150}\text{Nd}$ with respect to JNdi-1 (shown as LJO). Data from Carlson et al. (7) suggest that the anomalies observed in (I) are caused by domain-mixing rather than decay of $^{147}\text{Sm}$ at variable Sm/Nd ratios. A comprehensive ($n = 29$) study of La Jolla and JNdi-1, shown as LJB, demonstrates that they are identical within error. This is consistent with the MC-ICP-MS data in (I), which shows that when La Jolla is measured by TIMS and normalized using the exponential law it should exhibit small irresolvable deficits in $^{142}\text{Nd}$, $^{144}\text{Nd}$, and $^{150}\text{Nd}$ with respect to JNdi-1 (shown as LJO). Data from Carlson et al. (12) suggest that La Jolla could be enriched in $^{148}\text{Nd}$ and $^{150}\text{Nd}$ with respect to JNdi-1 (shown as LJC). The cause for this discrepancy between the studies, two of which were conducted on the same mass spectrometer, is not clear, and we speculate that it is a statistics of small numbers issue, because only four JNdi-1 measurements were performed in (I2). There is no known process that can generate variations along the $y$ axis in $^{148}\text{Nd}$ and $^{150}\text{Nd}$ without associated changes in $^{142}\text{Nd}$. Individual sample analyses of O’Neil et al. (2) are plotted in the insets, the best-fit line in (A) is the same for individual samples and lithology averages, whereas the data for the individual samples in (B) are too noisy to yield a best-fit line. The choice to average the sample data of O’Neil et al. (1) was made to investigate the effects of domain mixing that are smaller than the uncertainty on individual analyses (10). Since different lithologies show clustering in $^{148}\text{Nd}$/$^{144}\text{Nd}$ and $^{147}\text{Sm}$/$^{144}\text{Nd}$ (I) the data averages were calculated for each lithology. The data used for the averages are given in table S4 in (I). Eight $^{150}\text{Nd}$ data were excluded because of spike contamination.


Additional references:
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Fig. 2. Deviations in parts per million in Nd isotope composition from Nd standard for the averages of the five Nuvvuagittuq lithologies analyzed in (1) (normalized to La Jolla), Deccan Traps picrite BN 016 (10) (normalized to Caltech nNd-b), Isua metasediments (9) (normalized to Ames Nd), and Nuuk and Isua tonalites (13) (normalized to Ames Nd). All data are fractionation-corrected using the exponential law and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$; $^{144}\text{Nd}$ is omitted because of the large radiogenic variations. The shaded area indicates common levels of 2σ reproducibility (1, 7–9, 11–13); individual error bars have been omitted for clarity. The curves are best-fit model calculations, to the samples of the same color. Assuming the deviations in $^{142},^{145},^{148},^{150}\text{Nd}$ for a given sample relative to the standard are caused by neodymium evaporating from multiple domains on the filament, fractionated to differing extents, the domain-mixing lines (Fig. 1) yield a parabola-shaped isotope pattern in multi-isotope space, with roots at the normalizing isotopes $^{144}\text{Nd}$ and $^{146}\text{Nd}$. Convex parabolas imply larger degrees of domain mixing in the sample than in the standard, concave parabolas imply larger degrees of domain mixing in the standards than in the sample. The degree of curvature of the parabolas indicates the absolute difference in mixing between the sample and the standards. Note that all samples with reported negative $^{142}\text{Nd}$ values fall on mixing parabolas in contrast to the samples with reported positive $^{142}\text{Nd}$ anomalies, where the excess in $^{142}\text{Nd}$ cannot be attributed to mixing effects. Note also that the O’Neil et al. (1) samples showing no or small $^{142}\text{Nd}$ anomalies also show no or small anomalies in $^{148}\text{Nd}$ and $^{150}\text{Nd}$ relative to La Jolla, which suggests that there is no systematic difference between the La Jolla and JNd-1 standards.
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