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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 4280⁺⁵³₋₈₁ million years ago (Ma). They sampled an enriched reservoir that must have formed shortly after the formation of Earth 4567 Ma. These inferences hinge on the interpretation of the observed positive correlation between the ¹⁴⁷Sm/¹⁴⁴Nd and ¹⁴²Nd/¹⁴⁴Nd ratios for faux-amphibolites and gabbros, which suggests that 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 faux-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 faux-amphibolites and gabbros are not co-genetic and that the observed negative ¹⁴²Nd anomalies are an analytical artifact. The faux-amphibolites yield average depleted-mantle model ages [4290 ± 340 million years ago (Ma)] that appear distinct from the gabbros (3580 ± 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 faux-amphibolites data 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 faux-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 (= 0.7219) and estimates a “fractionation factor” that is used to calculate true values for other measured isotope ratios (¹⁴²Nd/¹⁴⁴Nd, ¹⁴³Nd/¹⁴⁴Nd, and so on). However, improper 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) metasediments 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 $\mu_{Nd}^{142}-\mu_{Nd}^{150}$ and $\mu_{Nd}^{142}-\mu_{Nd}^{148}$ 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 anomalies 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 [−3.1 ± 0.8 parts per million (ppm)], ¹⁴⁸Nd (−3.0 ± 0.8 ppm), and ¹⁵⁰Nd (−9.1 ± 2.2 ppm) [based on tables 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.

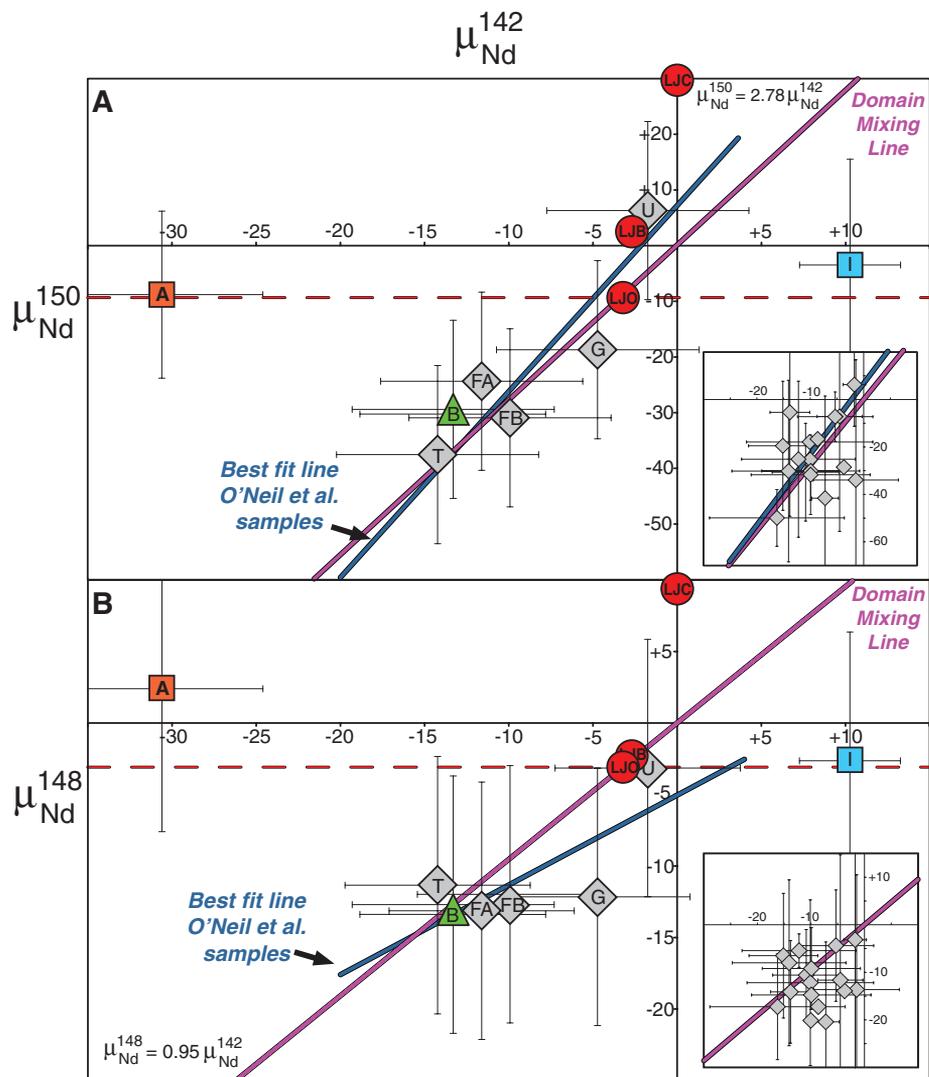
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Fig. 1. Parts per million (μ) deviations from standard Nd in $^{142}\text{Nd}/^{144}\text{Nd}$ ratios plotted against the respective deviations in $^{150}\text{Nd}/^{144}\text{Nd}$ (A) and $^{148}\text{Nd}/^{144}\text{Nd}$ (B) ratios. Shown are the averages of the five Nuvvuagittuq lithologies analyzed in (1). FA, faux-amphibolite; FB, felsic band; G, gabbro; T, tonalite; U, ultramafic [normalized to La Jolla (1)]. Also shown are Allende (A) [an average of analyses normalized to La Jolla, JNdi-1, and Caltech nNd- β (7, 8)]; Isua metasediments (I) [average of analyses normalized to Ames Nd (9)]; and an analysis of a Deccan Plateau picrite (B, BN 016) [normalized to Caltech nNd- β (10, 11)], for which the ^{142}Nd anomaly shown here could not be reproduced. Additionally, three analyses of La Jolla relative to JNdi-1 are plotted as LJO (1), LJB (7), and LJC (12). Variations in Nd isotopic composition caused by domain-mixing in the source of the mass spectrometer or mass-dependent isotope fractionation are plotted along curves passing through the origin. These curves have near-constant ratios between anomalies in the different Nd isotopes: $\Delta\mu_{\text{Nd}}^{148} \cong 0.95 \Delta\mu_{\text{Nd}}^{142}$, and $\Delta\mu_{\text{Nd}}^{150} \cong 2.78 \Delta\mu_{\text{Nd}}^{142}$. These values are obtained by taking two normal Nd isotopic compositions at different f -values, mixing them, and using the exponential law to fractionation correct to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. The resulting lines are called “domain-mixing” lines and are, in effect, mass-dependent fractionation lines. Anomalies in ^{142}Nd caused by the decay of ^{146}Sm at variable Sm/Nd ratios plot along the x axis or on a horizontal line going through a point on the domain-mixing line, exemplified here by a dashed line through LJO. The similarity between the domain-mixing lines and the best-fit lines for the O’Neil *et al.* (1) data and the co-variation of μ_{Nd}^{142} and $\mu_{\text{Nd}}^{148,150}$ suggest that the anomalies observed in (1) are caused by domain-mixing rather than decay of ^{146}Sm at variable Sm/Nd ratios. A comprehensive ($n = 29$) study of La Jolla and JNdi [(7), shown as LJB] demonstrates that they are identical within error. This is consistent with the MC-ICP-MS data in (1), which shows that when La Jolla is measured by TIMS and normalized using the exponential law it should exhibit small irresolvable deficits in ^{142}Nd , ^{148}Nd , and ^{150}Nd with respect to JNdi-1 (shown as LJO). Data from Carlson *et al.* (12) suggest that La Jolla could be enriched in ^{148}Nd and ^{150}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 (12). There is no known process that can generate variations along the y axis in ^{148}Nd and ^{150}Nd without



associated changes in ^{142}Nd . Individual sample analyses of O’Neil *et al.* (1) 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 in $^{148,150}\text{Nd}$. Since different lithologies show clustering in $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ (1) the data averages were calculated for each lithology. The data used for the averages are given in table S4 in (1); eight ^{150}Nd data were excluded because of spike contamination.

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10 December 2008; accepted 16 June 2009

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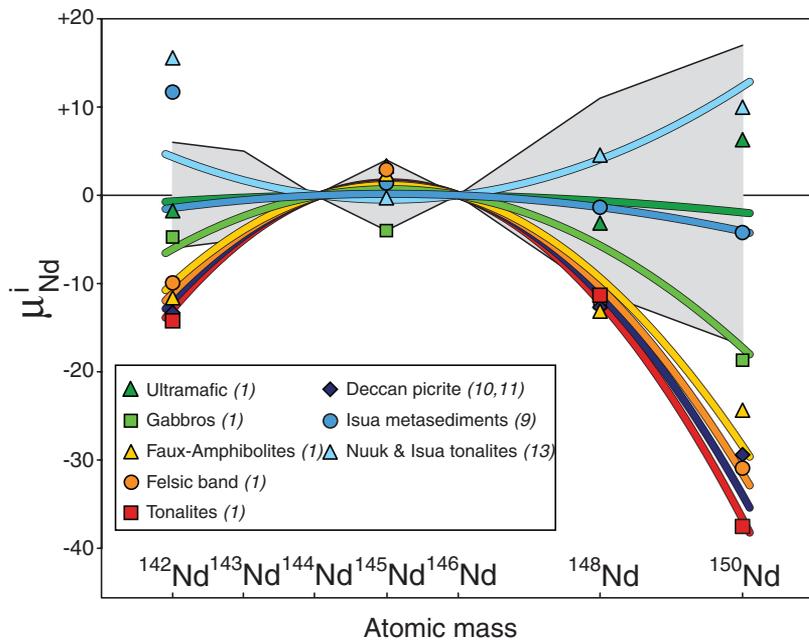


Fig. 2. Deviations in parts per million in Nd isotope composition from Nd standard for the averages of the five Nuvvuagittuq lithologies analyzed in (1) (normalized to La Jolla), Deccan Traps picrite BN 016 (10) (normalized to Caltech nNd- β), Isua metasediments (9) (normalized to Ames Nd), and Nuuk and Isua tonalites (13) (normalized to Ames Nd). All data are fractionation-corrected using the exponential law and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$; ^{143}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}Nd and ^{146}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}Nd values fall on mixing parabolas in contrast to the samples with reported positive ^{142}Nd anomalies, where the excess in ^{142}Nd cannot be attributed to mixing effects. Note also that the O’Neil *et al.* (1) samples showing no or small ^{142}Nd anomalies also show no or small anomalies in ^{148}Nd and ^{150}Nd relative to La Jolla, which suggests that there is no systematic difference between the La Jolla and JNdi-1 standards.