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## **Comment on "Neodymium-142 Evidence for Hadean Mafic Crust"**

Rasmus Andreasen<sup>1\*</sup> and Mukul Sharma<sup>2</sup>

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 <sup>142</sup>Nd anomalies that may be the result of an analytical artifact.

'Neil et al. (1) presented high-precision Nd isotope data for a suite of rocks from the Nuvvuagittug 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 fauxamphibolites and gabbros, which suggests that that the rocks sample a reservoir formed when short-lived  $^{146}$ Sm (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 <sup>142</sup>Nd 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 <sup>142</sup>Nd anomalies are an analytical artifact. The faux-amphibolites yield average depletedmantle model ages  $[4290 \pm 340 \text{ million years ago}]$ (Ma)] that appear distinct from the gabbros (3580  $\pm$ 580 Ma) [table S2 in (1)]. Thus, these two rock types, although spatially associated, are not cogenetic, 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 <sup>142</sup>Nd are artifacts of thermal ionization mass spectrometry (TIMS) analyses. The most relevant observation is that the Nuvvuagittuq samples that display negative <sup>142</sup>Nd anomalies also display negative <sup>148</sup>Nd and <sup>150</sup>Nd anomalies, whereas the ones that show no <sup>142</sup>Nd anomalies also show no anomalies in <sup>148</sup>Nd and <sup>150</sup>Nd. Indeed, the strong correlations between the <sup>142</sup>Nd anomalies and the <sup>148</sup>Nd and <sup>150</sup>Nd anomalies uggest 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  $^{146}$ Nd/ $^{144}$ Nd ratio to the "true"  ${}^{146}$ Nd/ ${}^{144}$ Nd ratio (= 0.7219) and estimates a "fractionation factor" that is used to calculate true values for other measured isotope ratios (<sup>142</sup>Nd/<sup>144</sup>Nd, <sup>143</sup>Nd/<sup>144</sup>Nd, 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 <sup>146</sup>Nd/<sup>144</sup>Nd is used for fractionation correction, increasing levels of mixing between different domains will lead to increases in <sup>142</sup>Nd/<sup>144</sup>Nd with collateral increases in <sup>148</sup>Nd/<sup>144</sup>Nd and <sup>150</sup>Nd/<sup>144</sup>Nd [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 <sup>142</sup>Nd, <sup>148</sup>Nd, and <sup>150</sup>Nd (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 <sup>148</sup>Nd and <sup>150</sup>Nd accompany the <sup>142</sup>Nd 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 spikecontaminated 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 <sup>142</sup>Nd anomaly (10) also fall in the cluster of Nuvvuagittuq lithologies. Subsequent analyses of this sample proved it to be normal with respect to <sup>142</sup>Nd 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 <sup>148</sup>Nd and <sup>150</sup>Nd 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 <sup>146</sup>Nd/<sup>144</sup>Nd ratio of La Jolla is 0.72174, which when the exponential law and  $^{146}$ Nd/ $^{144}$ Nd = 0.7219 are used, results in small negative anomalies in  $^{142}$ Nd [-3.1 ± 0.8 parts per million (ppm)],  $^{148}$ Nd (-3.0 ± 0.8 ppm), and  $^{150}$ Nd (-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 <sup>142</sup>Nd, it is enriched in <sup>148</sup>Nd by 9 ppm and in <sup>150</sup>Nd by 30 ppm with respect to JNdi-1. However, this inference is inconsistent with the expected depletions in <sup>142</sup>Nd, <sup>148</sup>Nd, and <sup>150</sup>Nd. 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 <sup>142</sup>Nd anomalies also exhibit pronounced associated negative anomalies in <sup>148</sup>Nd and <sup>150</sup>Nd, 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

- J. O'Neil, R. W. Carlson, D. Francis, R. K. Stevenson, Science 321, 1828 (2008).
- S. Moorbath, P. N. Taylor, N. W. Jones, Chem. Geol. 57, 63 (1986).
- 3. K. Habfast, Int. J. Mass Spectrom. 176, 133 (1998).
- W. A. Russell, D. A. Papanastassiou, T. A. Tombrello, Geochim. Cosmochim. Acta 42, 1075 (1978).
- S. M. Sharma, C. Chen, *Precambrian Res.* 135, 315 (2004).
- D. Upadhyay, E. E. Scherer, K. Mezger, J. Anal. At. Spectrom. 23, 561 (2008).

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**Fig. 1.** Parts per million  $(\mu)$  deviations from standard Nd in <sup>142</sup>Nd/<sup>144</sup>Nd ratios plotted against the respective deviations in <sup>150</sup>Nd/<sup>144</sup>Nd (A) and  $^{148}\mathrm{Nd}/^{144}\mathrm{Nd}$  (B) ratios. Shown are the averages of the five Nuvvuagittug 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-B (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- $\beta$  (10, 11)], for which the <sup>142</sup>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:  $\Delta \mu_{Nd}^{148} \cong 0.95 \ \Delta \mu_{Nd}^{142}$ , and  $\Delta \mu_{Nd}^{150} \cong 2.78 \ \Delta \mu_{Nd}^{142}$ . 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 <sup>142</sup>Nd caused by the decay of <sup>146</sup>Sm at variable Sm/Nd ratios plot along the x axis or on a horizontal line going through a point on the domainmixing line, exemplified here by a dashed line through LJO. The similarity between the domainmixing lines and the best-fit lines for the O'Neil et al. (1) data and the co-variation of  $\mu_{Nd}^{142}$  and  $\mu_{Nd}^{148,150}$  suggest that the anomalies observed in (1) are caused by domain-mixing rather than decay of <sup>146</sup>Sm at variable Sm/Nd ratios. A comprehensive (n = 29) study of La Jolla and JNdi (7), shown as L]B] 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 <sup>142</sup>Nd, <sup>148</sup>Nd, and <sup>150</sup>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

7. M. Boyet, R. W. Carlson, Science 309, 576 (2005).

9. G. Caro, B. Bourdon, J. L. Birck, S. Moorbath, Geochim.

8. R. Andreasen, M. Sharma, Science 314, 806

Cosmochim, Acta 70, 164 (2006).

(2006).

10. R. Andreasen, K. V. Subbarao, M. Sharma, Geochim.

- Cosmochim Acta 68 A747 (2004)
  - 11. R. Andreasen, M. Sharma, K. V. Subbarao, S. G. Viladkar, Earth Planet. Sci. Lett. 266, 14 (2008).
  - 12. R. W. Carlson, M. Boyet, M. Horan, Science 316, 1175 (2007).





13. V. C. Bennett, A. D. Brandon, A. P. Nutman, Science 318, 1907 (2007)

10 December 2008; accepted 16 June 2009 10.1126/science.1169604





 $\mu_{Nd}^{142}$ 



Atomic mass

**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 <sup>146</sup>Nd/<sup>144</sup>Nd = 0.7219; <sup>143</sup>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 <sup>142,145,148,150</sup>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 <sup>144</sup>Nd and <sup>146</sup>Nd. Convex 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 <sup>142</sup>Nd values fall on mixing parabolas in contrast to the samples with reported positive <sup>142</sup>Nd anomalies, where the excess in <sup>142</sup>Nd cannot be attributed to mixing effects. Note also that the O'Neil *et al.* (1) samples showing no or small <sup>142</sup>Nd anomalies also show no or small anomalies in <sup>148</sup>Nd and <sup>150</sup>Nd relative to La Jolla, which suggests that there is no systematic difference between the La Jolla and JNdi-1 standards.