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Tracking Hadean processes in modern basalts with 142-Neodymium

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17 Abstract

18 The short-lived ${}^{146}\text{Sm} \rightarrow {}^{142}\text{Nd}$ isotope system ($t_{1/2} = 103 \text{ Ma}$) can constrain terrestrial silicate fractionation during the early Hadean. Although some Archean terranes preserve variability in 19 20 ¹⁴²Nd/¹⁴⁴Nd, no anomalies have been previously resolved in young rocks. This study provides high 21 precision ¹⁴²Nd/¹⁴⁴Nd data on a suite of ocean island basalts from Samoa and Hawaii previously shown to have variable depletions in ¹⁸²W/¹⁸⁴W that are inversely correlated with ³He/⁴He ratios. 22 23 Improved analytical techniques and multiple replicate analyses of Nd show a variation in μ^{142} Nd 24 values between -1.3 and +2.7 in the suite, relative to the JNdi standard. Given the reproducibility of 25 the standard (±2.9 ppm, 2 SD), two Samoan samples exhibit resolved variability in their ¹⁴²Nd/¹⁴⁴Nd 26 ratios outside of their 95% confidence intervals, suggesting minor variability in the Samoan hotspot. One sample from Samoa has a higher μ^{142} Nd of +2.7, outside the 95% confidence interval (±1.0 ppm) 27 28 of the average of the standard. Limited, but resolved, variation in ¹⁴²Nd/¹⁴⁴Nd within the suite 29 suggests the preservation of early Hadean silicate differentiation in the sources of at least some basalts from Samoa. Larger variations of ¹⁸²W/¹⁸⁴W and ³He/⁴He ratios in the same samples suggest 30 31 that metal-silicate separation and mantle outgassing left a more persistent imprint on the accessible 32 mantle compared to ¹⁴²Nd/¹⁴⁴Nd ratios which are impacted by early silicate differentiation.

34 **1. Introduction**

35 Modern oceanic basalts preserve variations in the relative abundance of the daughter 36 products of short-lived radioactive isotopes that reflect chemical differentiation processes occurring 37 in the early Hadean (Mukhopadhyay, 2012; Rizo et al., 2016; Mundl et al., 2017). These isotopic tools 38 track different processes involved in Earth's earliest differentiation. For example, differences in the 39 ratio of 129 Xe/ 130 Xe (129 I $\rightarrow {}^{129}$ Xe, $t_{1/2}$ = 15 Ma) between some mid-ocean ridge basalts (MORB) and 40 some ocean island basalts (OIB) indicate that the source reservoirs for MORB and OIB experienced 41 different outgassing histories and were isolated from each other within the first 100 Ma of Earth 42 history (Mukhopadhyay, 2012; Pető et al., 2013; Tucker and Mukhopadhyay, 2014; Parai et al., 2015). The short-lived ${}^{182}\text{Hf} \rightarrow {}^{182}\text{W}$ isotope system (t_{1/2}=8.9 Ma) is sensitive to both early Hadean metal-43 44 silicate differentiation and silicate-liquid fractionation, as Hf is lithophile and less incompatible 45 during silicate melting, compared to W, which is also moderately siderophile. Ocean island basalts 46 from Samoa and Hawaii show variable depletions in ¹⁸²W/¹⁸⁴W that are negatively correlated with 47 their ³He/⁴He ratios (Mundl et al., 2017). By contrast, the 60 Ma basalts from Baffin Bay, Canada, characterized by the highest known ³He/⁴He ratios in terrestrial rocks, show elevated ¹⁸²W/¹⁸⁴W 48 ratios (Rizo et al., 2016). The causes of these variations are not yet clear, with suggested explanations 49 50 including sources differentially affected by the late addition of gas- and siderophile-rich meteoritic 51 components following core formation (e.g. Willbold et al., 2011), early-differentiated sources that 52 could include core metal (e.g. Porcelli and Halliday, 2001), or deep, undegassed, remnants of early 53 Earth differentiation events, possibly located in seismically anomalous zones near the core-mantle 54 boundary (e.g. Coltice et al., 2011; Mundl et al., 2017).

55 The short-lived 146 Sm \rightarrow 142 Nd system would be affected by early Hadean differentiation of the 56 silicate Earth, like the ¹⁸²Hf-¹⁸²W system. A shorter half-life of 68 Ma for ¹⁴⁶Sm was recently reported 57 by Kinoshita et al. (2012), but Marks et al. (2014) and Sanborn et al. (2015) showed that the previously used 103 Ma half-life (Friedman et al., 1966) appears to provide a better fit to meteoritic 58 data. The 103 Ma half-life is used in this paper, but the consequences of the different half-lives for 59 60 the modeling of early differentiation are minor compared to other uncertainties in our understanding of the processes and timing of early Earth differentiation. An important difference between the Sm-61 62 Nd and Hf-W systems, however, is that neither Sm or Nd are siderophile, unlike W, hence the Sm-Nd system is insensitive to metal-silicate separation. Even small changes (e.g., 5%) in Sm/Nd ratios by 63

64 silicate melting and crystal-liquid fractionation during the first few hundred million years of Earth's history should result in measureable (c.10 ppm) offsets in ¹⁴²Nd/¹⁴⁴Nd ratios between melt and 65 66 residue and/or cumulate. Consistent with this, enrichments and depletions of up to 20 ppm in ¹⁴²Nd/¹⁴⁴Nd have been measured in rocks from early Earth terranes, indicating that the oldest 67 preserved crust was derived from sources that experienced differentiation in the Hadean (Caro et al, 68 69 2006; Bennett et al., 2007; O'Neil et al., 2008; Rizo et al., 2012, 2013; Morino et al., 2017). The 70 magnitude of ¹⁴²Nd anomalies in ancient rocks appears to have decreased with time during the Archean, and has been interpreted as evidence that early fractionated mantle domains were mixed 71 72 away by the end of the Archean (Rizo et al., 2012; Debaille et al., 2013).

73 In modern rocks, no variations in ¹⁴²Nd/¹⁴⁴Nd have been resolved outside of an uncertainty 74 of, at minimum, ±5 ppm (Boyet and Carlson, 2006; Caro et al., 2006; Jackson and Carlson, 2012; Murphy et al., 2010; Rizo et al., 2016; de Leeuw et al., 2017). Whether ¹⁴²Nd variations in the sources 75 76 of modern rocks have been homogenized through >4.5 Ga of mantle convection, hide within the 77 analytical uncertainties of previous measurements, or reside in rocks not yet analyzed is unknown. 78 For this study, our approach targeted a small sample suite of OIB from Samoa and Hawaii that show 79 variability in W and He isotope compositions (Mundl et al., 2017). Our specific aim was to evaluate whether any samples that have anomalies in ¹⁸²W/¹⁸⁴W might also have resolvably different 80 ¹⁴²Nd/¹⁴⁴Nd. In order to increase the level of analytical resolution, we refined procedures for Nd 81 82 purification and isotopic analysis, and performed multiple replicate analyses of each sample to reduce the uncertainty on the ¹⁴²Nd/¹⁴⁴Nd composition of each sample, and to better understand the 83 84 earliest silicate fractionation history of OIB sources.

85 **2. Methods**

86 Sample aliquots for this study were taken from the same powders used in Mundl et al. (2017), in order to circumvent uncertainties from sample heterogeneity. These samples are described in the 87 Supplement. Approximately 100 mg of powder was dissolved in HF-HNO₃ in a closed PFA beaker at 88 89 130°C. Samples were dried, and re-dissolved successively in concentrated HNO₃ and HCl until a clear 90 solution without precipitates was obtained. We used a four-column procedure to purify Nd. First, 91 the rare earth element (REE) fraction was separated from major elements in 6M HCl using 2 mL of BioRad AG50Wx8 cation exchange resin. Cerium was removed from the REE fraction next using 92 oxidative chromatography after Hirahara et al. (2012). In this procedure, Ce in the REE fraction was 93 94 oxidized in a solution of 10M HNO₃+20mM NaBrO₃ and adsorbed onto 0.5 mL of Eichrom LN resin

95 (50-100 micron), while the trivalent REE were eluted and collected. This column procedure was repeated. From the resulting Ce-free REE fraction, sodium was removed using a protocol similar to 96 97 that used for the first group REE separation. Lastly, Nd was separated from the REE fraction on PFA columns using a 12 cm by 0.4 cm bed of *Eichrom LN* resin (20-50 micron) and 0.17-0.20 M HCl. This 98 purification scheme yielded undetectable Sm, ¹⁴⁰Ce/¹⁴⁴Nd ratios <3x10⁻⁶ and ¹⁴¹Pr/¹⁴⁴Nd <0.3. 99 Recoveries of Nd were between 75% and >90%. Prior to analysis by thermal ionization mass 100 101 spectrometry (TIMS), 1% of the final Nd fraction was measured on a Thermo iCAP-Q quadrupole ICP-102 mass spectrometer to determine the amount of Nd recovered, and to verify the absence of Ce and Sm.

103 Neodymium was analyzed using double Re filaments on a Thermo Triton TIMS instrument at the Department of Terrestrial Magnetism, Carnegie Institution for Science. The amount of Nd loaded 104 105 onto the filament was controlled to between 600-800 ng, and the intensity of ¹⁴²Nd was maintained between 3 to 6 x 10⁻¹¹ A during analysis. The Faraday cup configuration for multidynamic analysis is 106 shown in Table 1. A 4-step analysis program rotated masses 143, 144, 145 and 146 into the center 107 cup and, for each cycle, yielded two dynamic ratios for $^{142}Nd/^{144}Nd$, as well as two dynamic ratios 108 each for ¹⁴³Nd/¹⁴⁴Nd and ¹⁴⁸Nd/¹⁴⁴Nd, and three dynamic ratios for ¹⁴⁵Nd/¹⁴⁴Nd. Dynamic ratios for 109 110 ¹⁵⁰Nd/¹⁴⁴Nd were not calculated with this method, so static ¹⁵⁰Nd/¹⁴⁴Nd ratios are shown in the Supplementary Table. Intensities of ¹⁴⁰Ce and ¹⁴⁷Sm were measured and used to correct for 111 interferences on Nd isotopes; ¹⁴¹Pr was also monitored. A typical analysis of a given filament included 112 113 300-900 cycles and provided 600-1800 dynamic ¹⁴²Nd/¹⁴⁴Nd ratios. On-peak integration times were 8 s. Once every five blocks of 30 cycles, peaks were centered, the source was tuned and baselines 114 115 were collected for 30 s. Amplifiers were not electronically rotated between blocks, although 116 amplifier gains were calibrated each day.

117 Mass spectrometry data were reduced offline using baseline corrected intensities for each isotope. Mass fractionation was corrected using $^{146}Nd/^{144}Nd \equiv 0.7219$ and applying an exponential 118 equation. Ratios for ¹⁴⁶Nd/¹⁴⁴Nd typically increased throughout an analysis. Multidynamic ratios 119 normally would be calculated using ¹⁴⁶Nd/¹⁴⁴Nd obtained during a different time step within a 4-step 120 cycle. For example, to dynamically correct the $^{142}Nd/^{144}Nd$ measured in step 1 (using Faraday cups 121 L1 and H1), our analysis routine uses the ratio for ¹⁴⁴Nd/¹⁴⁶Nd collected in step 3 (in the same cups). 122 123 To better accommodate changing fractionation with time, we instead used a ¹⁴⁶Nd/¹⁴⁴Nd ratio 124 interpolated (using a linear interpolation) from that measured in step 3 within the same cycle and 125 from the previous cycle. Similarly, dynamic ratios for ¹⁴³Nd/¹⁴⁴Nd, ¹⁴⁵Nd/¹⁴⁴Nd and ¹⁴⁸Nd/¹⁴⁴Nd were 126 calculated using time-corrected ¹⁴⁶Nd/¹⁴⁴Nd. The equations used for the exponential mass

fractionation correction of these multidynamic ratios are given in the Supplement. Dynamic ratios calculated in this way eliminated inverse correlations between dynamic ¹⁴²Nd/¹⁴⁴Nd and ¹⁴⁸Nd/¹⁴⁴Nd ratios within a given analysis (Fig. 1) and among different analyses (Fig. 2), and reduced the systematic bias in the final average ratios of ¹⁴²Nd/¹⁴⁴Nd, ¹⁴³Nd/¹⁴⁴Nd, ¹⁴⁵Nd/¹⁴⁴Nd and ¹⁴⁸Nd/¹⁴⁴Nd that resulted from changing mass fractionation during the individual analyses. Two analyses of the JNdi standard that underwent the same chemical purification procedures as the samples are noted in the Supplementary Table and showed no detectable isotopic effects resulting from purification.

134 To further constrain accuracy and precision of sample analyses, one of the basalt samples was

artificially enriched with an known amount of 142 Nd and then processed through chemistry and

136 mass spectrometry using the procedures described above. The procedures and results of this

137 experiment are described in supplemental section S4.

138

139 3. Results

In order to better evaluate if differences in ¹⁴²Nd/¹⁴⁴Nd ratios could be resolved among the
 rock samples chosen for this study, we performed both replicate chemical dissolutions and replicate
 mass spectrometric analyses utilizing different filaments. The full Nd dataset for individual mass
 spectrometric analyses of samples and standards is provided in the Supplementary Table. An
 individual analysis consists of data obtained from one filament; measurement precision for an
 individual analysis is provided as 2SE. Ratios for ¹⁴²Nd/¹⁴⁴Nd are given as μ¹⁴²Nd, which are the
 deviations in parts per million (ppm) from the weighted average of JNdi standard analyses.

147 A weighted average was calculated for repeated measurements (N=12) of 600 ng of the JNdi 148 standard over the course of the analytical campaign. This weighted average gave 2 standard 149 deviations = ± 2.9 ppm for 142 Nd/ 144 Nd ratios, which represents the best precision that might be 150 expected for a single analysis of a sample or standard. The 95% confidence interval for this set of 151 measurements of JNdi is ± 1.0 ppm that is an estimate for the best precision that can be achieved by 152 combining the results from multiple analyses. The 95% confidence interval is calculated using:

153
$$\frac{1 SD}{\sqrt{N}} * t_{1-\frac{a}{2},2N-2}$$

where 1SD is the standard deviation of the set of replicate analyses, N is the number of analyses, and *t* is the Student's t factor for a significance level, *a*, in which *a*= 0.05 and the degrees of freedom is 2N-

156 2 (Ludwig, 2008). In the equation above, *a* is divided by 2 to provide the cumulative probability for 157 a two-sided test because it is not known if the "true" value is higher or lower than the average 158 (NIST/SEMATECH, 2012). For our standards data, as well any dataset in which the probability of fit 159 (chi square distribution) of the individual analyses is higher than 0.15, the dominant contributor to 160 the uncertainty of the weighted average is the measurement errors of the individual analyses. The 161 95% confidence interval for such high probabilities of fit is similar to the error-weighted 2S 162 uncertainty given by

163

$$\frac{1}{\sqrt{\sum \frac{1}{2SE_i^2}}}$$

where 2SE is the measurement uncertainty for each analysis, *i*. For probabilities of fit <0.15 for a set of individual replicate analyses, however, equation 2 will *under*estimate the error on the weighted mean, so equation 2 was not used to calculate the uncertainties on averages in this study. Following Ludwig (2008), we use the more conservative 95% confidence intervals to report the uncertainty of the weighted averages of sample replicates.

Each sample in this study has 3-5 replicate analyses. Results for individual analyses of each 169 170 sample are shown in Fig. 3. Replicate analyses and their individual measurement precisions (2SE) are combined to give a weighted average μ^{142} Nd for each sample and a corresponding uncertainty at 171 the 95% confidence level (Table 2 and Fig. 4). All the samples in this study have μ^{142} Nd values 172 173 between -1.3 and +2.7, with their individual 95% confidence intervals between 1.0 and 3.2 ppm. The total range of μ^{142} Nd reported here for these samples is smaller than measured in most previous 174 studies of young terrestrial rocks (Boyet and Carlson, 2006; Murphy et al., 2010; Jackson and Carlson, 175 176 2012; Rizo et al., 2016; de Leeuw et al., 2017), except for those reported in Caro et al. (2006). Unlike prior studies of ¹⁴²Nd/¹⁴⁴Nd, we sought to reduce analytical uncertainties by multiple analysis of a 177 178 given sample. The improvement in precision largely results from a combination of a more accurate 179 correction for mass bias and of more multidynamic data for each sample, both from longer individual 180 analyses and more replicates. Use of 95% confidence level to describe the precision of the weighted 181 average composition of each sample allows more robust comparison of the sample compositions. Consequently, results reported here are not easily compared with results from prior studies. 182

183 All seven samples chosen for this study had μ^{142} Nd within the 2SD of the JNdi standard (±2.9 184 ppm). Four of the samples examined here have μ^{142} Nd within the 95% confidence interval of the JNdi standard (±1.0 ppm). One basalt from the Samoan island of Ofu (Ofu-04-14) has a μ^{142} Nd value of 185 186 +2.7 ±1.3 that is higher than, and outside of the 95% confidence interval, of the value for JNdi. Of greatest note, a small (c. 4 ppm) difference is resolved between this basalt and a basalt from the 187 188 Samoan island of Ta'u (T33, -1.3 ±1.5). The average of the other sample from Ofu (OFU 04-15, +0.6 ±3.2), however, has a larger uncertainty that overlaps both T33 and OFU 04-14. Loihi sample LO-02-189 190 02 has a nominal μ^{142} Nd value similar to Ofu-04-14, but a larger 95% confidence interval. Therefore, no μ^{142} Nd values among the samples from Hawaii are resolved from one another, outside of their 191 192 95% confidence intervals.

193 **4. Discussion**

194 *4.1. Hadean vs. later processes.*

195 The samples in this study show a total variation in μ^{142} Nd that is quite small (<4 ppm) in spite of the fact that the samples span a large fraction of the range of W and He isotope compositions 196 observed in these OIB systems (Mundl et al., 2017). Nevertheless, the sample having 2.7 ppm higher 197 ¹⁴²Nd/¹⁴⁴Nd than the JNdi average, albeit near the limit of our resolution, is also characterized by a 198 199 3 He/ 4 He ratio that is among the highest, and μ^{182} W values that are among the lowest, of the Samoan suite (Fig. 5), although not all of the high ${}^{3}\text{He}/{}^{4}\text{He}$ and low $\mu^{182}\text{W}$ lavas have resolvable ${}^{142}\text{Nd}$ 200 anomalies. Because some high ${}^{3}\text{He}/{}^{4}\text{He}$, low μ^{182} W samples from Samoa and Hawaii show evidence 201 202 for early Hadean fractionation of Hf/W within the lifetime of ¹⁸²Hf, these samples are particularly 203 useful to evaluate whether their Nd isotope systematics are consistent with a similar early fractionation of Sm/Nd. Further, the combination of the long-lived system 147 Sm \rightarrow 143 Nd (t_{1/2} = 106 204 Ga) with the short-lived ¹⁴⁶Sm⁻¹⁴²Nd system offers the opportunity to separate the chemical 205 consequences of early Earth differentiation events from those occurring over most of Earth history, 206 207 for example crust production and recycling. For this assessment, however, the choice of the 208 composition of the bulk-silicate Earth (BSE) is important.

Estimates of the Sm-Nd systematics of the bulk silicate earth (BSE) are usually based on chondritic meteorites, given that both Sm and Nd are refractory lithophile elements. The more primitive of these meteorites show a very narrow range in Sm/Nd ratios and modern day ¹⁴³Nd/¹⁴⁴Nd (e.g., Jacobsen and Wasserburg, 1980; Bouvier et al., 2008) that form the basis for estimating that the 213 BSE has a ¹⁴⁷Sm/¹⁴⁴Nd = 0.1960 and present day ¹⁴³Nd/¹⁴⁴Nd = 0.512630 (Bouvier et al., 2008). Estimating the BSE ¹⁴²Nd/¹⁴⁴Nd, however, is not so straightforward. Chondritic meteorites show a 214 range in μ^{142} Nd values >30 ppm?, with nearly all measured values being lower than modern 215 terrestrial mantle-derived rocks (Boyet and Carlson, 2005; Carlson et al., 2007; Andreasen and 216 217 Sharma 2006; Gannoun et al., 2011; Burkhardt et al., 2016; Bouvier and Boyet, 2016). Only enstatite 218 chondrites are known to be characterized by ¹⁴²Nd/¹⁴⁴Nd ratios that overlap with those observed in 219 the modern mantle, and only a small subset of the data for this group extend to ratios as high as Earth's modern mantle. The range in μ^{142} Nd values seen in chondrites does not correlate with Sm/Nd 220 221 ratio. This observation, coupled with minor variability in other stable Nd isotope ratios, suggests that 222 the majority of the Nd isotopic variability measured in meteorites results from the incorporation of 223 different mixtures of *r*-process and *s*-process Nd produced by different nucleosynthetic processes 224 (Carlson et al., 2007; Burkhardt et al., 2016; Bouvier and Boyet, 2016). A correlation observed 225 between Nd and Mo isotopic compositions in enstatite and ordinary chondrites and the Earth provides evidence that the variability in μ^{142} Nd among chondrites is entirely nuclesynthetic in origin, 226 and suggests that the BSE has a μ^{142} Nd=0.3±2.6, if terrestrial Nd and Mo were derived from the same 227 planetary building blocks (Render et al., 2017). On the other hand, enstatite chondrites may have 228 229 small deficits in ¹⁴²Nd/¹⁴⁴Nd of a few to several ppm, either with no clearly resolvable anomalies in 230 the other stable Nd isotope ratios (Bouvier and Boyet, 2016) or after small corrections for s-process deficits in other stable Nd isotope ratios (Burkhardt et al., 2016). These results, combined, appear to 231 leave open the possibility that the ¹⁴²Nd/¹⁴⁴Nd of BSE could have deficits of up to several ppm, relative 232 233 to JNdi.

234 Even given the uncertainty in the ¹⁴²Nd composition of the BSE, we can examine the extent to 235 which the ¹⁴²Nd and ¹⁴³Nd histories of the samples in this study could be coupled. Figure 6 shows the 236 modern Nd isotope compositions that would be generated by single episodes of fractionation of 237 Sm/Nd at different times. The black lines show results for fractionation at 4.568 and 4.500 Ga, i.e., at 238 the start of Solar System history while ¹⁸²Hf was still extant, and at 4.42 Ga, after ¹⁸²Hf became extinct. 239 The latter age, an estimate for the timing of primordial differentiation of Earth's mantle based on ¹⁴²Nd in Archean rocks (e.g., Rizo et al., 2012; Caro et al, 2016; Morino et al., 2017), may represent a 240 minimum differentiation age, as ¹⁷⁶Hf/¹⁷⁷Hf ratios in the oldest zircons suggest the formation of crust 241 242 or proto-crust commenced by 4.4-4.5 Ga (Harrison et al., 2005; Kemp et al., 2010). These calculations 243 assume that both initial μ^{142} Nd and ϵ^{143} Nd compositions were 0, and model the effect of extraction of 0.3% to 1% melt from an upper mantle source composed of olivine, orthopyroxene and 244

clinopyroxene. Such melt extraction changes the ¹⁴⁷Sm/¹⁴⁴Nd ratio of the residue from 0.1960 to between 0.200 and 0.208, respectively, and might occur during crystallization of a magma ocean. To accommodate uncertainty in the BSE composition, the blue field in Fig. 6 extends the range of compositions that would be generated by early melt removal between 4.568 and 4.5 Ga in a BSE whose initial μ^{142} Nd was between 0 and -7. The lower value reflects the average μ^{142} Nd of enstatite chondrites (Boyet and Carlson, 2005; Carlson et al., 2007; Gannoun et al., 2011; Bouvier and Boyet, 2016; Burkhardt et al., 2016).

252 Four of the basalts examined here have μ^{142} Nd values that are within the ±1.0 ppm 95% confidence interval of the value of the JNdi standard. If the JNdi composition is representative of the 253 254 BSE composition, then these basalts would have retained no resolvable Nd imprint from early Earth processes, despite some having deficits in ¹⁸²W. The Samoan basalt OFU 04-14 extends the range in 255 256 μ^{142} Nd to +2.7. The e143Nd of all the samples, except for Samoan basalt ALIA 118-15, are all positive. The combination of m142Nd and e143Nd causes most of the basalts to plot to the right of the single-257 stage differentiation curves shown in figure 6 if the BSE has a m142Nd = 0. The ε^{143} Nd value for 258 259 Samoan basalt ALIA 118-15 is much lower than the other samples, and possible reasons for this are discussed below. The positive ε^{143} Nd values of the remaining samples studied here can be reconciled 260 with μ^{142} Nd = 0 for BSE if there was a later stage of increase in Sm/Nd ratio after the effective 261 extinction of ¹⁴⁶Sm at about 4 Ga. The conventional model for generating the positive ε^{143} Nd of the 262 263 MORB source is through its depletion in incompatible elements as a result of the extraction of 264 incompatible element-rich continental crust throughout Earth history (Jacobsen and Wasserburg, 1979; Allègre et al., 1983). The lower ε^{143} Nd of many OIB compared to MORB can then be explained 265 266 by either contamination of the depleted mantle with recycled crustal materials, or by mixing between depleted and primitive mantle, the latter with ε^{143} Nd \equiv 0 (Allègre, 1983; White, 1985). The ε^{143} Nd 267 values of these basalts are consistent with depleted mantle (0.58 ppm Nd, ε^{143} Nd=+10.9; Workman 268 269 and Hart, 2005) comprising 50-70% of the mantle source with the rest from primitive mantle (1.25 ppm Nd, ε^{143} Nd=0; deLeeuw et al., 2017). The sources for the sample with μ^{142} Nd of +2.7 may include 270 not only primitive mantle and MORB-type depleted mantle, but also a mantle domain depleted during 271 the early Hadean. Alternatively, if the BSE has μ^{142} Nd<0, then the 142 Nd- 143 Nd systematics permit that 272 all of these samples, except for the sample from Savai'i that has negative ε^{143} Nd, were derived, at least 273 in part, from mantle domains that formed during the early Hadean. 274

275 A good example of the consequences of the recycling of crustal materials is provided by 276 sample ALIA 118-15, a submarine lava collected off the coast of Savai'i, in western Samoa. This basalt has a far lower ε^{143} Nd value than the rest of the samples examined here and that is also substantially 277 278 subchondritic. The trace element contents, negative ε^{143} Nd, and radiogenic 87 Sr/ 86 Sr (=0.7186) 279 composition of this basalt are consistent with a mantle source that incorporated approximately 5% 280 of a subducted upper continental crust (UCC) component prior to melting (Jackson et al., 2007). 281 Further, this modelling suggests that approximately 40% of the Nd in the basalt melt may have been derived from this UCC endmember (Jackson et al., 2007). Incorporation of this fraction of UCC in the 282 source of the sample apparently had no resolvable effect on 142 Nd. Given that a range of about ± 20 283 284 ppm in ¹⁴²Nd/¹⁴⁴Nd is observed in Archean crustal rocks (Caro et al, 2006; Bennett et al., 2007; O'Neil 285 et al., 2008; Rizo et al., 2012, 2013; Morino et al., 2017), mixing of ambient mantle having μ^{142} Nd = 0 with 40% of a crustal component at the extreme of the compositions measured for Archean crust 286 287 would produce a melt with μ^{142} Nd of ±8 ppm, which would be well resolved in our data. Most Archean 288 rocks and all post-Archean continental crust measured to date, however, do not show μ^{142} Nd values resolved from zero, so the lack of an anomaly in μ^{142} Nd in ALIA 118-15 is not surprising. Additional 289 precise ¹⁴²Nd data on post-Archean continental crust would help to better characterize the possible 290 range of compositions of subducted UCC components. 291

292 These examples of ¹⁴²Nd-¹⁴³Nd systematics thus suggest that much of the Nd in these samples 293 has undergone post-Hadean processing during development of depleted mantle or the formation and 294 recycling of continental crust. Dilution of primordial ¹⁴²Nd variations, then, may help to explain why 295 ¹⁴²Nd/¹⁴⁴Nd ratios in these samples from Samoa and Hawaii vary by no more than a few ppm. Some 296 mantle domains sampled by these volcanic systems possibly are characterized by much larger ¹⁴²Nd 297 anomalies, but that heterogeneity could have been attenuated through vigorous mixing in hot plumes 298 during transit to the surface (Jackson et al., 2017). An alternative possibility is that the mantle sources of these magmas were sufficiently mixed by mantle convection over Earth history as to nearly 299 300 obliterate the evidence for early differentiation recorded by ¹⁴²Nd. Debaille et al. (2013) used 301 diminution of ¹⁴²Nd anomalies in late Archean rocks to argue for the end of a stagnant lid tectonic 302 regime for Earth and the subsequent rapid mixing away of mantle with anomalous ¹⁴²Nd resulting from the advent of modern plate tectonics. The very small variations ¹⁴²Nd observed here, therefore, 303 304 may indicate incomplete homogenization either within the plumes or by long-term mantle 305 convection.

306 Another possible contributor to limited variation in ¹⁴²Nd in these sources was insufficient fractionation of Sm/Nd in deep mantle sources while ¹⁴⁶Sm was extant. The presence of a range of 307 308 μ^{142} Nd ±20 ppm in Archean supracrustal rocks argues against this explanation, at least for the likely upper mantle sources of the supracrustal rocks. Crystallization of a basal magma ocean in the 309 presence of Ca-perovskite would be expected to generate domains having heterogeneous Sm/Nd 310 311 ratios in the solids and residual melts (Hirose et al., 2004; Corgne et al., 2005; Labrosse et al., 2007). If crystallization of the basal magma ocean occurred after the first 100-200 Ma of Earth history, then 312 313 sizable ¹⁴²Nd anomalies may never have been generated in deep mantle domains that may be 314 sampled by modern plumes. Magma ocean differentiation this late in Earth's history also would leave 315 no signature in ¹⁸²W and ¹²⁹I because both radioactive parents for these isotopes would have been 316 extinct by 4.45 to 4.50 Ga.

317 *4.2. Constraints on source materials.*

If the limited range in μ^{142} Nd results from mixing with "normal" upper mantle, then it must 318 be explained why the sources of these basalts preserve a far larger range in $^{182}W/^{184}W$, which must 319 320 also have been created early in Earth history. One possible source of high 3 He/ 4 He and low 182 W/ 184 W in some Samoa and Hawaii basalts is the core (e.g. Porcelli and Halliday, 2001), although the highly-321 322 siderophile-element abundances in these lavas are not easily reconciled with a direct core 323 contribution (Mundl et al., 2017). The lack of appreciable Nd in the core means that no correlation between ¹⁸²W and ¹⁴²Nd should be expected to result from core-mantle interaction. To explain the 324 325 variations in W and He isotope compositions, Mundl et al., (2017) speculated that the Samoa and 326 Hawaii OIB systems access rare, seismically distinct ultralow velocity zones (ULVZ) that may host 327 ancient deficits in ¹⁸²W and high ³He/⁴He ratios. These are attractive sites from which to extract the anomalous W and He because the largest ULVZs are located near the core-mantle boundary beneath 328 329 Hawaii and Samoa (Cottaar et al., 2012; Thorne et al., 2013). Further, the seismic profiles of the ULVZ are consistent with the presence of Fe-rich silicate or metallic melt (Rost et al., 2006; Wicks et al., 330 2010; Mao et al., 2006; Zhang et al., 2016). Early-formed metal, such as generated by 331 332 disproportionation reactions, that is trapped at the core-mantle boundary would likely be characterized by comparatively high W contents, low Hf/W and may have incorporated the low 333 μ^{182} W value of the mantle at the time of its isolation. Such metal might also have incorporated 334 primitive He, characterized by high 3 He/ 4 He (Bouhifd et al., 2013). Finally, in addition to overlying 335 ULVZ, the plumes associated with the Hawaii and Samoa hotspots simultaneously have high hotspot 336

337 buoyancy fluxes, high upper mantle temperatures and produce basalts with high ³He/⁴He ratios (Jackson et al., 2017). As the hottest and most buoyant plumes, they, therefore, may be best able to 338 339 entrain dense mantle domains residing near the core mantle boundary that, as a result of their density, are ideally suited for preserving early-formed reservoirs (Mukhopadhyay, 2012; Rizo et al., 340 2016; Jackson et al., 2017; Mundl et al., 2017). If the Samoan and Hawaiian ¹⁸²W and ³He/⁴He 341 342 anomalies are attributed to contributions to the plumes from primordial metal, then nonmetallic 343 components in the ULVZ might contribute the small ¹⁴²Nd anomalies. The small magnitude of the 142Nd variation may then either relate to limited Sm/Nd fractionation in the ULVZ material, or to Nd 344 345 concentrations that are not high enough to imprint their isotopic signature on the other components 346 present in the plume supplying the volcanism at these hot spots.

The only previous study of combined ¹⁸²W and ¹⁴²Nd in relatively young basalts examined 347 two picrites from the Baffin Bay area and a basalt from the Ontong Java plateau. The Baffin Bay area 348 hosts basalts that are considered to be an early manifestation of Iceland plume volcanism and have 349 the highest ³He/⁴He measured for any mantle-derived modern basalt (Stuart et al., 2003). Lavas from 350 351 the Ontong Java Plateau, the largest terrestrial volcanic province, sample a mantle source with a 352 primitive Pb-isotopic composition, similar to those from the Baffin Bay area (Jackson and Carlson, 353 2011). These samples, as well as an additional suite of basalts from same area, have μ^{142} Nd values within 8 ppm of [Ndi, but are not sufficiently precise to resolve whether this range is real (Rizo et al., 354 355 2016; deLeeuw et al., 2017). Rizo et al. (2016) reported elevated ¹⁸²W/¹⁸⁴W ratios in basalts from 356 both localities, in contrast with the depleted ¹⁸²W/¹⁸⁴W compositions of the OIB samples examined 357 here. These differences in ¹⁸²W are perhaps indicative that several sources with distinct early-Earth histories are involved in oceanic basalt genesis. 358

359 **5. Conclusions**

360 The data reported here support the presence of a limited range of ¹⁴²Nd/¹⁴⁴Nd in ocean island 361 basalts from Samoa and Hawaii. A small difference is resolved between two samples from the Samoa 362 hotpsot which, given the half-life of ¹⁴⁶Sm, implies preservation of Hadean silicate differentiation 363 events in the modern mantle. These samples show considerably variable and mostly negative $\mu^{182}W$ 364 (Mundl et al., 2017), in contrast to young oceanic basalts from Baffin Island and the Ontong Java 365 plateau that have positive $\mu^{182}W$ (Rizo et al., 2016). No single process can account for these observations. Any correlation between ¹⁸²W/¹⁸⁴W and ¹⁴²Nd/¹⁴⁴Nd is limited, which likely indicates 366 that different processes and different materials were involved in the generation of the Nd and W 367

368 anomalies. Early differentiation that included core-mantle segregation and mantle outgassing would dramatically affect W and He isotope evolution, respectively. The more subdued signal in μ^{142} Nd 369 370 could reflect more limited early Hadean differentiation of the silicate portion of the Earth, greater 371 homogenization during mantle convention or upwelling, or overprinting by recycled crust.

372 The search for modern ¹⁴²Nd anomalies should continue, especially coupled with ¹⁸²W data 373 on the same samples. Better characterization of the ¹⁴²Nd composition of the convecting upper mantle through more precise analysis of MORB, and the secular variation in upper continental crust 374 375 as recorded in sedimentary rocks, would be particularly useful. Replicate dissolutions and analyses 376 of individual samples offer the best way to resolve the small variations in ¹⁴²Nd in young rocks.

377

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	L4	L3	L2	L1	С	H1	H2	H3	H4
Step 1		(140)	(141)	142	143	144	145	146	(147)
Step 2	(140)	(141)	142	143	144	145	146	(147)	148
Step 3	(141)	142	143	144	145	146	(147)	148	(149)
Step 4	142	143	144	145	146	(147)	148	(149)	150

Table 1. Faraday cup configuration for multidynamic analysis of Nd.

			Probability		
	μ ¹⁴² Nd	95% conf.	of fit	Ν	
Samoa					
ALIA 115-18	0.5	1.0	0.64	5	
OFU 04-14	2.7	1.3	0.88	5	
OFU-04-15	0.3	3.0	0.10	4	
Т33	-1.3	1.5	0.96	4	
Hawaii					
J2-374-R5-A	-0.7	2.6	0.04	5	
LO-02-02	2.6	1.7	0.33	3	
ML 1868-9	-0.5	2.3	0.16	5	

 Table 2. Weighted means for each sample and 95% confidence intervals.

95% confidence intervals: see text for explanation

Probability of fit: Chi square calculated using 2 SE measurement uncertainties for individual analyses.

N: number of individual analyses

561

562



564

Figure 1. Moving averages (N=20) of dynamically corrected ratios of ¹⁴²Nd/¹⁴⁴Nd and ¹⁴⁸Nd/¹⁴⁴Nd from a single analysis of JNdi (a) normalized for mass fractionation using the ¹⁴⁶Nd/¹⁴⁴Nd ratio measured in the same cycle and (b) normalized using a time-corrected ¹⁴⁶Nd/¹⁴⁴Nd ratio interpolated from that measured within the same cycle and one from the previous cycle.



570 Figure 2. Data for μ^{142} Nd *vs.* μ^{148} Nd for the individual analyses of samples from Hawaii (squares) and 571 Samoa (circles) in this study. Error bars are 2 SE for each analysis. No correlation is observed between 572 these isotope ratios either for replicates analyses of same rock sample or for the whole dataset.



Figure 3. Results for ¹⁴²Nd/¹⁴⁴Nd of individual analyses of samples from Samoa (circles) and Hawaii (squares). Each symbol represents the results from analysis of one filament. Light blue field is 2SD of analyses (N=12) of 600 ng of the JNdi standard; the darker blue field is the 95% confidence interval for the weighted average of the standard analyses.



Fig. 4. Combined results for ¹⁴²Nd/¹⁴⁴Nd given as ppm deviation for the average JNdi standard value.
Individual mass spectrometric analyses are shown as small circles (Samoa) and squares (Hawaii),some
of which are partially hidden beneath the larger symbols. Large symbols for each sample are the
calculated weighted average for the individual analyses; error bars on these averages are 95%
confidence intervals; boxes enclosing each sample's data are 2 SD of the weighted average. Results for
600 ng loads of JNdi are given on the right, in which the larger region is 2 SD of the average and the

588 smaller, darker region is the 95% confidence interval.



591

Fig. 5. (a) Plot of μ^{142} Nd vs. μ^{182} W (Mundl et al., 2017). (b) Plot of μ^{142} Nd vs. ³He/⁴He (R/R_A) (Mundl et al., 2017 and references therein). There is no correlation between W or He isotope compositions with Nd isotope compositions. The Samoa sample that shows a small but resolved ¹⁴²Nd enrichment also has a larger ¹⁸²W deficit and higher ³He/⁴He, although Loihi samples with ¹⁸²W deficits and high ³He/⁴He do not have resolvably different ¹⁴²Nd.



Figure 6. A comparison of the modern Nd isotope compositions that would be generated by a single episode of melt depletion at 4.568 Ga (dashed black line), at 4.50 Ga (solid black line) and at 4.42 Ga (dotted black line). Starting composition for these calculations is a mantle reservoir with μ^{142} Nd and ϵ^{143} Nd = 0, and 147 Sm/ 144 Nd ratio= 0.196. For 147 Sm/ 144 Nd ratios of 0.196, 0.200, 0.204 and 0.208 after melt depletion, the ϵ^{143} Nd and μ^{142} Nd grow to those values shown as small black symbols. The blue field extends the possible starting composition of BSE to μ^{142} Nd =-7 (similar to the average for enstatite chondrites) and shows the range of compositions possible for fractionation between 4.568 Ga and 4.50

607 Ga., within the lifetime of ¹⁸²Hf. Data for Samoa are shown as circles; samples from Hawaii are squares.

609 Supplemental information.

610

611 S1. Samples

612

613 Four Samoan samples were characterized in this study: Ta'u island subaerial sample T33 (Workman et al., 2004), Ofu island subaerial samples Ofu-04-14 and Ofu-04-15 (Jackson et al., 614 615 2007a), and Savai'i island submarine sample ALIA-115-18 (Jackson et al., 2007b). Ofu-04-14 is an olivine (20%) and pyroxene (50%) cumulate, Ofu-04-15 is an ankaramite, T33 is an olivine basalt, 616 617 and ALIA-115-18 is a trachybasalt (further sample descriptions can be found elsewhere: Workman et al., 2004; Hart and Jackson, 2014; Koppers et al., 2008). Ages are provided only for sample ALIA-618 619 115-18 (5.29 Ma; Koppers et al., 2008). While ages of the Ta'u and Ofu lavas in this study are not available, prior work shows that subaerial lavas from Ta'u (<0.02 to 0.07 Ma) and Ofu (0.24 to 0.42 620 Ma) islands are relatively young (McDougall, 2010). Of usamples Ofu-04-14 and Ofu-04-15 have 621 among the lowest ⁸⁷Sr/⁸⁶Sr (0.704517 and 0.704559, respectively) and the highest 3He/4He (25.0 622 and 29.6 Ra) in Samoa, Ta'u sample T33 has slightly higher ⁸⁷Sr/⁸⁶Sr (0.704736) and intermediate 623 ³He/⁴He (16.6 Ra), and Savai'i submarine sample ALIA-115-18 has the one of the highest ⁸⁷Sr/⁸⁶Sr 624 ever measured in an OIB lava (0.718592) and a low ³He/⁴He ratio (4.3 Ra). Locations of these 625 samples are given in Table S1. 626

Hawaii: ML1868-9 is a picritic basalt sampled from a subaerial flow of the 1868
eruption from the SW rift of Mauna Loa (Kurz et al., 1995; Norman and Garcia, 1999). L002-02 is a basalt dredge sample from the submarine flank of Loihi (Norman and Garcia,
1999; Kent et al., 1999). J2-374-R5-A is a basalt dredge sample from Loihi (Mundl et al.,
2017). Its major and trace element composition is given in table S2. GPS coordinates were
not available for these samples.

634 635 636	<u>Table S1. GPS locations (degrees south, degrees west):</u>
637	T33 14.216°, 169.442°
638	Ofu-04-15 14.176°, 169.638°
639	Ofu-04-14 14.166°, 169.680°
640	ALIA-115-18 14.090°, 172.898° (dredged at 3220 m water depth).
641	
642	
643	

Table S2.	J2-374-R5-A			
SiO2	48.06			
TiO2	2.70			
AI2O3	13.69			
Fe2O3T	13.17			
MnO	0.20			
MgO	7.13			
CaO	11.16			
Na2O	2.81			
K2O	0.490			
P2O5	0.281			
Total	99.688			
LOI	0.15			
Sr	365			
Zr	126			
V	364			
Ni	915			
Cr	339			
Со	16			
Major elements in wt%				
Trace elements in ppm.				

S2. Data reduction

Below are equations used for offline calculation of multidynamic Nd isotope ratios using an exponential mass fractionation and time corrected ¹⁴⁶Nd/¹⁴⁴Nd. This data reduction is for a 4-step analysis scheme that uses the Faraday cup configuration given in Table 1 of the main text.

For dynamic correction of ¹⁴²Nd/¹⁴⁴Nd:

$$656 \qquad \frac{142Nd}{144Nd}(Dyn1_3)(i) = \frac{142Nd}{144Nd}St1(i) * \frac{146Nd}{144Nd}(True)^{(const1)} * \left[\frac{\frac{146Nd}{144Nd}St3(i) + \frac{146Nd}{144Nd}St3(i-1)}{2}\right]^{(-const1)}$$

$$658 \qquad \frac{142Nd}{144Nd}(Dyn2_4)(i) = \frac{142Nd}{144Nd}St2(i) * \frac{146Nd}{144Nd}(True)^{(const1)} * \left[\frac{\frac{146Nd}{144Nd}St4(i) + \frac{146Nd}{144Nd}St4(i-1)}{2}\right]^{(-const1)}$$

For dynamic correction of ¹⁴³Nd/¹⁴⁴Nd:

661
662
$$\frac{143Nd}{144Nd}(Dyn1_2_3)(i) = \frac{143Nd}{144Nd}(St2)(i)^{0.5} * \frac{143Nd}{144Nd}(St1)(i)^{0.5} * \frac{146Nd}{144Nd}(True)^{(0.5*const3)} *$$

$$\begin{cases} 0.625 * \frac{146Nd}{144Nd} St3(i) + 0.375 * \frac{146Nd}{144Nd} St3(i-1) \end{cases}^{(0.5*const3)}$$

$$665 \qquad \frac{143Nd}{144Nd} (Dyn2_3_4)(i) = \frac{143Nd}{144Nd} (St3)(i)^{0.5} * \frac{143Nd}{144Nd} (St2)(i)^{0.5} * \frac{146Nd}{144Nd} (True)^{(0.5*const3)} * \\ 666 \qquad \left\{ 0.625 * \frac{146Nd}{144Nd} St4(i) + 0.375 * \frac{146Nd}{144Nd} St4(i-1) \right\}^{(0.5*const3)}$$

$$\begin{cases} 666 \\ \begin{cases} 0.625 * \frac{146Nd}{144Nd} St4(i) \end{cases} \end{cases}$$

For dynamic correction of ¹⁴⁵Nd/¹⁴⁴Nd:

670
671
$$\frac{145Nd}{144Nd}(Dyn1_2)(i) = \frac{145Nd}{144Nd}(St1)(i)^{0.5} * \frac{145Nd}{144Nd}(St2)(i)^{0.5} * \frac{146Nd}{144Nd}(True)^{(0.5*const4)} *$$

672
$$\left\{ 0.875 * \frac{146Nd}{144Nd} St2(i) + 0.125 * \frac{146Nd}{144Nd} St2(i-1) \right\}^{(0.5*const4)}$$

$$674 \qquad \frac{145Nd}{144Nd}(Dyn2_3)(i) = \frac{145Nd}{144Nd}(St2)(i)^{0.5} * \frac{145Nd}{144Nd}(St3)(i)^{0.5} * \frac{146Nd}{144Nd}(True)^{(0.5*const4)} *$$

675
$$\left\{ 0.875 * \frac{146Nd}{144Nd} St3(i) + 0.125 * \frac{146Nd}{144Nd} St3(i-1) \right\}^{(0.5*const4)}$$

,

$$677 \quad \frac{145Nd}{144Nd} (Dyn3_4)(i) = \frac{145Nd}{144Nd} (St3)(i)^{0.5} * \frac{145Nd}{144Nd} (St4)(i)^{0.5} * \frac{146Nd}{144Nd} (True)^{(0.5*const4)} *
678 \qquad \left\{ 0.875 * \frac{146Nd}{144Nd} St4(i) + 0.125 * \frac{146Nd}{144Nd} St4(i-1) \right\}^{(0.5*const4)}$$

For dynamic correction of ¹⁴⁸Nd/¹⁴⁴Nd:

 $\frac{148Nd}{144Nd}(Dyn1_3)(i)$

683
$$= \frac{148Nd}{144Nd} (St3)(i) * \frac{146Nd}{144Nd} (True)^{(const2)}$$

$$684 \qquad \qquad * \frac{146Nd}{144Nd} St3(i)^{(-0.5*const2)} * \left[\frac{\frac{146Nd}{144Nd} St1(i) + \frac{146Nd}{144Nd} St1(i+1)}{2} \right]^{(-0.5*const2)}$$

 $\frac{148Nd}{144Nd}(Dyn2_4)(i)$

$$687 = \frac{148Nd}{144Nd} (St4)(i) * \frac{146Nd}{144Nd} (True)^{(const2)}$$

$$688 * \frac{146Nd}{144Nd} St4(i)^{(-0.5*const2)} * \left[\frac{\frac{146Nd}{144Nd} St2(i) + \frac{146Nd}{144Nd} St2(i+1)}{2}\right]^{(-0.5*const2)}$$

The value for ¹⁴⁶Nd/¹⁴⁴Nd (True)= 0.7219. Stx refers to a static Nd isotope ratio collected in Step x. $Dyn(x_y_z)$ refers to a multidynamic ratio calculated using static ratios measured in steps x, y, and z. The cycle number within a given block is given as *i*. Values for constants are as follows:

$$694 \quad \text{const1} = \frac{\log(\text{atomic weight 142Nd/atomic weight 144Nd})}{\log(\text{atomic weight 146Nd/atomic weight 144Nd})}$$

$$695 \\696 \quad \text{const2} = \frac{\log(\text{atomic weight 148Nd/atomic weight 144Nd})}{\log(\text{atomic weight 146Nd/atomic weight 144Nd})}$$

$$697 \\698 \quad \text{const3} = 2 * \frac{\log(\text{atomic weight 143Nd/atomic weight 144Nd})}{\log(\text{atomic weight 144Nd/atomic weight 144Nd})}$$

$$699 \\700 \quad \text{const4} = 2 * \frac{\log(\text{atomic weight 145Nd/atomic weight 144Nd})}{\log(\text{atomic weight 144Nd/atomic weight 144Nd})}$$

$$701$$

$$702$$

S4. Evaluation of possible systematic errors on Nd isotope compositions.

 A^{142} Nd-enriched spike was dissolved, diluted, and calibrated by isotope dilution using our AMES

707 Nd standard. A precisely weighed aliquot of this spike was added to powder of ALIA 115-18 and

- equilibrated during dissolution. Another aliquot of the same basalt with no added spike was
- 709 processed at the same time. Chemical separation and mass spectrometry followed the procedures
- 710 given in the Methods section. The results are shown in Figure S1and in the Supplemental Table.
- The weighted average of 5 analyses of this sample spiked with ¹⁴²Nd yielded μ^{142} Nd = +17.8 ±1.3 (05%) and the sample spiked sample spiked sample spiked set 0.5 ±1.0 mm (05%)
- (95% confidence limit); while 5 analyses of the unspiked sample yielded +0.5 ±1.0 ppm (95%
 confidence limit). This offset in ¹⁴²Nd between the spiked and unspiked samples is within the
- 713 confidence finity. This offset in ¹²Nd between the spiked and dispiked samples is within the 714 precision of the amount of spike added. This experiment confirms that, for our method, both
- 715 random and systematic errors in measured ¹⁴²Nd/¹⁴⁴Nd are within our stated precisions.



716

Figure S1. A comparison of μ¹⁴²Nd results for replicate analyses of (a) ALIA 115-18 with
added ¹⁴²Nd spike and (b) of the same sample with no ¹⁴²Nd spike. The light blue bands in
each figure show the weighed average and 95% confidence level for the replicate analyses.
The green box in (a) shows the offset in μ¹⁴²Nd (including the precision of the ¹⁴²Nd spike
calibration) expected from the amount of ¹⁴²Nd added. More detailed isotope data are given
in the Supplementary Table.

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