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Inherited ^{142}Nd anomalies in Eoarchean protoliths

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ABSTRACT

Geological records of the earliest history of the Earth are rare; rocks older than 3700 Ma comprise only a few percent of continental surfaces. Evidence is mounting, however, that vestiges of primordial planetary differentiation continued to influence the compositions of the oldest rocks during the Hadean and into the Archean. Here, we report new whole-rock ^{147,146}Sm–^{143,142}Nd data for the ancient Nuvvuagittuq Supracrustal Belt (NSB) in Québec (Canada) and confirm the ^{142}Nd deficits reported by O'Neil et al. (2008). We show that the assigned (O'Neil et al., 2008) and recently revised (Kinoshita et al., 2012) ^{142}Nd "age" of 4362^{+35}_{-54} Ma claimed for NSB amphibolites is at odds with the younger ^{147}Sm–^{143}Nd record. This discrepancy can be reconciled by partial Nd isotope equilibration of rocks with Hadean model ages of up to 4500 Ma during magmatic and metamorphic perturbations associated with the emplacement of the NSB at ca. 3750 Ma (Cates and Mojzsis, 2009). Our model further predicts a whole-rock ^{147}Sm–^{143}Nd age of 3800 Ma for other NSB lithologies in agreement with U-Pb zircon chronology (Cates and Mojzsis, 2007). Hence, ^{146}Sm–^{142}Nd systematics for the Eoarchean NSB rocks represent inheritance of a Hadean signature that was stored either in pre-existing crust or in early-enriched mantle sources. The decoupled ^{147,146}Sm–^{143,142}Nd systematics of the NSB is similar but complementary to the Hadean mantle isochron preserved in Eoarchean rocks from West Greenland (Bennett et al., 2007; Rizo et al., 2011).

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1. Introduction

Planetary mantle differentiation can be investigated by coupling the long- and short-lived isotope systems of samarium: ^{147}Sm–^{143}Nd [$T_{1/2}$=106 billion years (Gyr)] and ^{146}Sm–^{142}Nd [half-life $T_{1/2}$=68 million years (Ma) (Kinoshita et al., 2012)]. Samarium and Nd are refractory and lithophile, such that both condense at high temperature and are concentrated in the silicate portion of planets. Their relative abundances should, in principle, not be affected by planetary accretion and core segregation. However, these two rare earth elements fractionate from each other during partial melting or crystallization because of a small difference in their mineral–liquid partitioning behavior. As a result, enriched melts with low Sm/Nd will, over time, develop an unradiogenic Nd isotopic signature, whereas depleted sources with high Sm/Nd will yield an excess of radiogenic Nd. With its short half-life of 68 Ma, the extinct ^{146}Sm–^{142}Nd system can only trace early silicate differentiation that happened prior to about 4300 Ma. In contrast, the long-lived ^{147}Sm–^{143}Nd system provides a time-integrated record of Sm/Nd evolution until the present. Coupled variations in the abundances of ^{142}Nd and ^{143}Nd reveal both the timing and the degree of the earliest differentiation of planets into crust and mantle (Harper and Jacobsen, 1992; Caro et al., 2003), or possibly the fractionation due to crystallization of a magma ocean (Boyet and Carlson, 2005; Caro et al., 2005). Variations in the abundance of ^{142}Nd in planetary and meteoritic materials are below 100 ppm (ppm). This is to be expected because of the low initial ^{146}Sm/^{144}Sm ratio of 0.0085 ± 0.0007 in the solar system (Boyet et al., 2010), revised to 0.0094 ± 0.0005 (Kinoshita et al., 2012), and the small difference in the mineral–liquid partition coefficient between Sm and Nd. The ^{142}Nd excess of 18 ppm in the Earth relative to chondrites (Boyet and Carlson, 2005; Carlson et al., 2007) suggests that either Earth underwent early global differentiation at 4530 Ma and the complementary enriched reservoir has since remained hidden (Boyet and Carlson, 2005), or the earth formed from materials with super-chondritic Sm/Nd ratios (Caro et al., 2008; Caro and Bourdon, 2010).

Our planet has preserved Nd isotopic heterogeneities from its primordial silicate evolution in its oldest rocks. Early mantle depletion has been established from ^{142}Nd excesses of up to

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15 ppm relative to the modern terrestrial value in the ca. 3770 Ma Itsaq Gneiss Complex of West Greenland (Boyet et al., 2003; Caro et al., 2003, 2006; Rizo et al., 2011) as well as the Narryer Gneiss Complex in Western Australia (Bennett et al., 2007). Evidence for a complementary early-enriched reservoir characterized by ^{142}Nd deficits is, however, sparse (O'Neil et al., 2008; Upadhyay et al., 2009). O'Neil et al. (2008) reported ^{142}Nd deficits of as much as -15 ppm within pre-3750 Ma rocks from the Nuvvuagittuq Supracrustal Belt (NSB) in northern Québec (David et al., 2009; O'Neil et al., 2007). Based on a ^{142}Nd/^{144}Nd versus ^{147}Sm/^{144}Nd correlation, these authors derived an age of 4280^{+53}_{-81} Ma for a hornblende amphibolite and a cummingtonite (Ca-poor) amphibolite unit of possibly pyroclastic origin (Cates and Mojzsis, 2009; O'Neil et al., 2011). This age estimate is revised upward to 4362^{+35}_{-54} when using the recent shorter half-life determination for ^{146}Sm (Kinoshita et al., 2012). Nonetheless, the result is at variance with precise U-Pb zircon chronology on trondhjemite gneisses within the NSB, which yield a younger Eoarchean age of 3750 Ma (Cates and Mojzsis, 2007), and ^{147}Sm–^{143}Nd systematics for the same rocks that give similar ages ($\approx$3800 Ma). To explain this discrepancy, O'Neil et al. (2008) proposed a decoupling between the ^{146}Sm–^{142}Nd and ^{147}Sm–^{143}Nd systems due to metamorphic processes that would have shifted Sm/Nd ratios arbitrarily, and concluded that the NSB may be the oldest preserved crust on Earth. Andreasen and Sharma (2009) questioned these conclusions and argued that the apparent Hadean age is based on a correlation in the Sm–Nd isochron diagram between non-cogenetic rocks and that the observed ^{142}Nd deficits resulted from inappropriate corrections for mass fractionation during mass spectrometric analysis (Upadhyay et al., 2008). Subsequently, Upadhyay et al. (2009) reported ^{142}Nd evidence for an early-enriched reservoir in 1480 Ma alkaline rocks from India. Owing to the Proterozoic age of these rocks they concluded that such Hadean reservoirs could have been preserved for billions of years. More recently, O'Neil et al. (2012) have shown that by selecting 20% of their comprehensive Sm–Nd NSB data they could produce concordant ^{147,146}Sm–^{143,142}Nd ages of approximately 4300 Ma. In this approach, only some of the samples with an old Nd model age were arbitrarily plotted to define an age. Our view is that in order to better understand the nature of the ^{147,146}Sm–^{143,142}Nd data for the Nuvvuagittuq rocks, and to place firmer constraints on the likely time of emplacement of the NSB (3750 Ma versus 4300 Ma), a more robust analysis is required.

To explore further this potential record of Hadean reservoirs, we present new ^{147,146}Sm–^{143,142}Nd data for samples from the NSB and confirm the ^{142}Nd deficits reported by O'Neil et al. (2008). Our data set extends that of O'Neil et al. (2008) with felsic samples having low Sm/Nd ratios. Based on the combined data sets we show that the ^{147,146}Sm–^{143,142}Nd systematics in the NSB are disturbed and record a complex history. The ^{146}Sm–^{142}Nd system does not indicate the formation age of these rocks, as inferred by O'Neil et al. (2008). Instead, we propose a numerical model of isotopic equilibration simulating later metamorphic events at 3750 Ma that reconciles the discrepant Sm–Nd age assignments and demonstrates that the ^{142}Nd anomalies observed in the NSB and in different Eoarchean terranes worldwide are the inherited vestiges of Hadean mantle–crust differentiation.

2. Geological setting: the Nuvvuagittuq Supracrustal Belt

The NSB is located in the northeastern Superior Province in northern Québec, on the eastern shore of Hudson Bay. This province is dominated by the Minto Block, a series of volcanic arc and back arc terranes that accreted at the end of the Archean. The Minto Block is made of metamorphosed plutonic rocks, mostly of the tonalite, trondhjemite and granodiorite (TTG) suite, with numerous supracrustal enclaves. This block is subdivided into six major lithotectonic domains based on mapping and integration of structural and aeromagnetic data. The NSB is a dominantly mafic enclave of about 8 km^2 in the Inukjuak terrane, the westernmost domain of the Superior Province (O'Neil et al., 2007). The NSB is a volcano-sedimentary succession composed of basaltic amphibolites, layered ultramafic intrusions, ultramafic rocks, finely banded quartz–magnetite and other ferruginous quartz–pyroxene rocks of chemical sedimentary origin, and quartz–biotite schists of putative polymict conglomerate derivation. The NSB is surrounded and occasionally intruded by younger granitoids (Cates and Mojzsis, 2007 and references therein).

Reconnaissance geochronology on single zircons reported U–Pb ages of up to 3825 ± 16 Ma (David et al., 2002) for a trondhjemitic gneiss arbitrarily described as a "felsic band". Extensive in situ U-Pb ion microprobe measurements of igneous zircons from trondhjemitic gneisses at the Porpoise Cove outcrops were used to define a minimum age of 3750 Ma for the oldest gneissic components of the NSB (Cates and Mojzsis, 2009). Furthermore, U-Pb ages for detrital igneous zircons extracted from quartzites are statistically indistinguishable from other ca. 3800 Ma ages of transecting gneisses and therefore define the maximum age of the NSB (Cates et al., in press). The NSB represents the oldest rocks so far identified in the northeast Superior Province and overlap in age with the Isua Supracrustal Belt, West Greenland.

3. Methods

3.1. Chemical separation of Sm and Nd

Samarium and Nd were separated from bulk rock samples by ion-exchange chromatography following the procedures of Caro et al. (2006). About 100–250 mg of powdered rocks (equivalent to about 1 μg of Nd) were digested in concentrated HF–HNO_3 and HNO_3–$HClO_4$. The residues were then completely dissolved in 6M HCl. Iron was reduced with ascorbic acid to avoid later competition between the REE and trivalent Fe. The REE were separated from the rock matrix using TRU-Spec chromatographic columns. In order to lower isobaric interferences to negligible levels, Ce was removed from Nd by a highly efficient two-phase micro-extraction technique (Rehkämper et al., 1996). To this end, Ce was oxidized with sodium bromate and the tetravalent Ce was complexed by an organic solvent. The organic solvent was pipetted out from the Ce-free aqueous phase and discarded. AG50W-X8 cation exchange columns were used to remove the large amounts of Na previously added as sodium bromate. Samarium and Nd were finally separated from the remaining REE and collected individually using Ln-Spec chromatographic columns.

3.2. Neodymium mass spectrometry

Neodymium was measured as a positive metal ion (Nd^+) with the Thermo Triton (TIMS) at ETH Zurich. About 500 ng of Nd per sample were ionized on double rhenium filaments with a ^{142}Nd ion beam intensity of about 7.5 V (using 10^{11} Ω feedback resistors). Instrumental mass bias was corrected for with an exponential law using ^{146}Nd/^{144}Nd$=$0.7219. Isobaric interferences of ^{144,148,150}Sm and ^{142}Ce were monitored with, respectively, ^{147}Sm and ^{140}Ce and corrected for online. The ^{142}Ce/^{142}Nd and ^{144}Sm/^{144}Nd ratios never exceeded 1.79×10^{-6} and 1.12×10^{-6}, respectively. Fig. 1 shows the repeated ^{142}Nd/^{144}Nd measurements of the JNdi-1 standard over a period of 3 yr ($n=94$). A dynamic acquisition scheme using two magnet settings

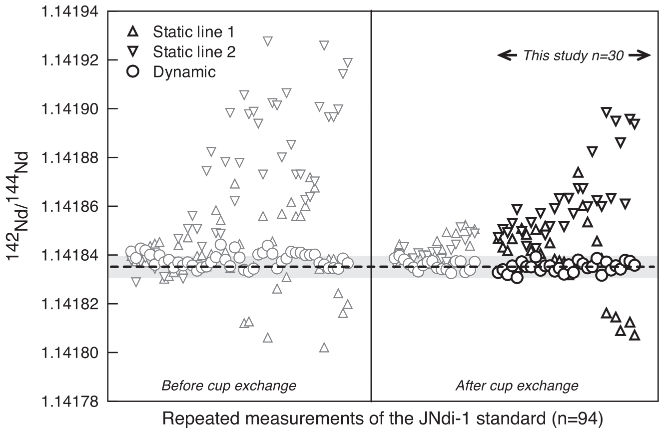

Fig. 1. Repeated measurements of the JNdi-1 standard for $^{142}Nd/^{144}Nd$. The value of the $^{142}Nd/^{144}Nd$ ratio acquired in static mode (triangles) drifted owing to slow degradation of the Faraday detectors. A dynamic acquisition scheme allowed this drift to be canceled (circles). The external precision was 5.1 ppm (2 SD) over a period of 3 yr ($n=94$). Over the course of this study (bold symbols), the external precision (shaded area) was ± 3.7 ppm ($n=30$) with a mean $^{142}Nd/^{144}Nd$ ratio of 1.1418351 (dashed line). Note that when the Faraday detectors were new (immediately after exchange), the values of the static and dynamic $^{142}Nd/^{144}Nd$ measurements were identical.

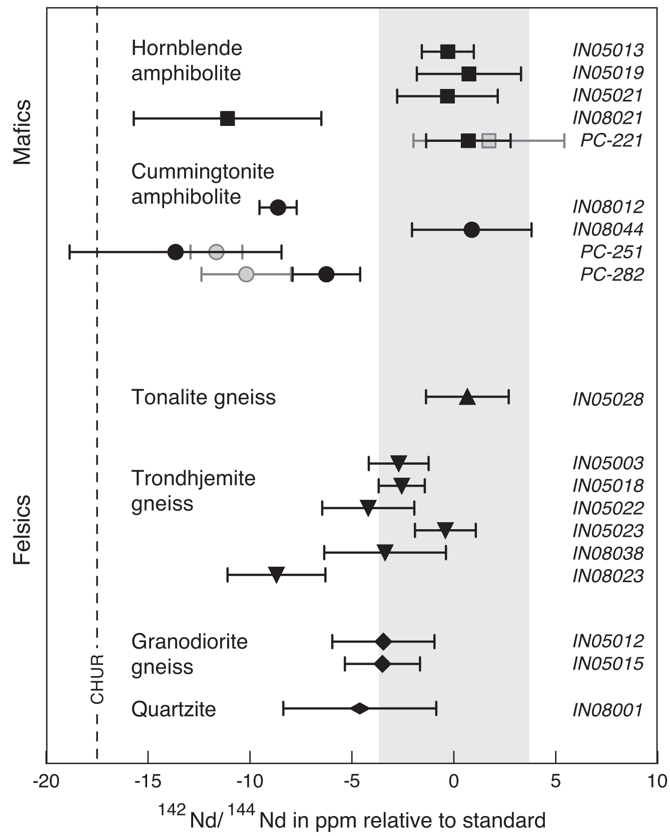

Fig. 2. $^{142}Nd/^{144}Nd$ for the NSB samples expressed in parts per million (ppm) deviations from the JNdi-1 Nd standard. The shaded area defines the external error of 3.7 ppm (2 SD) of the repeated measurements of the JNdi-1 standard ($n=30$). Samples are grouped according to their lithology and sample names are indicated in italics. Only the average value of replicate analyses is plotted. Error bars on individual samples are either the 2 SEM value when multiple analyses were done or the 2 SD of individual mass spectrometer runs for samples analyzed only once. The value of the chondritic uniform reservoir (CHUR) is indicated for reference. Samples IN08012, IN08021, IN08023, PC-251, and PC-282 show resolvable ^{142}Nd deficits down to -15 ppm. Replicate analyses of the same sample powder of the cummingtonite amphibolites PC-251 and PC-282, and the hornblende amphibolite PC-221, are consistent with the published values of O'Neil et al. (2008) shown with grey symbols.

(corresponding to ^{145}Nd and ^{143}Nd in the central detector) allowed gain biases caused by the degradation of the Faraday detectors to be canceled out and yielded an external precision of ± 5.1 ppm (2 SD). During the course of this study the external precision was ± 3.7 ppm ($n=30$), which is a factor of two smaller than that reported in O'Neil et al. (2008). The mean $^{142}Nd/^{144}Nd$ value of 1.1418351 ± 0.0000042 for our JNdi-1 standard is 3.5 ppm lower than the value reported by O'Neil et al. (2008) for the La Jolla standard. To further test the accuracy of our method, we also analyzed samples from the Isua Supracrustal Belt and rocks from elsewhere in the Itsaq Gneiss Complex of southern West Greenland for which ^{142}Nd excesses had previously been reported (Caro et al., 2006). Our data are in excellent agreement with those published earlier. The Nd isotopic compositions of the NSB samples are reported in Table S1.

3.3. *Sm and Nd concentrations*

Samarium and Nd concentrations were determined by isotope dilution. Aliquots of completely dissolved samples in 6 M HCl were spiked with an enriched, mixed ^{150}Nd–^{149}Sm tracer. Samarium and Nd were then separated following the same method as described above (omitting the two-phase micro-extraction technique of Ce) and their spiked isotopic compositions were measured with a Nu Instruments MC-ICP-MS at ETH Zurich. Replicate analyses of three separate digestions of the BCR-2 USGS standard gave Sm and Nd concentrations identical within errors to the published values (Wilson, 1997) with a mean $^{147}Sm/^{144}Nd$ ratio of $0.1374 \pm 0.2\%$ (2 SD). The concentrations of Sm and Nd in the NSB samples are reported in Table S1.

4. Results

The new NSB $^{147,146}Sm$–$^{143,142}Nd$ whole-rock data (Table S1) come from three hornblende amphibolites, two cummingtonite amphibolites, one tonalite gneiss, five trondhjemite gneisses, two granodiorite gneisses, and a quartzite. Fig. 2 shows the $^{142}Nd/^{144}Nd$ ratios of our samples expressed as ppm deviations from the JNdi-1 standard (assumed to be equal to the modern terrestrial value). Two cummingtonite amphibolites, PC-251 and PC-282 (with ^{142}Nd deficits), and one amphibolite, PC-221, yielded $^{142}Nd/^{144}Nd$ consistent with the data of O'Neil et al. (2008) using the same powder splits. Our cummingtonite amphibolite sample IN08012 shows a ^{142}Nd deficit of -8.6 ppm. All other analyzed NSB samples are identical within errors to the standard. Two samples collected by us from another ancient (unnamed) Inukjuak terrane supracrustal enclave located ~5 km northeast of the NSB have ^{142}Nd deficits, with the hornblende amphibolite IN08021 giving -11.1 ppm and the trondhjemite gneiss IN08023 giving -8.7 ppm.

In a ^{147}Sm–^{143}Nd isochron diagram (Fig. 3A) the NSB samples do not fall on a well-defined isochron. Rather, the mafic and felsic lithologies define a statistically imprecise array or "scatterchron" with an age of 3876 ± 191 Ma (MSWD$=$194). This apparent Eoarchean age is similar to the minimum age of 3750 Ma defined by U–Pb zircon chronology of trondhjemite gneisses in the belt (Cates and Mojzsis, 2007), as well as to the maximum age defined by detrital zircons (Cates et al., in press). Although the six lithologies form trends in the ^{147}Sm–^{143}Nd isochron diagram, they all define scatterchrons. The scatterchron of cummingtonite amphibolites (solid line) yields an age of 3891 ± 584 Ma (MSWD$=$75) similar to the age of the trondhjemite gneisses with 3802 ± 1144 Ma (MSWD$=$19). Hornblende amphibolites (dashed line), however,

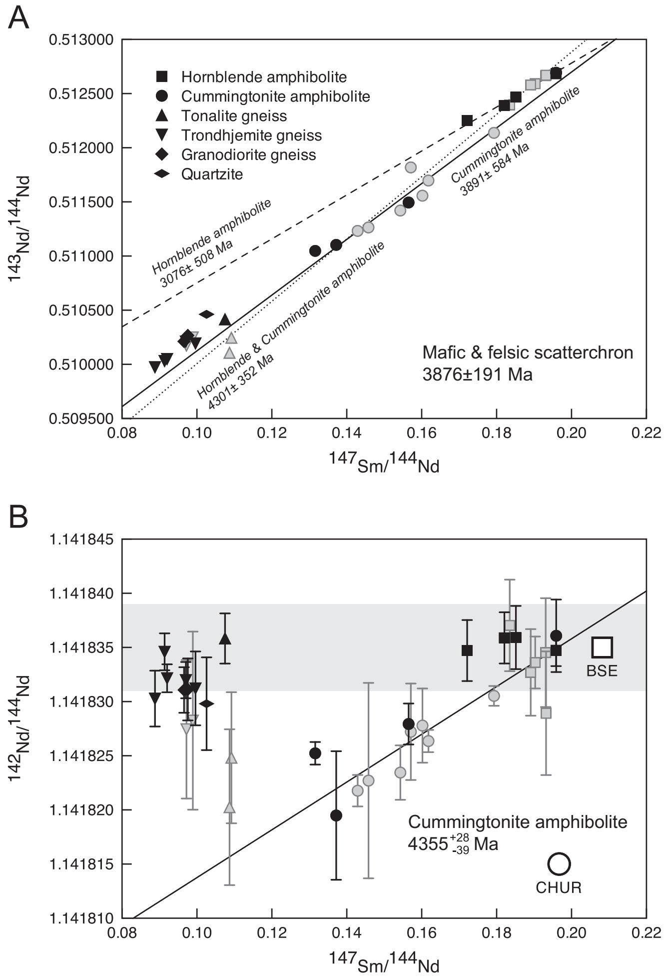

Fig. 3. Long-lived $^{147}Sm-^{143}Nd$ (panel A) and short-lived $^{146}Sm-^{142}Nd$ (panel B) isochron diagrams for NSB samples. The NSB samples from this study (black symbols) were combined with those of O'Neil et al. (2008) (grey symbols). The shaded area in the $^{146}Sm-^{142}Nd$ isochron diagram defines the external error of 3.7 ppm (2 SD) of repeated measurements of the Nd standard ($n=30$). Error bars are either the 2 SEM of multiple analyses or the 2 SD of the individual mass spectrometer run. Samples with no reported error bars have measurement errors about as large as the symbol size. The values of the super-chondritic bulk silicate Earth (BSE) (Caro and Bourdon, 2010) and the chondritic uniform reservoir (CHUR) (Bouvier et al., 2008) are shown for reference in panel B. The solid line in both isochron diagrams represents the best fit to the cummingtonite amphibolites. The dashed and the dotted lines in the $^{147}Sm-^{143}Nd$ isochron diagram represent the best fit to the hornblende amphibolites and the pooled hornblende amphibolites and cummingtonite amphibolites, respectively.

with an ostensibly younger age of 3076 ± 508 Ma (MSWD$=8$), fall above the scatterchron of the cummingtonite amphibolites. If the regressions of the hornblende amphibolites and the cummingtonite amphibolites are pooled (dotted line), an apparent age of 4301 ± 352 Ma (MSWD$=65$) is obtained, which is comparable to the result reported by O'Neil et al. (2008) when regressing their data in a $^{142}Nd/^{144}Nd$ versus $^{147}Sm/^{144}Nd$ diagram.

The $^{142}Nd/^{144}Nd$ data plotted against $^{147}Sm/^{144}Nd$ (Fig. 3B) for the mafic and felsic lithologies do not define a scatterchron similar to that observed in the $^{147}Sm-^{143}Nd$ isochron diagram. Hornblende amphibolites and our felsic lithologies have $^{142}Nd/^{144}Nd$ identical to the standard and do not correlate with $^{147}Sm/^{144}Nd$. O'Neil et al. (2008) reported ^{142}Nd deficits of as much as -13 ppm for two ca. 3600 Ma tonalite gneisses with relatively high $^{147}Sm/^{144}Nd$. Remarkably, ^{142}Nd deficits down to -15 ppm for the cummingtonite amphibolites appear to correlate with the $^{147}Sm/^{144}Nd$ ratios (O'Neil et al., 2008). The solid line shown in the $^{146}Sm-^{142}Nd$ isochron diagram yields an apparent age of 4355^{+28}_{-39} Ma (MSWD$=6$). A drawback with the interpretation of the Sm–Nd systematics of O'Neil et al. (2008) is that the hornblende amphibolite and the cummingtonite amphibolite units, as already argued by Andreasen and Sharma (2009), are not cogenetic because they have different $^{147}Sm-^{143}Nd$ ages of, respectively, 3076 ± 508 Ma and 3891 ± 584 Ma (see Fig. 3A). O'Neil et al. (2009) agreed with this viewpoint and admitted that the two mafic lithologies should not be fitted with a single isochron forced through the super-chondritic bulk silicate Earth (BSE) composition. In this context, one can argue further that the $^{147}Sm-^{143}Nd$ and $^{146}Sm-^{142}Nd$ of the cummingtonite amphibolites are discordant, unless one excludes most of the data points as done by O'Neil et al. (2012). To draw an analogy with the field of U–Pb zircon geochronology, there is little in favor of the notion that zircons with discordant ^{238}U and ^{235}U ages provide trustworthy age estimates. The reason for this discordance in Sm–Nd is explored quantitatively in what follows.

5. Discussion

5.1. Accuracy of ^{142}Nd measurements

Andreasen and Sharma (2009) argued that the apparent ^{142}Nd deficits in the NSB samples relative to the La Jolla Nd standard reported by O'Neil et al. (2008) were the outcome of an analytical artefact resulting from the evaporation of Nd from multiple domains with variable extents of fractionation, as described in Upadhyay et al. (2008). This phenomenon yielded inaccurate mass bias corrections and correlated $^{142,148,150}Nd$ deficits in the samples. Andreasen and Sharma (2009) modeled these analytical artefacts assuming a higher degree of domain mixing in the standards than in the samples. In response, O'Neil et al. (2009) argued that the problem lied with the non-exponential mass fractionation of the La Jolla Nd standard – induced during chemical separation – and not with the samples themselves. In this study we have reproduced the deficits in ^{142}Nd using the same sample powders of the cummingtonite amphibolites PC251 and PC282 as analyzed and reported by O'Neil et al. (2008), as well as the modern terrestrial composition of the amphibolite PC221 (Fig. 2). We thus corroborate the accuracy of the Nd isotopic measurements of O'Neil et al. (2008) for these samples. As shown in Fig. 4, our measurements of samples with ^{142}Nd deficits are free of correlations between $^{142,148,150}Nd$ deficits and thus were not affected by any artefacts from the mass fractionation correction procedure.

5.2. A new model for $^{147,146}Sm-^{143,142}Nd$ systematics

O'Neil et al. (2008) argued qualitatively that the $^{146}Sm-^{142}Nd$ system is insensitive to small late metamorphic perturbations of the Sm/Nd ratio, which, in contrast, will reset $^{147}Sm-^{143}Nd$ isochrons to younger apparent ages. We formulated a new numerical model of partial isotope equilibration for the coupled $^{147,146}Sm-^{143,142}Nd$ systematics. Our approach is similar to that developed for oxygen isotopes (Criss et al., 1987), while our objective is to explain the incongruity between the apparent ^{142}Nd and ^{143}Nd ages for the cummingtonite amphibolites using a quantitative means of tracking Nd isotope exchange. The output of this model is used to propose a complementary link between the positive and negative ^{142}Nd anomalies that have so far been documented in Eoarchean rocks.

Our model assumes that the rate of isotope exchange between several interacting phases depends on the difference in their isotope compositions. This approach has been validated theoretically by Cole

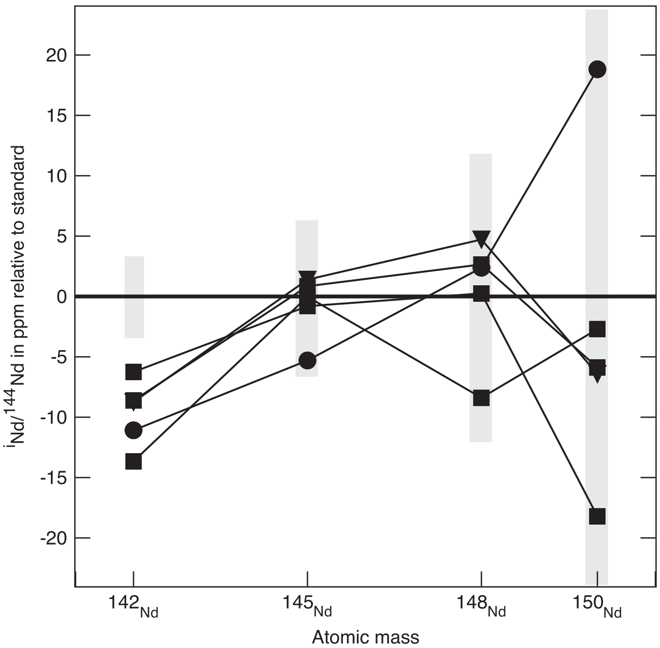

Fig. 4. Nd isotopic composition of the samples expressed in parts per million (ppm) deviations from the JNdi-1 Nd standard. Only samples with deficits in ^{142}Nd are shown. Grey bars show the external error (2 SD) of repeated measurements of the Nd standard. ^{142}Nd/^{144}Nd were measured in dynamic mode, while ^{145}Nd/^{144}Nd, ^{148}Nd/^{144}Nd, and ^{150}Nd/^{144}Nd were measured in static mode. All data were mass fractionation-corrected using the exponential law with ^{146}Nd/^{144}Nd = 0.7219. ^{143}Nd/^{144}Nd is omitted because of the large radiogenic variations. Samples with ^{142}Nd deficits are free of correlated ^{142,148,150}Nd deficits and thus were not affected by inaccurate corrections for mass fractionation. Note that the ^{150}Nd/^{144}Nd ratio is measured only with the static line 1 of the dynamic sequence and thus has a larger external error that may hinder the detection of mixing effects for this atomic mass.

et al. (1983) for fluid–mineral systems and does not require knowledge of the relative diffusivities in solid phases. In addition, we assume that there is no significant isotope fractionation between the isotopes of Nd, an assumption that we justify by the fact that all compositions are corrected to a fixed ^{146}Nd/^{144}Nd value during analysis. The solids (with isotope ratios r_1 and r_2, respectively) interact with an aqueous fluid phase with an isotope composition r_f that is assumed to be equal to the bulk composition of solids. In this context, the present model is equivalent to a system in which the various solids can re-equilibrate with each other isotopically, while the bulk composition of the system remains constant. This model is thus ideal for investigating resetting of isochrons during heating events. It should also be noted that in this system the Sm/Nd ratios of the various solids do not vary since they are fixed by the relative partition between mineral phases in a closed system. It is further emphasized that it is virtually impossible to predict variations in Sm/Nd during metamorphism as shown by Rosing (1990). The input parameters used in the model are reported in Table S2. The equations for isotope exchange between three phases can be written for isotope ratios as follows:

$$\frac{dr_1}{dt} = k_1(r_f - r_1)$$
$$\frac{dr_2}{dt} = k_2(r_f - r_2)$$
$$\frac{dr_f}{dt} = -\frac{X_1}{X_f}k_1(r_f - r_1) - \frac{X_2}{X_f}k_2(r_f - r_2)$$

where X_i represents the mass fraction of phase i, r_i is the ^{142}Nd/^{144}Nd (or ^{143}Nd/^{144}Nd) ratio of phase i, and k_i is the rate constant of phase i. The phase f represents a fluid phase that facilitates isotope exchange at grain boundaries. Two sets of such equations can be written for the ^{146}Sm–^{142}Nd and ^{147}Sm–^{143}Nd systems and solved simultaneously using a MATLAB™ script. Complete isotope reequilibration would lead to a flat line in the isochron diagram resulting from this model. The model is then used to simulate the Nd isotope systematics in the case of a thermal event that would have partially (or fully) equilibrated the isotope composition without modifying the Sm/Nd ratios (simple isotope exchange). Prior to isotope exchange, each sample was assumed to evolve with a Sm/Nd ratio corresponding to the BSE composition (^{147}Sm/^{144}Nd = 0.2082, as in Caro and Bourdon 2010). In this model, all materials start out evolving with chondritic ^{142}Nd/^{144}Nd and ^{143}Nd/^{144}Nd ratios, assumed to be representative of the Solar System as a whole. At time T_p, the protolith forms and this event is associated with Sm/Nd fractionation. At this point, the Nd isotope composition is calculated using the decay equation for a given Sm/Nd ratio. At the time of the thermal event, the equations above are used to calculate a partially reset Nd isotope composition,

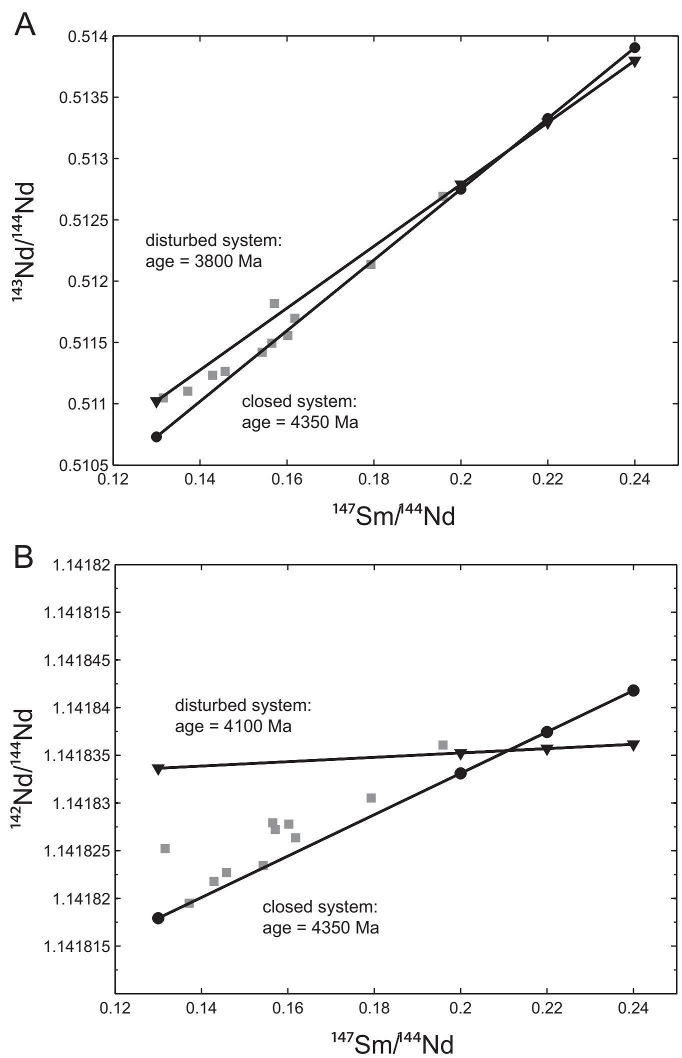

Fig. 5. (A) Synthetic ^{147}Sm–^{143}Nd isochron diagram showing (i) a closed system formed at 4350 Ma (solid circles) and (ii) a system formed at 4350 Ma and disturbed by a thermal event at 3750 Ma (solid triangles). The thermal event produces isotope equilibration (see text for details) that shifts the slope of the isochron to yield a slope with an age of approximately 3800 Ma. (B) Synthetic ^{146}Sm–^{142}Nd isochron diagram showing (i) a closed system formed at 4350 Ma (solid circles) and (ii) a system formed at 4350 Ma and disturbed by a thermal event at 3750 Ma (solid triangles). In the case of ^{146}Sm–^{142}Nd, the age of the disturbed system becomes 4100 Ma, showing that if ^{147}Sm–^{143}Nd is disturbed, ^{146}Sm–^{142}Nd is greatly affected and cannot, therefore, record the original age of the rocks. Grey symbols in panels A and B are the measured data for the cummingtonite amphibolites.

after which a decay equation is again used to calculate the present-day Nd isotope composition using the measured Sm/Nd ratios.

5.3. Disturbed ^{147,146}Sm–^{143,142}Nd systematics in the NSB

First, we consider a scenario similar to that proposed by O'Neil et al. (2008) whereby the starting ^{142}Nd and ^{143}Nd ages of the mafic rocks are 4350 Ma. Second, we assume a thermal event at 3750 Ma that partially resets the ^{147}Sm–^{143}Nd age to 3800 Ma, as evidenced by mineral-pair and Ti-in-zircon thermometry and zircon U-Pb chronology (Cates and Mojzsis, 2009). Third, we examine the consequence of this event on the ^{142}Nd/^{144}Nd scatterchron. Fig. 5 shows that it is not possible to obtain a ^{147}Sm–^{143}Nd age of 3800 Ma without also strongly affecting the ^{146}Sm–^{142}Nd system. In the case where a ^{147}Sm–^{143}Nd age becomes partially reset to approximately 3800 Ma, the ^{142}Nd age decreases to 4100 Ma. However, this age is only theoretical as the maximum relative difference in ^{142}Nd/^{144}Nd ratios between the samples with extreme Sm/Nd is up to 3 ppm, a difference that is analytically indistinguishable with current instrumentation. Our isotope exchange model suggests that the ^{146}Sm–^{142}Nd fit to the cummingtonite amphibolites with an assigned Hadean age cannot be interpreted as an isochron because the ^{146}Sm–^{142}Nd system is not robust against resetting. The ^{147,146}Sm–^{143,142}Nd systematics in the NSB hence are disturbed and it is difficult to extract the age information from the two decoupled chronometers.

To examine further the hypothesis of disturbed ^{147,146}Sm–^{143,142}Nd systematics in the NSB and its relation to inherited ^{142}Nd deficits, it is useful to compare calculated ^{143}Nd/^{144}Nd and ^{142}Nd/^{144}Nd of the samples at the time provided by U–Pb zircon chronology (Cates and Mojzsis, 2007, 2009). A snapshot of the samples in a ^{142}Nd/^{144}Nd versus ^{143}Nd/^{144}Nd diagram at 3750 Ma shows that they define a broad array with compositions ranging between the super-chondritic BSE and two enriched components marked A and B (Fig. 6). The cummingtonite amphibolites do not fall on a linear trend, as would be expected if the Sm–Nd system had remained closed, and hence suggest open system behavior or incomplete isotopic equilibration.

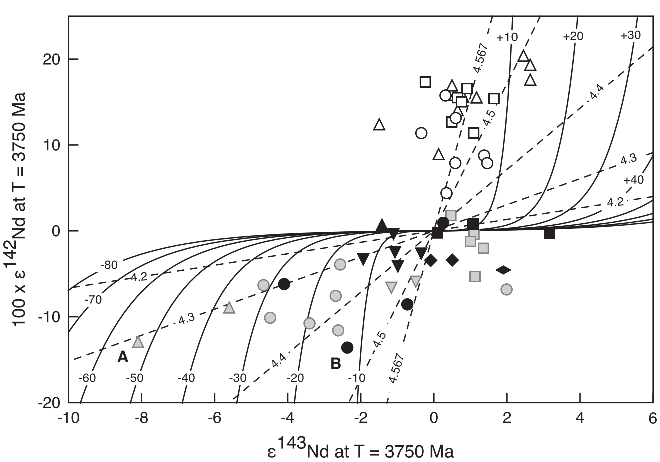

Fig. 6. Diagram showing ^{142}Nd/^{144}Nd versus ^{143}Nd/^{144}Nd for the NSB samples recalculated at 3750 Ma using their measured Sm/Nd ratios. The NSB samples from this study (black symbols) were combined with those of O'Neil et al. (2008) (grey symbols). Dashed lines are loci of equal differentiation ages, while solid curves are loci of equal extent of fractionation referenced in percent relative to the present-day ^{147}Sm/^{144}Nd ratio. Samples from the NSB define a broad array with compositions ranging between the super-chondritic BSE and two enriched components marked A (felsic rocks) and B (cummingtonite amphibolites). West Greenland and Western Australian samples (Bennett et al., 2007, open triangles), Isua metasediments (Caro et al., 2006, open squares), and undisturbed Isua amphibolites (Rizo et al., 2011, open circles) have early-depleted signatures that are complementary to the NSB samples characterized by early-enriched signatures.

The following scenario explains the decoupled ^{147,146}Sm–^{143,142}Nd systematics of the cummingtonite amphibolites: First, these rocks formed at 3750–3780 Ma from variable mixtures of a mantle-derived melt with super-chondritic BSE composition with either Hadean crust or enriched mantle produced at ca. 4500 Ma. In the diagram shown in Fig. 6, binary mixing would simply be represented by a straight line between the 4500 Ma old enriched protolith and the BSE. Because the magma in question has crystallized since its extraction from the mantle, one does not expect to observe a correlation between ^{142}Nd/^{144}Nd (or ^{143}Nd/^{144}Nd) ratios and 1/Nd, as argued by O'Neil et al., (2012). The mechanism of interaction could be magma mixing and/or assimilation, so that rocks have an apparent age of ca. 4500 Ma in the Sm–Nd isochron diagram. A more detailed description of this mixing model is given in Guitreau et al. (in press). Second, at

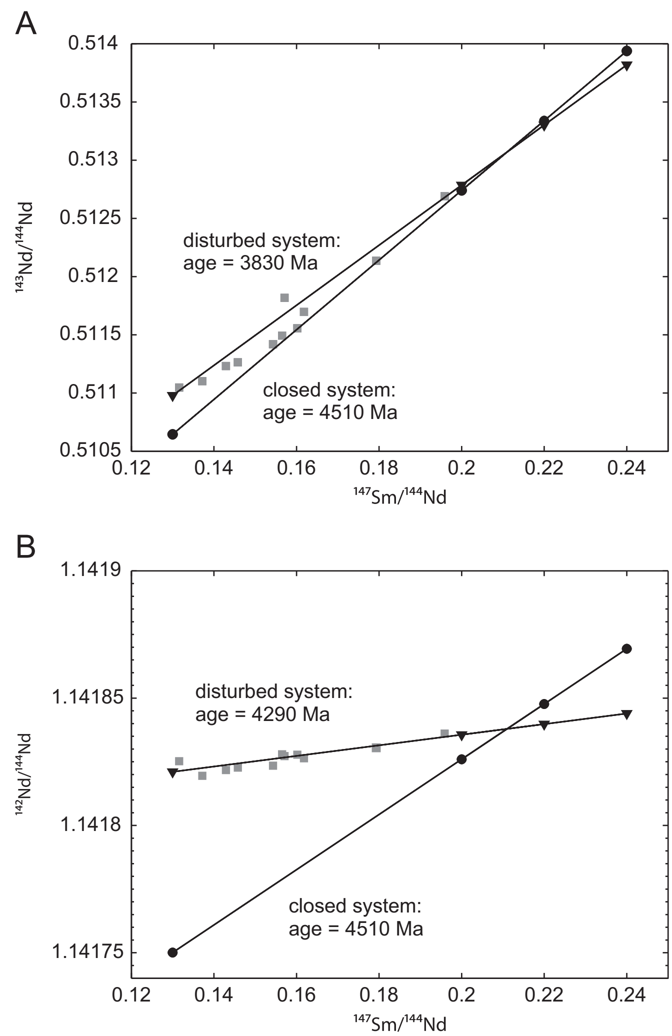

Fig. 7. (A) Synthetic ^{147}Sm–^{143}Nd isochron diagram showing (i) a closed system formed at ca. 3750 Ma by variable mixtures of a mantle-derived melt of super-chondritic BSE composition with either Hadean crust or enriched mantle produced at ca. 4510 Ma (solid circles) and (ii) an identical system disturbed by a thermal event at 3750 Ma (solid triangles). The thermal event produces partial isotope equilibration (see text for details) that shifts the slope of the "isochron" to yield a slope with an age of ca. 3830 Ma. (B) Synthetic ^{146}Sm–^{142}Nd isochron diagram showing (i) a closed system formed at ca. 3750 Ma by variable mixtures of a mantle-derived melt of super-chondritic BSE composition with either Hadean crust or enriched mantle produced at ca. 4510 Ma (solid circles) and (ii) an identical system disturbed by a thermal event at 3750 Ma (solid triangles). In the case of the ^{146}Sm–^{142}Nd system, the age of the disturbed system becomes 4290 Ma. Grey symbols in panels A and B are the measured data for the cummingtonite amphibolites.

the time the amphibolites formed, their Nd isotope compositions were partially reset according to the formalism introduced here, ultimately yielding ages of 4290 Ma for the ^{146}Sm–^{142}Nd system and 3830 Ma (consistent with U-Pb zircon ages) for the ^{147}Sm–^{143}Nd system (Fig. 7).

Hornblende amphibolites and felsic lithologies with no resolvable ^{142}Nd deficits simply derived at 3750–3780 Ma from a super-chondritic BSE mantle source. O'Neil et al. (2008) proposed that their trondhjemite gneisses (their "felsic band" samples *PC*-101, *PC*-102) with ^{142}Nd deficits as low as -13 ppm include rocks that formed as Eoarchean partial melts of the cummingtonite amphibolites. However, this scenario does not account for their ^{143}Nd/^{144}Nd isotopic composition at 3750–3780 Ma. As shown in Fig. 6, the trondhjemite gneisses have ^{143}Nd/^{144}Nd ratios as much as 3 parts per ten thousand lower than the cummingtonite amphibolites. We rather argue that the trondhjemite gneisses for which precise U-Pb zircon ages are available also formed at 3750–3780 Ma similarly to the cummingtonite amphibolites, but from variable mixtures of a mantle-derived melt of super-chondritic BSE composition with either Hadean crust or enriched mantle produced at ca. 4300 Ma with a large Sm/Nd fractionation (component A in Fig. 6) induced by melting.

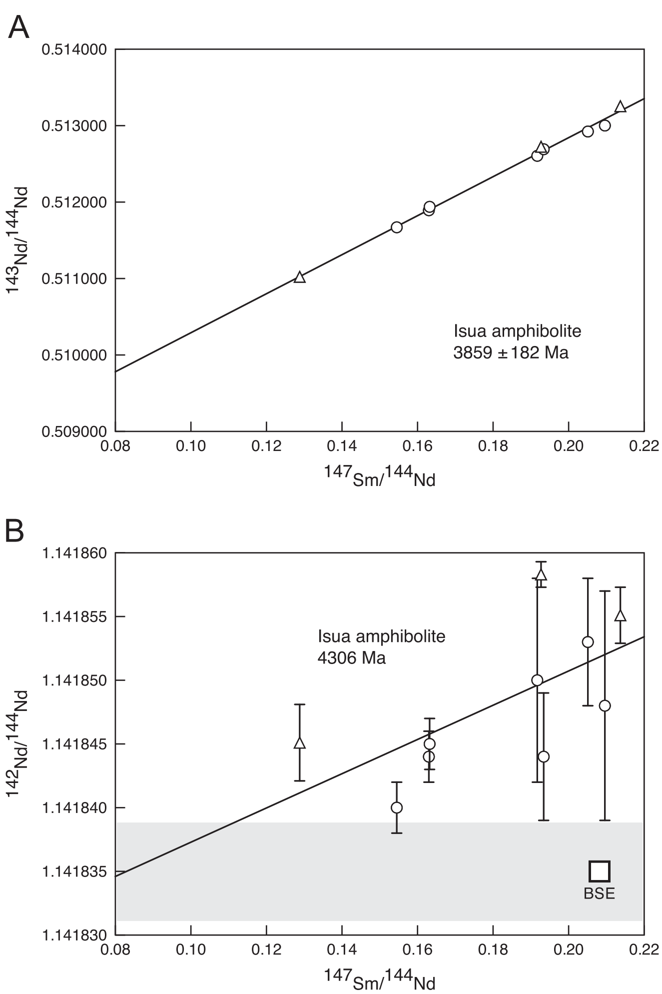

Fig. 8. Long-lived ^{147}Sm–^{143}Nd (panel A) and short-lived ^{146}Sm–^{142}Nd (panel B) isochron diagrams for amphibolite samples from Isua, West Greenland. Open circles are undisturbed Isua amphibolites from Rizo et al. (2011) and open triangles are Isua amphibolites from Bennett et al. (2007). The shaded area in the ^{146}Sm–^{142}Nd isochron diagram defines the modern ^{142}Nd terrestrial value. The super-chondritic bulk silicate Earth (BSE) is shown for reference. Error bars are 2 SD. Samples with no error bars have measurement errors of the size of the symbols. The solid line in both isochron diagrams represents the best fit to Isua amphibolites.

6. Implications

Amphibolites of the NSB were derived from Hadean sources with a model age of ca. 4500 Ma, whether of crustal or enriched mantle origin, with significant magmatic and metamorphic overprints. In such a scenario, the ^{146}Sm–^{142}Nd isochron does not record a true age since the true age of the protolith could be as old as 4500 Ma. Felsic samples with ^{142}Nd deficits were derived from younger Hadean sources (4300 Ma) with a higher degree of Sm/Nd fractionation. This proposed history for the NSB resembles that of the Itsaq Gneiss Complex in West Greenland, which has preserved complementary excesses of ^{142}Nd (Bennett et al., 2007; Rizo et al., 2011). A compilation of Sm–Nd isotope data for those amphibolites (Fig. 8) shows that their apparent but poorly defined ^{146}Sm–^{142}Nd "age" would be 4306 Ma (MSWD = 20), while their ^{147}Sm–^{143}Nd age is only 3859 ± 182 Ma (MSWD = 15), in agreement with inferences made from geological observations. We suggest that magmatic and metamorphic disturbances have also altered the Sm–Nd ages of the rocks of the Itsaq Gneiss Complex and that the ^{142}Nd signature represents the vestige of a corresponding depleted Hadean protolith or mantle source. In sum, Hadean mantle isochrons provide new prospects for understanding primordial differentiation, but the ^{142}Nd ages should not be interpreted at face value. That Eoarchean amphibolites from different localities worldwide (Nuvvuagittuq, Itsaq, Narryer) follow similar patterns in their decoupled ^{147,146}Sm–^{143,142}Nd systematics, strongly testifies to the lingering on into the Eoarchean of the last vestiges of enriched and depleted components in what was the termination of more than 700 Ma of Hadean crustal evolution.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.epsl.2012.11.023.

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