NEODYMIUM ISOTOPES AND EVOLUTION OF EARLY TERRESTRIAL CRUST

A Dissertation Submitted to

ETH ZURICH

For the Degree of
Doctor of Sciences

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2013
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The evolution of early terrestrial crust was investigated using the coupled $^{147,146}$Sm-$^{143,142}$Nd systems. With its short half-life of 68 Ma, the extinct $^{146}$Sm-$^{142}$Nd system is highly sensitive to early silicate Earth differentiation taking place prior to about 4100 Ma. Isotopic compositions of Nd and the concentrations of Sm and Nd in whole-rock samples were measured by Thermal Ionisation Mass Spectrometry (TIMS) and Multiple Collector - Inductively Coupled Plasma - Mass Spectrometry (MC-ICP-MS), respectively. A dynamic acquisition scheme during TIMS analyses allowed gain biases caused by the degradation of the Faraday detectors to be cancelled out and yielded an external precision of ±4.3 ppm (2 SD; n = 50) with a mean $^{142}$Nd/$^{144}$Nd value of 1.1418357 for the JNd1 Nd standard. Preparation of rock samples (wet chemistry) involved the separation of Nd from its matrix and in particular from Sm and Ce to lower isobaric interferences to negligible levels during analyses.

Our new $^{147,146}$Sm-$^{143,142}$Nd data for the pre-3750 Ma Nuvvuagittuq Supracrustal Belt (Canada) confirmed the $^{142}$Nd deficits as low as -15 ppm reported by O'Neil et al. (2008). Based on the $^{146}$Sm-$^{142}$Nd system, these authors derived a Hadean age of 4362 Ma, which was at odds with younger $^{147}$Sm-$^{143}$Nd records and U-Pb zircon geochronology. We reconciled this discrepancy by partial Nd isotope equilibration of rocks associated with the emplacement of the belt at ca. 3750 Ma. The $^{146}$Sm-$^{142}$Nd systematics for Nuvvuagittuq thus represents the inheritance of an early-enriched crust with Hadean model age of up to ca. 4500 Ma. New $^{176}$Lu-$^{176}$Hf data acquired by Dr M. Guitreau (ENS in Lyon) yielded a consistent Eoarchean age of 3864±70 Ma. Combined Nd-Hf data defined a mixing hyperbola at ca. 3800 Ma with end-member compositions representative of the compositional groups for the Nuvvuagittuq rocks. Deficits in $^{142}$Nd could have developed in response to the formation of enriched melts with low Sm/Nd ratios in a fractionated mantle domain at ca. 4500 Ma.

Our new $^{147,146}$Sm-$^{143,142}$Nd data for the ancient Acasta Gneiss Complex (Canada) yielded a $^{143}$Nd age of ca. 3400 Ma with initial $\epsilon^{143}$Nd of -5.6±2.1 and $^{142}$Nd deficits of -9.6±4.8 ppm (2 SD) for the oldest ca. 4000 Ma rocks. We reconciled the age discrepancy between the Paleoarchean $^{147}$Sm-$^{143}$Nd record and the Eoarchean U-Pb zircon chronology by partial Nd isotope equilibration of rocks associated with a meta-
morphic event at ca. 3400 Ma. A Hadean model age of ca. 4300 Ma was derived for the early-crust from which Acasta rocks inherited low $^{143}$Nd and $^{142}$Nd compositions. This early crust is 190 Ma younger than those reported in Nuvvuagittuq and Isua and did not show the decoupled Nd-Hf pattern characteristics of the crystallization of an early magma ocean. This suggests that formation and recycling of early crust happened over short timescales.

Our new $^{147,146}$Sm-$^{143,142}$Nd data for the 1.48 Ga Khariar alkaline rocks (India) did not confirm the $^{142}$Nd deficits as low as -13 ppm reported by Upadhyay et al. (2009). Rapid sample fractionation during TIMS analyses has biased $^{142}$Nd data toward negative values relative to the terrestrial standard in that study. After applying an approximate correction for this effect, only one of the samples retained a small negative $^{142}$Nd anomaly. This, in conjunction with the new anomaly-free data measured at low fractionation rates, led to the conclusion that the earlier reported anomalies are analytical artifacts. The absence of negative $^{142}$Nd anomalies in these rocks relaxes the need for a mechanism (other than crust formation) that can isolate a Nd reservoir from the convective mantle for billions of years.
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L’évolution de la croûte terrestre précoce a été étudiée avec les systèmes couplés du $^{147,146}$Sm-$^{143,142}$Nd. Avec une période radioactive courte de 68 Ma, le système éteint du $^{146}$Sm-$^{142}$Nd est très sensible à la différentiation silicatée de la terre précoce avant environ 4100 Ma. La composition isotopique du Nd et les concentrations en Sm et Nd des roches totales ont été mesurées par spectrométrie de masse TIMS (Thermal Ionisation Mass Spectrometry) et MC-ICP-MS (Multiple Collector - Inductively Coupled Plasma - Mass Spectrometry), respectivement. Un schéma d’acquisition dynamique durant les mesures TIMS a permis d’annuler le biais des gains causés par la dégradation des détecteurs de Faraday. Une précision externe de $\pm 4.3$ ppm (2 SD; $n = 50$) et un rapport $^{142}$Nd/$^{144}$Nd moyen de 1.1418357 ont été obtenus pour le standard de Nd JNdI-1. La préparation des échantillons de roche (chimie en solution aqueuse) a nécessité la séparation du Nd de la matrice, en particulier du Sm et du Ce, afin de réduire les interférences isobares à des niveaux négligeables pendant les analyses.

Nos nouvelles données en $^{147,146}$Sm-$^{143,142}$Nd pour la chaîne de croûte supérieure de Nuvvuagittuq (Canada) d’un âge minimum de 3750 Ma ont confirmé les déficits en $^{142}$Nd de -15 ppm rapportés par O’Neil et al. (2008). Ces auteurs avaient conclu à un âge Hadéen de 4362 Ma sur la base du système $^{146}$Sm-$^{142}$Nd qui est en désaccord avec les enregistrements plus jeunes du $^{147}$Sm-$^{143}$Nd et de la chronologie U-Pb dans les zircons. Nous avons réconcilié cette différence d’âge par une équilibration des isotopes du Nd dans les roches de la chaîne associée à son emplacement à ca. 3750 Ma. La systématique du $^{146}$Sm-$^{142}$Nd de Nuvvuagittuq représente ainsi un héritage de croûte précoce enrichie d’un âge modèle Hadéen de ca. 4500 Ma. Les nouvelles données en $^{176}$Lu-$^{176}$Hf acquises par Dr M. Guitreau (ENS de Lyon) donnent un âge Eoarchéen cohérent de 3864±70 Ma. Les données combinées en Hf-Nd définissent une hyperbole de mélange à ca. 3800 Ma avec des compositions extrêmes similaires à celles des roches de Nuvvuagittuq. Les déficits en $^{142}$Nd se sont certainement développés en réponse à la formation de magmas enrichis avec des rapports Sm/Nd bas à partir d’une portion fractionnée de manteau à ca. 4500 Ma.

Nos nouvelles données en $^{147,146}$Sm-$^{143,142}$Nd pour le complexe gneissique d’Acasta (Canada) donnent un âge $^{147}$Sm-$^{143}$Nd de ca. 3400 Ma avec un initial $\epsilon^{143}$Nd de
Résumé

-5.6±2.1 et des déficits en $^{142}$Nd de -9.6±4.8 ppm (2 SD) pour les roches les plus anciennes d’âge ca. 4000 Ma. Cette différence d’âge Paléoarchéen pour le $^{147}$Sm-$^{143}$Nd, et Eoarchéen pour la chronologie U-Pb dans les zircons, a été réconciliée par une équilibration des isotopes du Nd dans les roches d’Acasta associée à un évènement métamorphique à ca. 3400 Ma. Un âge modèle Hadéen de ca. 4300 Ma a été estimé pour la croûte précoce enrichie qui a donné aux roches d’Acasta leurs compositions basses en $^{143}$Nd and $^{142}$Nd. Cette croûte précoce est plus jeune de 190 Ma que celles observées à Nuvvuagittuq et Isua et ne montre pas de signature découpée en Nd-Hf caractéristique de la cristallisation d’un océan de magma précoce. Cela suggère que la formation et le recyclage de la croûte précoce se sont produits à des échelles de temps réduits.

Nos nouvelles données en $^{147,146}$Sm-$^{143,142}$Nd pour les roches alkalines de Khariar (Inde) d’un âge de 1.48 Ga n’ont pas confirmé les déficits en $^{142}$Nd de -13 ppm rapportés par Upadhyay et al. (2009). Un fractionnement rapide des échantillons lors des analyses TIMS avait biaisé leurs données en direction de valeurs anormalement basses comparées à celle de leur standard terrestre. Après avoir corrigé de manière approximative leurs données de cet effet, seulement un de leurs échantillons retient une petite anomalie négative. Ceci, en conjonction avec les nouvelles données sans anomalies mesurées à des taux de fractionnement suffisamment bas pour ne pas causer de biais, conduit à la conclusion que les anomalies rapportées avaient été le produit d’un artefact analytique. L’absence d’anomalies négatives en $^{142}$Nd dans ces roches affranchit du besoin d’un mécanisme (autre que celui de la formation de croûte) qui peut isoler un réservoir de Nd du manteau convectif durant des milliards d’années.
1 Introduction

This dissertation consists of four research projects focusing on the early differentiation of the Earth. We developed and applied analytical techniques in radiogenic isotope geochemistry on natural rock samples to date the formation and trace the evolution of early terrestrial crust. Samples were from the Nuvvuagittuq Supracrustal Belt in Québec (Canada), the Acasta Gneiss Complex in Slave Province (Canada), and the Khariar Alkaline Complex in southeastern India. We measured the abundance of radiogenic nuclides by isotope-ratio mass spectrometry produced in these rocks by the long- and short-lived radioactive decay of Sm and the long-lived radioactive decay of Lu. The four research projects are presented in the following four chapters:

Chapter 3. Inherited $^{142}$Nd anomalies in Eoarchean protoliths

Chapter 4. A legacy of Hadean silicate differentiation inferred from Hf isotopes in Eoarchean rocks of the Nuvvuagittuq Supracrustal Belt (Québec, Canada)

Chapter 5. New $^{147,146}$Sm-$^{143,142}$Nd constraints on the lifetime of early terrestrial crust

Chapter 6. Revisiting the $^{142}$Nd deficits in the 1.48 Ga Khariar alkaline rocks (India)

Versions of these chapters are or will be published in peer-reviewed scientific journals as four independent articles. This dissertation also includes two general chapters entitled Introduction and Methods.

1.1 Differentiation of the Earth

The architecture of the Earth is essentially identical to that of a “spherical egg”, the shell corresponding to the crust, the white to the mantle, and the yellow to the core. The bulk chemical composition of the Earth is about chondritic, i.e., similar to primitive meteorites that have elemental abundances that match that of the Sun, except for the most volatile elements (e.g. McDonough & Sun, 1995). The crust, mantle, and core have different compositions. The continental crust and the mantle are made of silicates and have large differences in the abundance of major elements such as Mg, Al, and Si. The core is an alloy mostly made of Fe and Ni but includes also
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A fraction of lighter elements. The transformation of a homogenous planetary body into a body with stratified regions of different compositions is the result of igneous processes that grouped under the term “differentiation”.

The Earth formed ca. 4550 million years (Ma) ago (e.g. Allègre et al., 1995) by accretion of smaller bodies that orbited the young Sun (e.g. Canup, 2008). Gravitational energy released during giant collisions provided sufficient heat to induce global melting (e.g. Tonks & Melosh, 1993). The metal-loving elements segregated from the molten Earth into a central core. The molten bulk silicate Earth (BSE) possibly underwent fractional crystallization (e.g. Caro et al., 2005) and differentiated into an early crust enriched in incompatible elements (low Sm/Nd ratio) and a mantle depleted in those elements (high Sm/Nd ratio). Although core formation was a transient process, the differentiation of the BSE continued throughout Earth history.

Heat produced by radioactive decay has driven the convection of the mantle until today. As mantle rises due to buoyancy forces, it undergoes partial melting and produces basaltic magmas with compositions richer in incompatible elements compared to the upper mantle. These magmas emerge at mid-ocean ridges and form the oceanic crust. At convergent margins, the oceanic crust is subducted and recycled back into the mantle. The dehydration of subducted crust produces partial melts that rise to the surface. After fractional crystallization in magma chambers, these melts erupt or are trapped as andesitic magmas and form the continental crust. Oceanic crust is relatively young and has been recycled continually. The continental crust is old and was derived from the reworking and differentiation of juvenile and earlier crusts over many eons.

Partial melting and fractional crystallization has induced continuous differentiation of the BSE such that crust and mantle are chemically complementary (e.g. Hofmann, 1988): the crust is enriched in incompatible elements, whereas the mantle is depleted in those elements. Continental crust is even more enriched than oceanic crust. Growth models for the continental crust and estimates of its composition through time are yet poorly constrained (e.g. Taylor & McLennan, 1995).

1.2 Early terrestrial crust

The dynamic of the Earth reworked most—if not all—of early-formed enriched crust and complementary depleted mantle. Geological records of the earliest history of the Earth are thus rare. Rocks older than ca. 3700 Ma comprise only a few percent of continental surfaces. They are preserved in stable regions called cratons. The oldest rocks are up to ca. 4000 Ma (e.g. van Kranendonk et al., 2007). In the geological time
scale, they informally define the border between the Archean and the Hadean eon (meaning “origin” or “beginning” in ancient Greek). Tiny zircon minerals represent the only direct record from the Hadean times. They have ages of up to ca. 4400 Ma and were found in Archean rocks of sedimentary origins (Wilde et al., 2001).

Archean rocks were metamorphosed. They underwent solid-state recrystallization by heat and pressure and show different textures and mineral assemblages than their original parent rocks, called protoliths. Even though their appearance has changed, their bulk chemical composition remained mostly pristine. Archean terranes worldwide occur in accretionary orogens and are thought to have formed by subduction and accretion processes similar to those occurring in modern plate tectonic. Most Archean rocks are tonalite-trondhjemite-granodiorite gneisses and derived from the melting of hydrous mafic crust at high pressure. A review of the oldest rocks and terrains is given in van Kranendonk et al. (2007).

The geological term “early terrestrial crust” mostly refers to the Hadean crust that formed during the first ca. 550 Ma of Earth’s history, possibly by fractional crystallization of a magma ocean or by differentiation of the primitive mantle. Rock samples of the early terrestrial crust are yet missing in the geological record. One way to study the early crust is thus to examine its last chemical vestiges that have been preserved in old rocks in the form of small variations in the abundances of radiogenic isotopes.

1.3 Radiogenic isotope geochemistry

Radiogenic isotopes are powerful means to date and trace the long-term (e.g. DePaolo & Wasserburg, 1976) and early (e.g. Harper & Jacobsen, 1992) differentiation of the BSE. Radioactive nuclides (parents) transform into radiogenic products (daughters) according to the law of radioactive decay (Rutherford & Soddy, 1902):

\[-\frac{dn}{dt} = \lambda n\]

The decay rate is proportional to the number of parent atoms \( n \) at time \( t \) and to the constant of proportionality \( \lambda \) called decay constant. The decay constant corresponds to the probability of a parent atom to decay within a given interval of time \( dt \). This constant is specific to each radioactive nuclide and can also be expressed as a half-life \( (T_{1/2}) \), which is the time required for half of the parent atoms to decay:
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\[ T_{1/2} = \frac{\ln 2}{\lambda} \]

Long-lived radioactive nuclides with half-lives within about an order of magnitude identical to the age of the Earth can be used as absolute chronometers to date and trace ancient geological processes. In the case of a closed system, one can derive from the law of radioactive decay the following equation:

\[ D = D_0 + n(e^{\lambda t} - 1) \]

where \( D \) represents the total number of daughter atoms after time \( t \) and \( D_0 \) is the number of initial daughter atoms at \( t = 0 \). This equation serves as a basis for absolute radiometric dating. Relative abundances of parent and daughter atoms are measured by isotope-ratio mass spectrometry and elemental abundances by isotope dilution for a series of cogenetic rocks. If daughter atoms have been produced by the decay of parent atoms in a closed system over time (i.e. no gains or losses), data series of samples with variable parent to daughter ratios plotted in a daughter versus parent normalized atoms diagram—called isochron diagram—will show a positive linear correlation. The slope of this correlation is equal to \( e^{\lambda t} - 1 \) and can be used to calculate an age of parent-daughter fractionation, whereas the y-intercept corresponds to the initial abundance of daughter atoms. This initial abundance can be used to trace processes such as the degree of enrichment or depletion of a sample relative to a reference value, e.g., the BSE.

Short-lived radioactive nuclides have half-lives much shorter than the age of the Earth and they can be used as relative chronometers to date and trace early processes, such as the \(^{146}\text{Sm}-^{142}\text{Nd}\) system for the early differentiation of the BSE (e.g. Caro et al., 2003). Their parent atoms only decayed during the early Earth’s history and are since then extinct. Relative chronometers thus offer the highest temporal resolution for the oldest events. Their application requires estimating the initial abundances of parent atoms at a given time in the early solar system. Meteorites whose ages were determined with absolute chronometers are usually used as anchors for the initial abundance of parent atoms.
1.3 Radiogenic isotope geochemistry

1.3.1 Uranium-lead dating in zircons

A common way to estimate the age of igneous rocks is to determine the crystallization age of their zircons using the two long-lived isotope systems of uranium: $^{238}\text{U}-^{206}\text{Pb}$ [$T_{1/2} = 4.47 \text{ Ga}$] and $^{235}\text{U}-^{207}\text{Pb}$ [$T_{1/2} = 704 \text{ Ma}$]. Zircons ($\text{ZrSiO}_4$) are robust accessory minerals that crystallize from felsic magmas. They incorporate U that substitutes Zr, but not Pb. Their abundances in $^{206}\text{Pb}$/$^{238}\text{U}$ daughter isotopes are thus in principle only controlled by in-situ decays of $^{238}\text{U}$ parent isotopes. The daughter to parent ratios (i.e. $^{207}\text{Pb}/^{235}\text{U}$ or $^{206}\text{Pb}/^{238}\text{U}$) in zircons are therefore direct indicators of their crystallization age. Trustworthy ages can be derived when both U-Pb chronometers are concordant, indicating that minerals remained closed since they formed. Formation of Archean terranes is often studied by zircon U-Pb geochronology before using other techniques such as the Sm-Nd and Lu-Hf systems.

1.3.2 Samarium-neodymium systems

The differentiation of the BSE can be investigated by coupling the long- and short-lived isotope systems of Sm: $^{147}\text{Sm}-^{143}\text{Nd}$ [$T_{1/2} = 106 \text{ Ga}$] and $^{146}\text{Sm}-^{142}\text{Nd}$ [$T_{1/2} = 68 \text{ Ma}$ (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 (REE) fractionate from each other during partial melting or crystallization because of a small difference in their mineral-liquid partitioning behavior. As a result, melts are enriched in Nd relative to Sm (low Sm/Nd ratio) and 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 $^{146}\text{Sm}-^{142}\text{Nd}$ system can only trace early silicate differentiation that happened prior to about 4100 Ma. In contrast, the long-lived $^{147}\text{Sm}-^{143}\text{Nd}$ system provides a time-integrated record of Sm/Nd evolution until the present. Coupled variations in the abundances of $^{142}\text{Nd}$ and $^{143}\text{Nd}$ reveal both the timing and the degree of the earliest differentiation of planets into crust and mantle (Harper & Jacobsen, 1992; Caro et al., 2003), or possibly the fractionation due to crystallization of a magma ocean (Boyet & Carlson, 2005; Caro et al., 2005). Variations in the abundance of $^{142}\text{Nd}$ in planetary and meteoritic materials are below 100 parts per million (ppm). This is to be expected because of the low initial $^{146}\text{Sm}/^{144}\text{Sm}$ 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 $^{142}\text{Nd}$ excess of 18
ppm in the Earth relative to chondrites (Boyet & Carlson, 2005; Carlson et al., 2007) suggests that either the Earth underwent early global differentiation at 4530 Ma and the complementary enriched reservoir has since remained hidden (Boyet & Carlson, 2005), or the Earth formed from materials with super-chondritic Sm/Nd ratios (Caro et al., 2008; Caro & Bourdon, 2010). The difference between the Earth and chondrites could also have resulted from a heterogeneous distribution of $^{142}\text{Nd}$ in the solar nebula (Gannoun et al., 2011). The Earth has preserved Nd isotopic heterogeneities from its early silicate differentiation in its oldest rocks. Early mantle depletion has been established from $^{142}\text{Nd}$ excesses of up to 15 ppm relative to the modern terrestrial value in the ca. 3770 Ma Itsaq Gneiss Complex of West Greenland (Caro et al., 2003, 2006; Rizo et al., 2011) as well as in the Narryer Gneiss Complex in Western Australia (Bennett et al., 2007). Evidence for complementary early-enriched crust characterized by $^{142}\text{Nd}$ deficits is, however, sparse (O’Neil et al., 2008; Upadhyay et al., 2009; Rizo et al., 2012) and implications for the early history of the Earth are controversial.

1.3.3 Lutetium-hafnium system

The differentiation of the BSE can also be studied using the long-lived isotope system of lutetium: $^{176}\text{Lu} - ^{176}\text{Hf} \ [T_{1/2} = 37 \text{ Ga}].$ Lutetium (REE) and Hf (high-field strength element, i.e. element with large ionic valences) are incompatible elements and thus have geochemical behaviors similar to Sm and Nd. They also fractionate from each other during partial melting or crystallization because of a small difference in their mineral-liquid partitioning behavior. Enriched melts with low Lu/Hf will, over time, develop an unradiogenic Hf isotopic signature, whereas depleted sources with high Lu/Hf will yield an excess of radiogenic Hf. The $^{176}\text{Lu} - ^{176}\text{Hf}$ system thus provides a time-integrated record of Lu/Hf evolution until the present, similar to what the $^{147}\text{Sm} - ^{143}\text{Nd}$ does for Sm/Nd. The two long-lived Sm-Nd and Lu-Hf systems are therefore - under normal circumstances - coupled. Very unradiogenic $^{176}\text{Hf}$ in early Archean and Hadean zircons suggests that early-enriched crust existed on Earth by 4300 Ma ago (e.g. Amelin et al., 1999; Scherer et al., 2001). In a $^{176}\text{Hf} - ^{143}\text{Nd}$ diagram, the terrestrial array lies above the BSE. This together with elevated radiogenic $^{176}\text{Hf}$ and $^{143}\text{Nd}$ signatures of the Archean mantle may indicate that the Earth underwent massive differentiation and segregation of early crust (Vervoort & Blichert-Toft, 1999), or that the Earth has a super-chondritic composition (Caro & Bourdon, 2010).
1.4 Aims and outlines

The two first research projects focused on the ancient Nuvvuagittuq Supracrustal Belt (NSB) in northern Québec (Canada). O’Neil et al. (2008) reported $^{142}$Nd deficits of as much as -15 ppm in pre-3750 Ma rocks from the NSB. This was the first evidence for an early-enriched crustal reservoir that is complementary to the early-depleted mantle. Based on the short-lived $^{146}$Sm-$^{142}$Nd chronometer, these authors derived a $^{142}$Nd/$^{144}$Nd versus $^{147}$Sm/$^{144}$Nd correlation yielding a Hadean age of ca. 4300 Ma for intermediate rocks with Sm/Nd ratios from 0.14 to 0.17. This result stands in contrast to the precise U-Pb zircon chronology on felsic rocks within the NSB, which yields a younger Eoarchean age of 3750 Ma (Cates & Mojzsis, 2007), and the long-lived $^{147}$Sm-$^{143}$Nd chronometer for the same rocks that give similar ages of ca. 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 & Sharma (2009) argued, however, that the Hadean age is based on a correlation in the Sm-Nd isochron diagrams between non-cogenetic rocks and that the observed $^{142}$Nd deficits resulted from an analytical artifact (Upadhyay et al., 2008). 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 formation of the NSB (3750 Ma vs. 4300 Ma), a more robust analysis was required.

The first research project focused on the $^{147,146}$Sm-$^{143,142}$Nd analysis of a new set of NSB samples and also included sample aliquots from the same rock-powders studied by O’Neil et al. (2008). The accuracy of the O’Neil et al. (2008) data was assessed using a different analytical protocol and the two data sets were combined. A new numerical model of partial isotope equilibration for the coupled $^{147,146}$Sm-$^{143,142}$Nd systematics was developed to explain the discrepancy between the two chronometers in the NSB and in other Eoarchean localities. The second research project focused on new $^{176}$Lu-$^{176}$Hf analyses of the same set of NSB samples performed by Dr M. Guitreau (ENS in Lyon). The age defined with the $^{176}$Lu-$^{176}$Hf chronometer was compared to Sm-Nd ages and U-Pb zircon geochronology of the NSB. The likely time of formation of the Nuvvuagittuq Supracrustal Belt was reassessed. The Lu-Hf and Sm-Nd data were then combined to trace and date the Hadean source of the NSB protoliths.

The third research project focused on the ancient Acasta Gneiss Complex in the westernmost Slave Province (Canada). Acasta is one of the oldest outcrops of continental crust discovered so far and consists of late-Hadean/Eoarchean terranes with zircon U-Pb ages of up to ca. 4000 Ma (e.g. Bowring & Housh, 1995). Comprehensive
whole-rock $^{147}\text{Sm}$$-^{143}\text{Nd}$ systematics for Acasta, however, yielded a much younger age of ca. 3300 Ma (Bowring & Housh, 1995; Moorbath et al., 1997) and very unradiogenic $^{143}\text{Nd}$ compositions. This suggests that Acasta protoliths were derived from an early-enriched crustal source. First $^{146}\text{Sm}$$-^{142}\text{Nd}$ studies of three Acasta rocks did not reveal $^{142}\text{Nd}$ anomalies (McCulloch & Bennett, 1993; Caro et al., 2006). It was thus difficult to precisely define the age of enrichment simply based on the $^{147}\text{Sm}$$-^{143}\text{Nd}$ system. This research project focused on the $^{147,146}\text{Sm}$$-^{143,142}\text{Nd}$ analysis of a set of Acasta samples that were previously studied with the $^{176}\text{Lu}$$-^{176}\text{Hf}$ system and U-Pb zircon geochronology (Guitreau, 2013). This integrated approach aimed to explain the discrepancy between $^{147}\text{Sm}$$-^{143}\text{Nd}$ systematics and the U-Pb zircon geochronology and precisely date the Hadean source of Acasta protoliths.

The fourth research project focused on the 1.48 Ga Khariar Alkaline Complex (India). Upadhyay et al. (2009) reported the surprising finding of as much as -12 ppm negative $^{142}\text{Nd}$ anomalies in these rocks. These authors inferred that an early enriched, low-Sm/Nd reservoir must have contributed to the mantle source of Khariar. Owing to the Proterozoic age of the rocks, they concluded that such a Hadean reservoir had remained isolated from the convective mantle for billion of years. This research project focused on attempting to replicate the negative $^{142}\text{Nd}$ anomalies in the Khariar rocks using a different analytical protocol. It was shown here that the $^{142}\text{Nd}$ data reported by Upadhyay et al. (2009) are inaccurate and the possible sources of analytical bias were discussed.
2 Methods

This chapter describes the techniques that were used to prepare whole-rock samples for Nd isotopic analyses and the analytical protocols that were developed to measure the isotopic composition of Nd and the concentrations of Sm and Nd. The provenance of the samples and my fieldwork experience in the Nuvvuagittuq Supracrustal Belt are also mentioned.

2.1 Sample provenance / fieldwork

Nuvvuagittuq Supracrustal Belt (Canada)

Prof S. Mojzsis and Dr N. Cates (University of Colorado, Boulder) sampled rocks from the Nuvvuagittuq Supracrustal Belt (NSB) during fieldworks in summers 2005 and 2008. From these two sample suites, three hornblende amphibolites, two cummingtonite amphibolites, one tonalite gneiss, five trondhjemite gneisses, two granodiorite gneisses, and a quartzite were studied for Sm-Nd systematics. Samples were crushed and powdered at ETH Zurich. Dr J. O’Neil (McGill University, Montréal) sent powdered-rock samples of one hornblende amphibolite and two cummingtonite amphibolites for replicate analyses.

Prof S. Mojzsis, Dr N. Cates, Dr G. Caro (CRPG in Nancy) and myself went to Nuvvuagittuq in August 2012. The main purpose of this seven-days fieldwork was to sample rocks from another ancient (so far unnamed) Inukjuak terrane supracrustal enclave located about 5 km northeast of the NSB. We spent the first two days to study the geology of the NSB and made ourselves familiar with the different lithologies. Dr G. Caro sampled mafic and ultramafic rocks possibly for whole-rock \(^{147}\text{Sm-}^{143}\text{Nd}\) analysis. The third day, we walked to the enclave located inland from our basecamp on the shore of Porpoise Cove. During two days we sampled felsic, intermediate and mafic rocks and mapped portions of the supracrustal sequence. None of the rocks we sampled during this fieldwork were studied in this dissertation and they were saved for future studies.
2 Methods

**Acasta Gneiss Complex (Canada)**

Prof S. Mojzsis and Dr M. Guitreau (ENS in Lyon) sampled rocks from Acasta during fieldwork in summer 2009. From this sample suite, eleven granitoid gneisses and two plagioclase-hornblende schists were studied for Sm-Nd systematics. Rock samples were already powdered.

**Khariar Alkaline Complex (India)**

Prof E. Scherer (WWU Münster) sent powdered samples of two mesocratic nepheline-syenites and two nepheline-syenites for replicate analyses. The Khariar samples were collected by Dr D. Upadhyay as part of his doctoral studies. The exact locations, petrography, major and trace element geochemistry, Nd-Sr isotope systematics, and U-Pb zircon ages of the samples has been published by Upadhyay et al. (2006). The samples were analyzed at WWU Münster for $^{146}\text{Sm} - ^{142}\text{Nd}$ systematics not because they were suspected of being anomalous, but rather because the studies of Upadhyay et al. (2008) and Upadhyay et al. (2009) needed Nd-rich samples for setting up and testing the Sm-Nd chemistry and analytical methods. Dr D. Upadhyay had the samples in-hand from his doctoral work, and the Nd-rich samples allowed many analyses to be performed on single digestions. The apparent finding of negative $^{142}\text{Nd}$ anomalies (Upadhyay et al., 2009) in some of these rocks was therefore serendipitous.

### 2.2 Sample preparation

Whole-rock Sm and Nd isotopic analyses required separation of Sm and Nd from all other elements that composed the sample matrix. Separation was achieved by ion exchange chromatography (wet chemistry) combined with a solvent extraction. The protocols were based on the work of Caro et al. (2006) and further developed at ETH Zurich with Dr M. Touboul. Samples were first powdered and then dissolved in acids.

#### 2.2.1 Sample powdering

Whole-rock samples from the NSB were crushed and powdered in agate mortars that were pre-cleaned with quartz sand and subsequently conditioned with small sample aliquots prior to powdering of the main sample mass. Splits from homogenized powders were then divided for separate Sm-Nd and Lu-Hf isotope works at ETH Zurich and ENS in Lyon, respectively. Rock samples from Acasta and Khariar were received for analysis already powdered.
2.2 Sample preparation

2.2.2 Sample dissolution

For each sample, about 50 to 250 mg of powdered rock (containing about 1 µg of Nd) were weighed in a Teflon Savillex beaker and digested in up to 40 ml of a 24 M HF and 14 M HNO₃ 5:1 mixture. After 48 hours of digestion at 180 °C, few drops of HClO₄ were added to re-dissolve fluorides and the mixture was dried down at 210 °C. The residue was subsequently completely dissolved in up to 40 ml of 6 M HCl and the sample solution weighed.

2.2.3 Aliquot for isotope dilution

About 2-5% of the sample solution was pipetted out and weighed in a Teflon Savillex beaker. The aliquot was spiked with an optimized amount of the isotopically enriched and mixed ¹⁵₀Nd-¹⁴⁹Sm tracer (Hiro 2). The amount of spike was optimized so that the aliquot-tracer mixture had ¹⁵₀Nd/¹⁴⁴Nd and ¹⁴⁹Sm/¹⁵²Sm ratios close to 1. The aliquot-tracer mixture was then weighed to determine the exact amount of added spike. Samarium and Nd were separated following the same protocol as described bellow (omitting the two-phase solvent extraction technique of Ce).

2.2.4 Chemical separation of Sm and Nd

During ion exchange chromatography, the REE were separated from each other between a liquid (mobile) and a solid (stationary) phase. The liquid phase was typically an acid where REE together with the rock matrix ions were in solution. The solid phase was an organic substrate (resin) that had exchangeable sites onto which ions can be fixed. The affinity of an ion to remain in solution or to be retained in the resin depended on its electric charge, the resin type, the acid type (e.g. HCl, HNO₃ or HF) and the acid molarity. Ion exchange took place in a column where acid percolated through the resin bed. Column shape and resin mesh size influenced percolation rate. Ions with different affinities travelled in the column at different effective speeds and consequently were separated from each other. A typical ion exchange procedure consisted of five steps. The resin bed was first cleaned with acids. The resin was then “pre-conditioned” with an acid that had the same properties as the sample solution. The sample solution was loaded in the column. Undesired elements were washed with acids. Elements of interest were eluted and collected. Prior to sample processing, columns were calibrated in order to define the elution curves of the elements of interest.

In the following, the detailed description of the protocols for separation of Sm and Nd from whole-rock solutions and aliquot-tracer solutions are given.
2 Methods

Iron reduction

Ferric iron was reduced with ascorbic acid to avoid later competition between the REE and trivalent Fe in the ion exchange columns. 30 mg of ascorbic acid per 100 mg of rock was added to the loading solution of the first chromatographic column (separation of REE from rock matrix; 3 ml of 3 M HNO₃). To test if Fe was completely reduced, one drop of 0.2 M ammonium thiocyanate was added to the solution. If the solution turned red because of residual trivalent Fe, more ascorbic acid was added and the colorimetric test was repeated until complete Fe reduction.

Separation of REE from rock matrix

The REE were separated from the rock matrix using TRU-Spec chromatographic columns (Eichrom) with a resin volume of 1 ml (dry mesh size of 100-150 µ). The chromatographic protocol is reported in Table 2.1.

Removal of Ce

To lower ¹⁴²Ce isobaric interferences to negligible levels during analysis of ¹⁴²Nd/¹⁴⁴Nd isotopic composition, Ce was removed from Nd using an efficient two-phase solvent extraction technique described in Rehkämper et al. (1996). To this end, Ce was oxidized with sodium bromate in an aqueous solution (HNO₃ acid) and the tetravalent Ce was then complexed by an organic solvent (HDEHP-heptane). The detailed procedure was as follows: each REE cut previously collected after the TRU-Spec chromatographic

<table>
<thead>
<tr>
<th>TRU-Spec chromatography column</th>
<th>AG50W-X8 chromatography column</th>
<th>LN-Spec chromatography column</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step</td>
<td>Acid</td>
<td>Volume [ml]</td>
</tr>
<tr>
<td>Cleaning</td>
<td>2 M HNO₃</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>10</td>
</tr>
<tr>
<td>Pre-conditioning</td>
<td>3 M HNO₃</td>
<td>10</td>
</tr>
<tr>
<td>Loading</td>
<td>3 M HNO₃</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>2 M HNO₃</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>2 M HNO₃</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>REE elution</td>
<td>H₂O</td>
<td>10</td>
</tr>
</tbody>
</table>

|                               |                 |             | Rinsing                       | 0.18 M HCl       | 1           | Rinsing                       | 0.4 M HCl        | 3.5         |

Table 2.1 Protocols for the TRU-Spec chromatographic column (separation of REE from rock matrix), the AG50W-X8 cation exchange column (removal of Na) and the Ln-Spec chromatographic column (separation of Sm and Nd).
2.2 Sample preparation

columns was dissolved in 100 µl of 10 M HNO$_3$ and transferred into a 1.5-ml centrifuge tube containing 500 µl of 5 mM NaBrO$_3$-10 M HNO$_3$. 500 µl of 0.3 M HDEHP-heptane was added and the immiscible mixture was emulsified by shaking for 3 minutes. After a settling time of about 2 minutes, the organic solvent (top layer) was pipetted out from the Ce-free aqueous phase (bottom layer) and discarded. The extraction using 500 µl of 0.3 M HDEHP-heptane was repeated twice. The aqueous phase was then scrubbed with 500 µl heptane to remove possible trace of HDEHP containing tetravalent Ce. The Ce-free aqueous phase was finally pipetted out (bottom layer), transferred into a Teflon Savillex beaker and dried down. The overall extraction technique was repeated twice. The separation factor (i.e final concentration divided by initial concentration) of Ce after one extraction was $9.6 \times 10^{-4}$. This is almost identical to the value of $1.0 \times 10^{-3}$ reported by Rehkämper et al. (1996).

**Encountered difficulty:** The extraction technique required some dexterity in pipetting out the organic solvent from the aqueous phase. The separation efficiency mostly depends on removing all buoyant organic solvent containing tetravalent Ce without pipetting out Nd in the underneath aqueous phase. The meniscus at the phase boundary caused difficulty in pipetting. Few µl of organic solvent were thus systematically not pipetted out and remained during the next extraction steps.

**Removal of Na**

Large amounts of Na added as sodium bromate during the previous step were removed using AG50W-X8 cation exchange columns (Bio Rad) with resin volume of 2 ml and dry mesh size of 100-200 µ. The chromatography protocol is reported in Table 2.1.

**Separation of Sm and Nd**

Samarium and Nd were separated from the remaining REE and individually collected using Ln-Spec chromatographic columns (Eichrom) with resin volume of 2 ml and dry mesh size of 100-150 µ. The chromatography protocol is reported in Table 2.1. Acid molarities were carefully determined by acid-base titration because of the small differences in acid concentrations between steps of the ion exchange procedure. Samarium and Nd fractions were then dried down and then taken up several times in HNO$_3$-H$_2$O$_2$ to oxidize and remove any residual organic matter. Samarium and Nd chemistry yields were > 80% and total procedural blank for Nd was about 150 pg.
Encountered difficulties: Efficient removal of Ce from the Nd fraction using Ln-Spec chromatographic columns was not possible. Figure 2.1 shows the elution curves for Ce and Nd (loads of 1 µg) that were washed with 0.21 M HCl and 0.18 M HCl. With a 0.21 M HCl wash, the Ce fraction eluted between 4 to 11 ml and Nd between 6 to 21 ml. The elution curves overlapped between 6 to 11 ml when relative concentration of Ce was up to 1. About 50% of the total Ce was thus eluted together with Nd. With a 0.18 M HCl wash, the Ce fraction eluted between 10 to 23 ml and Nd started eluting from 18 ml. The elution curves overlapped between 10 to 18 ml when relative concentration of Ce was up to 0.6. About 20% of the total Ce was thus eluted together with Nd. Acid elution with lower HCl molarity than 0.18 M broadened the elution curves of the two REE and did not improve the separation of Ce from Nd. The best separation factor of Ce using Ln-Spec chromatographic column was thus only about 0.20. This explains the necessity of separating Ce from Nd using the efficient two-phase solvent extraction technique prior to collecting Sm and Nd using the Ln-Spec chromatographic columns.

Large amounts of organic matter were occasionally eluted together with the Sm and Nd fractions from the Ln-Spec chromatographic columns and could not be completely removed with the HNO$_3$-H$_2$O$_2$ oxidation step. This caused problems when loading sample for isotopic analysis and yielded unstable signal during measurement. To solve this problem, small amounts of pre-filter resin (uncoated resin beads) were added at the bottom of the columns. This prevented eluting large amounts of organic material when collecting the Sm and Nd fractions.

2.3 Sample and standard measurements

Isotopic composition of Nd and the concentrations of Sm and Nd in whole-rock samples were measured by Thermal Ionization Mass Spectrometry (TIMS) and Multiple Collector - Inductively Coupled Plasma - Mass Spectrometry (MC-ICP-MS), respectively. Isotope-ratio mass spectrometry involved ionizing the element of interest, accelerating the ions through a high potential (10 kV for the TIMS instrument), separating the ions according to their mass-to-charge ratio, and measuring the electric currents produced by the resulting ion beams collected in Faraday detectors. Ions were separated with a magnet and collected simultaneously with array of Faraday detectors (multi-collection). Neodymium measurements by TIMS (isotope composition) were analytically demanding because the resolution of $^{142}$Nd/$^{144}$Nd variations among natural rock samples required achieving a long-term standard reproducibility of 5 ppm (2 SD) or better. Samarium and Nd isotope dilution measurements by MC-ICP-MS
2.3 Sample and standard measurements

![Elution curves of Ce (grey symbols) and Nd (black symbols) using Ln-Spec chromatographic columns (loads of 1 µg) with acid wash of 0.21 M HCl (upper panel) and 0.18 M HCl (lower panel). The separation factors of Ce from Nd were about 0.5 and 0.2 for 0.21 M HCl and 0.18 M HCl, respectively (see details in text). The dashed line in the lower panel shows the start of the Nd elution (17.9 ml of 0.18 M HCl acid wash) as it was defined in the protocol.](image)

(Sm and Nd concentrations) required a precision of 0.5% (2 SD) or better for the $^{147}$Sm/$^{144}$Nd ratio and thus were less analytically demanding.

2.3.1 Neodymium mass spectrometry (TIMS)

Neodymium was measured as a positive metal ion (Nd$^+$) with the Thermo Triton (TIMS) at ETH Zurich. This instrument is a solid source mass spectrometer where Nd sample (solid) was ionized by heating a zone refined rhenium filament assembly. A double filament assembly was used because Nd evaporates at lower temperature than it ionizes. The sample solution was loaded onto one filament (evaporation) and
2 Methods

was heated until it started evaporating. The other filament (ionization) was heated to even higher temperature (1670 °C) and ionized the vaporized Nd atoms. Zone-refined rhenium filaments were used because of the high work function of this metal. Filaments were previously degassed in a vacuum chamber with a maximum current of 5 A during 90 minutes.

Sample and standard loading

Nd fractions (containing about 1 µg of Nd) collected using Ln-Spec chromatographic columns (last columns) were dried down. Under a binocular microscope and with the help of a micropipette, each cut was dissolved in 2 µl 6 M HCl and the solution was split into two aliquots. Each aliquot (i.e. about 500 ng of Nd) was loaded onto one filament of a double rhenium filament assembly that was heated with a maximum current of 0.6 A. One µl of 0.01% H$_3$PO$_4$ (activator) was subsequently added. This helped increasing the evaporation temperature of Nd during TIMS analysis (by transforming Nd chloride into Nd phosphate) and thus enhanced signal intensity and stability. Loading of JNdi-1 Nd standards (500 ng) followed the same procedure.

Measurement protocol

A typical session lasted 10 days and consisted of measuring nine samples, nine JNdi-1 standards and a standard rock (BCR-2 USGS standard, SM/GR/97/31 and 155774a from the Isua Supracrustal Belt) that were altogether loaded onto the sample wheel of the Thermo Triton. Each session started with the measurement of few JNdi-1 standards in order to assess the state of the instrument. Samples were usually measured over day and standards over night.

The gain factors for the current amplifiers ($10^{11}$ Ω feedback resistors) were determined before every TIMS analysis. Gain factor for each individual amplifier did not vary by more than a few ppm over the course of one session but varied by about 10 ppm between sessions. Rotation of the virtual amplifier matrix was therefore used in order to cancel variation among amplifier gains for static analyses. During TIMS analysis, the ionization filament was heated to 5500 mA at a rate of 200 mA per minute. The evaporation filament was then heated at the same rate to typically 1600 mA until obtaining a $^{142}$Nd ion beam of about 7.5 volts. The evaporation filament was automatically reheated when signal intensity dropped below 80% of the initial signal intensity. Mass fractionation was corrected with the exponential law using a $^{146}$Nd/$^{144}$Nd = 0.7219 as a reference. Isobaric interferences from $^{144,148,150}$Sm and $^{142}$Ce were monitored by measuring $^{147}$Sm and $^{140}$Ce, respectively, and corrected on-
line. The $^{142}\text{Ce}/^{142}\text{Nd}$ and $^{144}\text{Sm}/^{144}\text{Nd}$ mean values for all sample analyses reported in this dissertation never exceeded $1.98 \times 10^{-6}$ and $1.05 \times 10^{-6}$, respectively. Corrections for isobaric interferences were thus always below 2 ppm in average. As there are variations in efficiency among the Faraday collectors and their associated amplifiers, a dynamic acquisition scheme using two magnet settings (corresponding to $^{145}\text{Nd}$ and $^{143}\text{Nd}$ in the axial detector) was used to reduce the effects of these variations on measured isotope ratios to negligible levels. The amplifier rotation feature on the Triton can cancel variation among amplifier gains even for static analyses, but it cannot correct for differences in cup efficiencies. Table 2.2 shows the collector configuration and measurement conditions for the dynamic Nd isotope analyses. The integration time was 8.4 seconds for each magnet setting. The two magnet settings were separated with an idle time of 4.0 seconds. The coincidences of each mass with its appropriate Faraday collector were optimized for the first magnet setting. To precisely align the beams into the detectors for the second magnet setting, the dispersion quadrupole was set to a value of 7.5 to 8.5 V. A measurement consisted of 24 to 80 blocks with 20 cycles per block, and lasted 4 to 14 hours. Amplifiers were rotated to the left after every block. The peaks were centered in the central detector every three blocks using the $^{145}\text{Nd}$- (magnet setting 1) and $^{143}\text{Nd}$-beam (magnet setting 2). Lens focusing using $^{145}\text{Nd}$ in central detector was done every three blocks. Electronic baselines (with deflected ion beams so that no ions reached collectors) were measured before every block with 30 integrations of 1 second. Over the course of one session, the means of individual baseline measurements for each individual cup did not vary by more than 90 $\mu$V (i.e. 12 ppm for a signal intensity of 7.5 V). In average, the difference between two consecutive averages of individual baseline measurements for each individual cup did not vary by more than 12 $\mu$V (i.e. 1.6 ppm for a signal intensity of 7.5 V), which was negligible.

<table>
<thead>
<tr>
<th>Magnet setting</th>
<th>Faraday collectors</th>
<th>Integration time [s]</th>
<th>Number of integrations</th>
<th>Idle time [s]</th>
<th>Peak centre</th>
<th>Lens focus</th>
<th>Zoom optics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$^{143}\text{Nd}$ $^{143}\text{Nd}$ $^{144}\text{Nd}$ $^{144}\text{Nd}$ $^{144}\text{Sm}$ $^{144}\text{Nd}$ $^{144}\text{Nd}$</td>
<td>8.39</td>
<td>1</td>
<td>4.0</td>
<td>$^{144}\text{Nd}$ $^{144}\text{Nd}$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>$^{144}\text{Ce}$ $^{144}\text{Nd}$ $^{144}\text{Nd}$ $^{144}\text{Nd}$ $^{144}\text{Sm}$ $^{144}\text{Nd}$ $^{144}\text{Nd}$</td>
<td>8.39</td>
<td>1</td>
<td>4.0</td>
<td>$^{145}\text{Nd}$ none</td>
<td>0.0</td>
<td>8.0</td>
</tr>
</tbody>
</table>

**Table 2.2** Collector configuration and measurement conditions for the dynamic Nd isotope analyses by TIMS.
2 Methods

Data reduction

Signal intensities were corrected online for amplifier gain, baselines and isobaric interferences. Static Nd isotope ratios for magnet setting 1 and 2 were calculated for every cycle and corrected with the exponential law as follows:

\[
\left( \frac{^{144}Nd}{^{144}Nd} \right)_{\text{static}} = \left( \frac{^{144}Nd}{^{144}Nd} \right)_{S} \times \left( \frac{m_{144}}{m_{144}} \right) ^{\ln \left( \frac{^{144}Nd}{^{144}Nd} \right)_{\text{nat}}} \left( \frac{m_{144}}{m_{144}} \right) ^{\ln \left( \frac{^{146}Nd}{^{144}Nd} \right)_{S}} \]  

(2.1)

where \(^{144}Nd_{\text{static}}\) is either \(^{142}Nd\), \(^{143}Nd\), \(^{145}Nd\), \(^{148}Nd\) or \(^{150}Nd\), \(^{144}Nd_{\text{static}}\) is the mass bias corrected static \(^{144}Nd_{/144}Nd_{\text{value}}, \(^{144}Nd_{/144}Nd_{S}\) is the \(^{144}Nd_{/144}Nd_{\text{measured in magnet setting 1 or 2}}, \(^{144}Nd_{/144}Nd_{\text{nat}}\) is the natural \(^{144}Nd_{/144}Nd_{\text{value used for normalization}, \(^{144}Nd_{/144}Nd_{S}\) is the \(^{144}Nd_{/144}Nd_{\text{ratio measured in magnet setting 1 or 2}}, \text{and } m\) is the exact mass of the specified Nd isotope.

The dynamic \(^{142}Nd_{/144}Nd_{\text{ratios were calculated for every cycle and corrected with the exponential law as follows:}}

\[
\left( \frac{^{144}Nd}{^{144}Nd} \right)_{\text{dyn}} = \left( \frac{^{144}Nd}{^{144}Nd} \right)_{S2} \times \left( \frac{m_{144}}{m_{144}} \right) ^{\ln \left( \frac{^{146}Nd}{^{144}Nd} \right)_{\text{nat}}} \left( \frac{m_{144}}{m_{144}} \right) ^{\ln \left( \frac{^{146}Nd}{^{144}Nd} \right)_{S1}} \]  

(2.2)

where \(^{144}Nd_{\text{dyn}}\) is the corrected dynamic \(^{144}Nd_{/144}Nd\) value, \(^{144}Nd_{S2}\) is the \(^{144}Nd_{/144}Nd\) measured in magnet setting 2, \(^{144}Nd_{\text{nat}}\) is the natural \(^{144}Nd_{/144}Nd\) value used for normalization, \(^{144}Nd_{S1}\) is the \(^{144}Nd_{/144}Nd\) ratio measured in magnet setting 1 and \(m\) is the exact mass of the specified Nd isotope.

Static and dynamic isotope ratios were then filtered at 2 standard deviations (SD) and averaged. Numbers of rejected ratios were always less than 5.6% of the total number of cycles. Internal errors were reported as 2 standard errors of the mean (SEM).

Neodymium isotope ratios were expressed as part per ten thousands (\(\epsilon\)-notation) or part per million (\(\mu\)-notation) deviations from the JNd-1 standard as follows:

\[
\epsilon^{144}Nd = \left( \frac{\left( \frac{^{144}Nd}{^{144}Nd} \right)_{\text{sample}}}{\left( \frac{^{144}Nd}{^{144}Nd} \right)_{\text{standard}}} - 1 \right) \times 10^{000} 
\]

(2.3)
2.3 Sample and standard measurements

\[ \mu^{142}Nd = \left( \frac{(^{142}Nd/^{144}Nd)_{sample}}{(^{142}Nd/^{144}Nd)_{standard}} - 1 \right) \times 1'000'000 \]  

(2.4)

where \(^{142}Nd\) is either \(^{142}Nd\), \(^{143}Nd\), \(^{145}Nd\), \(^{148}Nd\) or \(^{150}Nd\), \((^{142}Nd/^{144}Nd)_{sample}\) is the Nd isotope ratio measured for the sample and \((^{142}Nd/^{144}Nd)_{standard}\) is the Nd isotope ratio measured for the JNd-1 Nd standard.

Reproducibility of the JNd-1 Nd standard

The repeated measurements of the JNd-1 standard for \(^{142}Nd/^{144}Nd\) are shown in Figure 2.2. The value of the \(^{142}Nd/^{144}Nd\) ratio acquired in static mode (triangles) drifted by up to 130 ppm owing to slow degradation of the Faraday detectors. A dynamic acquisition scheme as explained above allowed this drift to be cancelled (circles). The external precision was ±4.9 ppm (2 SD) over a period of more than four years (n = 115) with a mean \(^{142}Nd/^{144}Nd\) value of 1.1418367. Over the course of this study (bold symbols) the external precision was ±4.3 ppm (n = 50) with a mean \(^{142}Nd/^{144}Nd\) ratio of 1.1418357 (dashed line). Grey bands with the letters A, B and C show the JNd-1 standards that were measured during the NSB study (n = 30), the Khariar study (n = 7) and the Acasta study (n = 13), respectively. 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, which supports the idea that the degradation of the Faraday collectors explains the drift in the static measurements. Repeated measurements of the JNd-1 standard shows that the protocol for Nd TIMS analysis is capable of reproducing long-term \(^{142}Nd/^{144}Nd\) values with a precision of about ±4 ppm.

Reproducibility of the rock standards

Figure 2.3 shows the \(^{142}Nd/^{144}Nd\) for rock standards expressed in parts per million (ppm) deviations from the JNd-1 Nd standard. The shaded area defines the external error of ±4.3 ppm (2 SD) of the repeated measurements of the JNd-1 standard (n = 50). Values for single analyses are plotted. Error bars are 2 SEM of individual mass spectrometer runs. The six replicates of the BCR-2 USGS standards (square symbols) are identical within errors to the JNd-1 Nd standard and have a mean value of -1.7±4.5 ppm (2 SD). The four replicates of the sample SM/GR/97/31 from the Isua supracrustal belt (circle symbols) show a \(^{142}Nd\) excess of 7.9±1.7 ppm (2 SD) that is
2 Methods

Fig. 2.2 Repeated measurements of the JNdi-1 standard for $^{142}\text{Nd}/^{144}\text{Nd}$. The value of the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio acquired in static mode (triangles) drifted. A dynamic acquisition scheme allowed this drift to be cancelled (circles). Over the course of this study (bold symbols) the external precision was ±4.3 ppm (n = 50) with a mean $^{142}\text{Nd}/^{144}\text{Nd}$ ratio of 1.1418357 (dashed line). Grey bands with the letters A, B and C show the JNdi-1 standards that were measured during the NSB study (n = 30), the Khariar study (n = 7) and the Acasta study (n = 13), respectively.

lower than the value of 14±2 ppm (n=1) reported in Caro et al. (2006). Measurement of sample 155574a from the Isua supracrustal belt (triangle symbol) shows a $^{142}\text{Nd}$ excess of 7.0±2.4 identical within errors to the value of 8.9±3.3 (n = 1) reported in Caro et al. (2006). Repeated measurements of rock standards shows that the protocol for Nd TIMS analysis is capable of reproducing modern terrestrial $^{142}\text{Nd}/^{144}\text{Nd}$ values for the BCR-2 USGS standard and resolving positive $^{142}\text{Nd}/^{144}\text{Nd}$ anomalies of about 8 ppm for standard rocks from the Isua supracrustal belt.

Example of a TIMS analysis

Figure 2.4 shows the dynamic $^{142}\text{Nd}/^{144}\text{Nd}$, the $^{146}\text{Nd}/^{144}\text{Nd}$ measured in magnet setting 1 (not corrected for mass fractionation) and the $^{142}\text{Ce}/^{142}\text{Nd}$ ratios acquired during TIMS analysis (1200 cycles) of one sample (IN05015) that had small isobaric interferences of $^{142}\text{Ce}$. Dynamic $^{142}\text{Nd}/^{144}\text{Nd}$ ratios are not filtered and have a mean value of 1.1418325±0.0000022, which corresponds to an unresolvable -2.8±1.9 ppm deviation from the JNdi-1 Nd standard. Dynamic $^{142}\text{Nd}/^{144}\text{Nd}$ ratios filtered at 2 SD (4.0% of total number of cycles removed; not shown in Fig. 2.4) have within errors an identical mean value of 1.1418331±0.0000025. Over 1200 cycles (about 12
2.3 Sample and standard measurements

Fig. 2.3 The $^{142}\text{Nd}/^{144}\text{Nd}$ ratio for the BCR-2 USGS standards (square symbols), SM/GR/97/31 (circle symbols) and 155574a (triangle symbol) standard rocks from the Isua supracrustal belt expressed in ppm deviations from the JNdI-1 Nd standard. The shaded area defines the external error of ±4.3 ppm (2 SD) of the repeated measurements of the JNdI-1 Nd standard (n = 50). Values for single analyses are plotted. Error bars are internal errors of individual mass spectrometer runs (2 SEM). Replicates of the BCR-2 USGS standard show identical $^{142}\text{Nd}/^{144}\text{Nd}$ values to the JNdI-1 Nd standard. Replicates of the standard rocks from the Isua supracrustal belt show positive $^{142}\text{Nd}/^{144}\text{Nd}$ anomalies of about 8 ppm.

hours of analysis) the $^{146}\text{Nd}/^{144}\text{Nd}$ ratios increased from about 0.720 to 0.724 (normal fractionation) and crossed the natural $^{146}\text{Nd}/^{144}\text{Nd}$ value of 0.7219. This increase in $^{146}\text{Nd}/^{144}\text{Nd}$ ratio is what is expected because the evaporation of $^{146}\text{Nd}$ is slower than that of $^{144}\text{Nd}$. At the beginning of the analysis, the $^{142}\text{Ce}/^{142}\text{Nd}$ value was 3 ppm and decreased to 1.5 ppm after 300 cycles. This example of a TIMS analysis shows that the correction for about 5.5% difference in mass fractionation did not induce drift in the dynamic $^{142}\text{Nd}/^{144}\text{Nd}$. The sample did not experience apparent “reverse” fractionation, and the residual Ce rapidly evaporated after about 300 cycles. Note that most analyses reported in this dissertation had no significant isobaric interferences of $^{142}\text{Ce}$ and did not show “reverse” fractionation.

Encountered problem: Vibrations emitted from the construction site of the LEE building at ETH Zurich perturbed the measurements with the Thermo Triton during spring and summer 2011. Blasting for basement excavation caused lateral displacements of the Faraday detectors and up to 30% drop in signal intensity when ion beams were aligned with one edge of their respective detectors. As a consequence, the Thermo
2 Methods

Fig. 2.4 Dynamic \(^{142}\text{Nd}/^{144}\text{Nd}\) (panel A), \(^{146}\text{Nd}/^{144}\text{Nd}\) measured in magnet setting 1 (panel B) and \(^{142}\text{Ce}/^{142}\text{Nd}\) in ppm (panel C) acquired during TIMS analysis (1200 cycles) for one sample that showed small isobaric interferences of \(^{142}\text{Ce}\). Dynamic \(^{142}\text{Nd}/^{144}\text{Nd}\) ratios are not filtered and have a mean value of 1.1418325±0.0000022, which corresponds to an unresolvable -2.8±1.9 ppm deviation from the JNdI-1 standard. Over 1200 cycles the values of the \(^{146}\text{Nd}/^{144}\text{Nd}\) ratios increases from about 0.720 to 0.724. At the beginning of the analysis, the value of the \(^{142}\text{Ce}/^{142}\text{Nd}\) ratio was 3 ppm and decreased to 1.5 ppm after 300 cycles.
Triton was placed on a vibration-free platform. Note that none of the analyses reported in this dissertation were measured during blasting events.

2.3.2 Samarium and Nd isotope dilutions (MC-ICP-MS)

Samarium and Nd concentrations were determined by isotope dilution mass spectrometry with the Nu Instruments MC-ICP-MS at ETH Zurich. This instrument is a plasma source mass spectrometer. The sample was dissolved in weak acid and nebulized with a desolvating unit. The sample was then transported with an argon gas flow to the plasma where it was ionized.

**Measurement protocol**

Samarium and Nd were measured as positive metal ions with $^{149}$Sm and $^{150}$Nd beam intensities of up to 8 volts (using Faraday detectors and $10^{11}$ Ω feedback resistors). The desolvating unit was a Cetac Aridus II. Uptake rate was set to 50 µl per minute. Radio frequency power was set to 1300 W with usually less than 3 W reflected power. High-voltage 1 and 4 were set to 4000 V and 2449 V, respectively. Other lens settings were adjusted for maximum sensitivity and best alignment of beams into the detectors. Samples and standards were measured in 0.1 M HNO$_3$ solutions. Baselines were measured in 0.1 M HNO$_3$ blank solution and lasted the same time as sample and standard measurements. Molarities of rinse solutions were 2 M HNO$_3$ and 0.1 M HNO$_3$. Samples and standards were measured with approximately same signal intensities.

**Samarium**

Individual Sm isotope measurement consisted of 30 cycles of 5 seconds integration time. Instrumental mass bias was corrected for normalizing to $^{147}$Sm/$^{152}$Sm = 0.56081 (e.g. Nyquist et al., 1995). Isobaric interferences from Gd were monitored on mass 157 and were negligible. For isotope dilution calculations, the average $^{149}$Sm/$^{152}$Sm composition obtained for multiple analyses ($n \geq 5$) of the Sm standard (Alfa Aesar) was used as the natural composition. Table 2.3 shows the collector configuration for the Sm isotope measurement. Instrument settings such as torch position, gas flow and zoom optics were adjusted to give maximum sensitivity of about 220 V·ppm$^{-1}$.

**Neodymium**

Individual Nd isotope measurement consisted of 30 cycles of 5 seconds integration time. Instrumental mass bias was corrected relative to $^{146}$Nd/$^{144}$Nd = 0.7219. Isobaric interferences from Sm were monitored on mass 147 and were negligible. For isotope dilution
2 Methods

calculations, the average $^{150}\text{Nd}/^{144}\text{Nd}$ composition obtained for multiple analyses ($n \geq 5$) of the Nd standard (Alfa Aesar) was used as natural composition. Table 2.3 shows the collector configuration for the Nd isotope measurement. Instrument settings such as torch position, gas flow and zoom optics were adjusted to give maximum sensitivity of about 200 V·ppm$^{-1}$.

<table>
<thead>
<tr>
<th>Collector configuration for the analysis of Sm concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>L4</td>
</tr>
<tr>
<td>$^{165}\text{Nd}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Collector configuration for the analysis of Nd concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
</tr>
<tr>
<td>$^{144}\text{Nd}$</td>
</tr>
</tbody>
</table>

Table 2.3 Collector configurations for the analyses of Sm and Nd concentrations by MC-ICP-MS.

Reproducibility of BCR-2 USGS standard

Replicate analyses of three separate digestions of the BCR-2 USGS standard (Table 2.4) yielded Sm and Nd concentrations identical within errors to the published values (Wilson, 1997) with a mean $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of 0.1374±0.2% (2 SD).

<table>
<thead>
<tr>
<th>Sm [ppm]</th>
<th>Nd [ppm]</th>
<th>$^{147}\text{Sm}/^{144}\text{Nd}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.4</td>
<td>28.3</td>
<td>0.1372</td>
</tr>
<tr>
<td>6.5</td>
<td>28.6</td>
<td>0.1375</td>
</tr>
<tr>
<td>6.5</td>
<td>28.6</td>
<td>0.1374</td>
</tr>
<tr>
<td>6.7±0.3</td>
<td>28±2</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.4 Sm and Nd concentrations and $^{147}\text{Sm}/^{144}\text{Nd}$ ratio for three replicates of the BCR-2 USGS standard. Recommended concentrations are shown in bold (Wilson, 1997).

2.4 Conclusions

Whole-rock Sm and Nd isotopic analyses required separation of Sm and Nd from sample matrix by ion exchange chromatography. Removal of Ce from Nd was achieved with a two-phase solvent extraction technique because the separation factor of Ce using
Ln-Spec chromatographic columns was only about 0.20. The analytical protocol for Nd TIMS measurements used a dynamic acquisition scheme to reduce the effects of variations in efficiency among the Faraday collectors on measured isotope ratios to negligible levels. The repeated measurements of the JNd-1 Nd standard showed that the protocol was capable of reproducing long-term $^{142}\text{Nd}/^{144}\text{Nd}$ values with a precision of about ±4 ppm (2 SD). The TIMS protocol was also capable of reproducing modern terrestrial $^{142}\text{Nd}/^{144}\text{Nd}$ values for the BCR-2 USGS standard and resolving positive $^{142}\text{Nd}/^{144}\text{Nd}$ anomalies of about 8 ppm for standard rocks from the Isua Supracrustal Belt. Samarium and Nd concentrations were determined by isotope dilution MC-ICP-MS. The protocol for isotope dilution was capable of reproducing published Sm and Nd concentrations for the BCR-2 USGS standard. In conclusion, the analytical techniques that were developed are reliable and can be used to study $^{147,146}\text{Sm}-^{143,142}\text{Nd}$ systematics in natural rock samples.
3 Inherited \(^{142}\)Nd anomalies in Eoarchean protoliths*

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 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 & 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 & 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 are similar but complementary to the Hadean mantle isochron preserved in Eoarchean rocks from West Greenland (Bennett et al., 2007; Rizo et al., 2011).

3.1 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

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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 $^{146}\text{Sm}-^{142}\text{Nd}$ system can only trace early silicate differentiation that happened prior to about 4300 Ma. In contrast, the long-lived $^{147}\text{Sm}-^{143}\text{Nd}$ system provides a time-integrated record of Sm/Nd evolution until the present. Coupled variations in the abundances of $^{142}\text{Nd}$ and $^{143}\text{Nd}$ reveal both the timing and the degree of the earliest differentiation of planets into crust and mantle (Harper & Jacobsen, 1992; Caro et al., 2003), or possibly the fractionation due to crystallization of a magma ocean (Boyet & Carlson, 2005; Caro et al., 2005). Variations in the abundance of $^{142}\text{Nd}$ in planetary and meteoritic materials are below 100 parts per million (ppm). This is to be expected because of the low initial $^{146}\text{Sm}/^{144}\text{Sm}$ 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 $^{142}\text{Nd}$ excess of 18 ppm in the Earth relative to chondrites (Boyet & 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 & Carlson, 2005), or the Earth formed from materials with super-chondritic Sm/Nd ratios (Caro et al., 2008; Caro & 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 $^{142}\text{Nd}$ excesses of up to 15 parts per million 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 in the Narryer Gneiss Complex in Western Australia (Bennett et al., 2007). Evidence for a complementary early-enriched reservoir characterized by $^{142}\text{Nd}$ deficits is, however, sparse (O’Neil et al., 2008; Upadhyay et al., 2009). O’Neil et al. (2008) reported $^{142}\text{Nd}$ deficits of as much as -15 ppm within pre-3750 Ma rocks from the Nuvvuagittuq Supracrustal Belt (NSB) in northern Quebec (David et al., 2009; O’Neil et al., 2007). Based on a $^{142}\text{Nd}/^{144}\text{Nd}$ versus $^{147}\text{Sm}/^{144}\text{Nd}$ correlation, these authors derived an age of 4280 Ma for a hornblende amphibolite and a cummingtonite (Ca-poor) amphibolite unit of possibly pyroclastic origin (Cates & Mojzsis, 2009; O’Neil et al., 2011). This age estimate is revised upward to 4362
3.1 Introduction

Ma 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 & 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 & 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 vs. 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.
3 Inherited $^{142}\text{Nd}$ anomalies in Eoarchean protoliths

## 3.2 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 eight 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 & 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 & 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. (2012) in revision). 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.

## 3.3 Methods

### 3.3.1 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...
3.3 Methods

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.

3.3.2 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 ¹⁴²Nd ion beam intensity of about 7.5 volts (using 10¹¹ Ω feedback resistors). Instrumental mass bias was corrected for with an exponential law using ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219. Isobaric interferences of ¹⁴⁴,¹⁴⁸,¹⁵⁰Sm and ¹⁴²Ce were monitored with, respectively, ¹⁴⁷Sm and ¹⁴⁰Ce and corrected for online. The ¹⁴²Ce/¹⁴²Nd and ¹⁴⁴Sm/¹⁴⁴Nd ratios never exceeded 1.79 × 10⁻⁶ and 1.12 × 10⁻⁶, respectively. Figure 3.1 shows the repeated ¹⁴²Nd/¹⁴⁴Nd measurements of the JNdi-1 standard over a period of three years (n=94). A dynamic acquisition scheme using two magnet settings (corresponding to ¹⁴⁵Nd and ¹⁴³Nd in the central detector) allowed gain biases caused by the degradation of the Faraday detectors to be cancelled 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 ¹⁴²Nd/¹⁴⁴Nd 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 analysed samples from the Isua Supracrustal Belt and rocks from elsewhere in the Itsaq Gneiss Complex of southern West Greenland for which ¹⁴²Nd 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 A.3.1.

3.3.3 Samarium and Nd concentrations

Samarium and Nd concentrations were determined by isotope dilution. Aliquots of completely dissolved samples in 6M HCl were spiked with an enriched, mixed ¹⁵⁰Nd-¹⁴⁹Sm 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-
3 Inherited $^{142}$Nd anomalies in Eoarchean protoliths

![Repeated measurements of the JNdi-1 standard (n=94)](image)

**Fig. 3.1** 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 cancelled (circles). The external precision was 5.1 ppm (2 SD) over a period of three years (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.

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±0.2 % (2 SD). The concentrations of Sm and Nd in the NSB samples are reported in Table A.3.2.

### 3.4 Results

The new NSB $^{147,146}$Sm-$^{143,142}$Nd whole-rock data (Table A.3.1) come from three hornblende amphibolites, two cummingtonite amphibolites, one tonalite gneiss, five trondhjemite gneisses, two granodiorite gneisses, and a quartzite. Figure 3.2 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.
3.4 Results

Fig. 3.2 $^{142}\text{Nd}/^{144}\text{Nd}$ 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 $^{142}\text{Nd}$ 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.

![Diagram](image)

In a $^{147}\text{Sm}-^{143}\text{Nd}$ isochron diagram (Fig. 3.3A) 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 $3876\pm191\text{ Ma}$ (MSWD = 194). This apparent Eoarchean age is similar to the minimum age of 3750 Ma defined by U-Pb zircon chronology of trond-
3 Inherited $^{142}$Nd anomalies in Eoarchean protoliths

Hjelmit gneisses in the belt (Cates & Mojzsis, 2007), as well as to the maximum age defined by detrital zircons (Cates et al. (2012) in revision). 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 $3891 \pm 584$ Ma (MSWD = 75) similar to the age of the trondhjemite gneisses with $3802 \pm 1144$ Ma (MSWD = 19). Hornblende amphibolites (dashed line), however, with an ostensibly younger age of $3076 \pm 508$ 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 $4301 \pm 352$ 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. 3.3B) 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 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 & 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. 3.3A). 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.

3.5 Discussion

3.5.1 Accuracy of $^{142}$Nd measurements

Andreasen & 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
3.5 Discussion

Fig. 3.3 Long-lived $^{147}\text{Sm}-^{143}\text{Nd}$ (panel A) and short-lived $^{146}\text{Sm}/^{142}\text{Nd}$ (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 $^{146}\text{Sm}/^{142}\text{Nd}$ 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 & 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 $^{147}\text{Sm}-^{143}\text{Nd}$ isochron diagram represent the best fit to the hornblende amphibolites and the pooled hornblende amphibolites and cummingtonite amphibolites, respectively.
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yielded inaccurate mass bias corrections and correlated $^{142,148,150}$Nd deficits in the samples. Andreasen & Sharma (2009) modelled 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 analysed and reported by O’Neil et al. (2008), as well as the modern terrestrial composition of the amphibolite PC221 (Fig. 3.2). We thus corroborate the accuracy of the Nd isotopic measurements of O’Neil et al. (2008) for these samples. As shown in Fig. 3.4, 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.

**Fig. 3.4** Nd isotopic composition of the samples expressed in parts per million (ppm) deviations from the JNd-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.
3.5 Discussion

3.5.2 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 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 reequilibrate 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 A.3.3. The equations for isotope exchange between three phases can be written for isotope ratios as follows:

\[
\begin{align*}
\frac{dr_1}{dt} &= k_1(r_f - r_1) \\
\frac{dr_2}{dt} &= k_2(r_f - r_2) \\
\frac{dr_f}{dt} &= -\frac{X_1}{X_f}k_1(r_f - r_1) - \frac{X_2}{X_f}k_2(r_f - r_2)
\end{align*}
\]

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

3.5.3 Disturbed $^{147,146}$Sm-$^{143,142}$Nd systematics in the Nuvvuagittuq supracrustal belt

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 & Mojzsis, 2009). Third, we examine the consequence of this event on the $^{142}$Nd/$^{144}$Nd scatterchron. Figure 3.5 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 an 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 & 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. 3.6). 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 behaviour or incomplete isotopic equilibration.
Fig. 3.5 (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.

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. 3.6, 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
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Fig. 3.6 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.

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. (2013). Second, at 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. 3.7).

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. 3.6, the trondhjemite gneisses have
Fig. 3.7 (A) Synthetic $^{147}\text{Sm}-^{143}\text{Nd}$ 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 $^{146}\text{Sm}-^{142}\text{Nd}$ 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 $^{146}\text{Sm}-^{142}\text{Nd}$ 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.

$^{143}\text{Nd}/^{144}\text{Nd}$ 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.
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with either Hadean crust or enriched mantle produced at ca. 4300 Ma with a large Sm/Nd fractionation (component A in Fig. 3.6) induced by melting.

3.6 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. 3.8) 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.
3.6 Implications

Fig. 3.8 Long-lived $^{147}\text{Sm} - ^{143}\text{Nd}$ (panel A) and short-lived $^{146}\text{Sm} - ^{142}\text{Nd}$ (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 $^{146}\text{Sm} - ^{142}\text{Nd}$ isochron diagram defines the modern $^{142}\text{Nd}$ 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.
### Appendix

Table A.3.1 Nd isotope compositions of the NSB samples. The table shows the Nd isotope ratios measured for the static line 1 and the dynamic $^{142}$Nd/$^{144}$Nd ratio. All Nd isotope ratios are mass-fractionation corrected using $^{146}$Nd/$^{144}$Nd = 0.7219. Isobaric interferences are expressed in ppm. Errors are 2 SD. Also listed are 30 measurements of the JNd-1 Nd standard, four replicates of the BCR-2 USGS standard, three replicates of sample SM/GR/97/31 from the Isua Supracrustal Belt, one replicate of sample 155774 from the Amitsoq Gneiss, and three replicates of samples from O’Neil et al. (2008). Letters after sample names denote separate digestions, while numbers denote separate analyses of a given digestion.

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<th>$^{143}$Nd/$^{144}$Nd</th>
<th>$^{145}$Nd/$^{144}$Nd</th>
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Errors are 2 SD. Also listed are 30 measurements of the JNd-1 Nd standard, four replicates of the BCR-2 USGS standard, three replicates of sample SM/GR/97/31 from the Isua Supracrustal Belt, one replicate of sample 155774 from the Amitsoq Gneiss, and three replicates of samples from O’Neil et al. (2008). Letters after sample names denote separate digestions, while numbers denote separate analyses of a given digestion.
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<th>145Nd/144Nd</th>
<th>143Nd/144Nd</th>
<th>144Nd/143Nd</th>
<th>148Nd/144Nd</th>
<th>150Nd/144Nd</th>
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<td>0.5109660 ± 9</td>
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<td>0.2415851 ± 7</td>
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Table A.3.1: Continued.
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**Table A.3.1: Continued.**
Table A.3.2 Concentrations of Sm and Nd in the NSB samples. Errors are 2SD. Also listed are three replicates of the BCR-2 USGS standard.
### Table A.3.3 Parameters used in the isotope equilibration model.

<table>
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<th>Meaning</th>
<th>Unit</th>
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<th>Value model 2&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>$T_f$</td>
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<tr>
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<td>yr</td>
<td>3.75 Gyr</td>
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<tr>
<td>$k_i$</td>
<td>rate of isotope equilibration</td>
<td>$[T]^{-1}$</td>
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<sup>a</sup> model 1 corresponds to the model where the $^{146}$Sm-$^{142}$Nd age for amphibolite is assumed to be the age of rock formation as in O’Neil et al. (2008).

<sup>b</sup> model 2 corresponds to the model where the age of rock formation is assumed to be a free parameter, adjusted to match the $^{147}$Sm-$^{143}$Nd and $^{146}$Sm-$^{142}$Nd ages.
4 A legacy of Hadean silicate differentiation inferred from Hf isotopes in Eoarchean rocks of the Nuvvuagittuq supracrustal belt (Québec, Canada)*

Abstract

New Lu-Hf isotopic data for mafic and felsic rocks from the Nuvvuagittuq supracrustal belt (NSB) in northern Québec (Canada) yield an Eoarchean age of 3864±70 Ma consistent with both zircon U-Pb and whole-rock $^{147}$Sm-$^{143}$Nd chronology, but in disagreement with ca. 4400 Ma ages inferred from the $^{146}$Sm-$^{142}$Nd chronometer (O'Neil et al., 2008, 2012). The Lu-Hf result is interpreted as the mean emplacement age of the different autochthonous units of the NSB. An observed alignment of the data along a Lu-Hf “scatterchron” precludes a Hadean age for the NSB because its isotopic characteristics appear to be controlled by long-term radiogenic ingrowth. Emplacement of the NSB in the Hadean (e.g., 4362 Ma if the decay constant of $^{146}$Sm of Kinoshita et al. (2012) is used with the O’Neil et al. (2008) data) should instead have caused age differences of hundreds of millions of years to manifest as strong deviations from the Lu-Hf scatterchron. Combined Lu-Hf and Sm-Nd data on the same NSB amphibolite samples (Ca-poor cummingtonite- and hornblende-bearing) define a mixing hyperbola at ca. 3800 Ma with end-member compositions representative of the compositional groups identified for these lithologies (O’Neil et al., 2011). Anomalously low $^{142}$Nd/$^{144}$Nd values relative to bulk silicate Earth are endemic to a group of rocks in the NSB termed “low-TiO$_2$” cummingtonite-amphibolites; this is attributable to an ancient multi-stage history of their mantle source. Modeling shows that the $^{142}$Nd/$^{144}$Nd deficits could have developed in response to a re-fertilization episode within a previously fractionated mantle domain at 4510 Ma.

4 Hadean silicate differentiation inferred from Hf isotopes in the NSB

4.1 Introduction

What little is known of our planets formation and early evolution is severely limited by the
 fact that the terrestrial rock record appears to end around the Eoarchean-Hadean boundary
 at about 4 billion years ago (Bowring & Williams, 1999). Thus far, this temporal barrier has
 prevented direct observations of the primitive Earth based on actual rocks. Evidence from
 ancient detrital zircons in quartzites of the Narryer Gneiss Complex in Western Australia,
 however, shows that some Hadean crust lingered on into the Archean (Compston & Pidgeon,
 1986; Froude et al., 1983). The ancient Australian zircons testify to the existence of an
 evolved felsic crust and surface conducive to the stability of liquid water (Mojzsis et al.,
 2001), the presence of relatively cool geothermal gradients (Hopkins et al., 2008) and oxidized mantle
 conditions (Trail et al., 2011), all within about 150-200 Myr after Earth formed (Harrison,
 2009; Kemp et al., 2010). It should be noted that because zircons are generally prevalent in
 granitic rocks, e.g., Hoskin & Schaltegger (2003), the Hadean mineral record almost certainly
 represents a biased sampling of a crust that was composed of a wide variety of rock types
 ranging in composition from ultramafic to felsic. Understanding the origin and fate of this
 primordial crust would greatly enhance what we know of Hadean geodynamics.

An essential complement to the Hadean zircon work has been the discovery of the anomalous
 ly high $^{142}$Nd/$^{144}$Nd isotope ratios reported from rocks collected in the Eoarchean (3770-
 3850 Ma) terranes of West Greenland and Western Australia (Bennett et al., 2007; Boyet
 et al., 2003; Caro et al., 2003, 2006; Rizo et al., 2011). The development of such anomalies resulted
 from Sm/Nd fractionation due to early silicate differentiation during the first few hundred million
 years of Earth history, followed by ingrowth of $^{142}$Nd produced by the decay of $^{146}$Sm ($T_{1/2}$ =
 68 million years; Kinoshita et al. (2012)). The ca. 3800 Ma West Greenland rocks show enrichments of up to 15 ppm in
 $^{142}$Nd/$^{144}$Nd (expressed as positive $\mu^{142}$Nd) compared to BSE. An overall 18 ppm difference in $\mu^{142}$Nd between Earth and chon-
 drites reported by Boyet & Carlson (2005) has been ascribed to the existence of an early
 terrestrial magma ocean that fractionated Sm and Nd by crystallization and has remained
 hidden and untapped since then as a complementary enriched reservoir (Boyet et al.,
 2003; Chase & Patchett, 1988). Another viewpoint holds that the $\mu^{142}$Nd difference between BSE
 and chondrites instead derives from an initial suprachondritic Sm/Nd ratio for the Earth
 which would have been fractionated from the chondritic value; within this framework, no
 hidden reservoir is required to explain the difference between Earth (or BSE) and CHUR
 (Caro et al., 2008; Caro & Bourdon, 2010; O’Neill & Palme, 2008).

An important discovery was made by O’Neil et al. (2008), who found $^{142}$Nd/$^{144}$Nd ratios lower than
 the terrestrial standard (expressed as negative $\mu^{142}$Nd) from rocks of the
 Nuvvuagittuq supracrustal belt (NSB) in northern Qu´ebec (Canada). These authors pro-
 posed a Hadean age for the NSB based on a positive correlation between $^{142}$Nd/$^{144}$Nd and
 $^{147}$Sm/$^{144}$Nd, which yielded a (revised) scatterchron age of 4388 Ma (O’Neil et al., 2012).
Conversely, the long-lived $^{147}\text{Sm}-^{143}\text{Nd}$ chronometer for the same rocks indicates an age of 3819±270 Ma, which is more consistent with the surrounding geology (Cates & Mojsis, 2007, 2009; Cates et al., 2012; David et al., 2002, 2009; Roth et al., 2013a).

To better understand the actual age of emplacement for the NSB and thereby the meaning of the coupled $^{147,146}\text{Sm}-^{143,142}\text{Nd}$ systematics of these rocks, high-precision whole-rock Lu-Hf isotope measurements were performed on a diverse collection of supracrustal samples previously analyzed for $^{147,146}\text{Sm}-^{143,142}\text{Nd}$ by Roth et al. (2013a) and described in Cates et al. (2012). The Lu-Hf isotope data are compared to new and existing Sm-Nd results for the NSB (David et al., 2009; O’Neil et al., 2008, 2012; Roth et al., 2013a), to previous data for the ca. 3800 Ma Isua Supracrustal Belt (ISB) in southern West Greenland (Caro et al., 2006; Rizo et al., 2011), and to U-Pb zircon chronology and whole-rock geochemistry (Cates & Mojsis, 2007, 2009; Cates et al., 2012). The principal goal of this integrated approach was to shed new light on how and when the isotopic signatures of Hadean silicate differentiation could have formed, and how these were subsequently incorporated and preserved in the oldest terranes.

### 4.2 Samples and analytical techniques

The analyzed samples reported here, as well as details of the geological setting are referenced in Cates et al. (2012) and Roth et al. (2013a). They comprise five hornblende amphibolites (IN05013, IN05019, IN05021, IN8019, IN08021), two cummingtonite amphibolites (IN08012, IN08044), one tonalitic gneiss (IN05028), six trondhjemitic gneisses (IN05003, IN05018, IN05022, IN05023, IN08023, IN08038), two granodioritic gneisses (IN05012, IN05015), and one fuchsitic (Cr-rich) quartzite (IN08001) from the Nuvvuagittuq locality and an adjacent (unnamed) belt also within the Inukjuak terrane (Table A.4.1). Whole-rock samples were crushed and powdered either at the Department of Geological Sciences of the University of Colorado at Boulder (CUB) or at ETH Zurich in agate mortars that were pre-cleaned with quartz sand and subsequently conditioned with small sample aliquots prior to powdering of the main sample mass. Splits from homogenized powders were divided for major, minor, and trace element geochemistry, and further subdivided for separate Sm-Nd and Lu-Hf isotope work at ETH Zurich and the Ecole Normale Supérieure in Lyon (ENSf), respectively. All Lu-Hf chemical separation and isotopic analyses were performed at ENSf. After dissolution in Parr bombs, Lu and Hf were separated from ca. 250 mg aliquots of whole-rock powder by ion-exchange column chromatography and measured for their isotopic compositions by MC-ICP-MS (Nu Plasma HR) according to the procedures previously described by Blichert-Toft et al. (1997, 2002) and Blichert-Toft (2001). Lutetium and Hf concentrations were determined by isotope dilution using a >98% pure mixed $^{176}\text{Lu}-^{180}\text{Hf}$ spike added to the samples prior to dissolution. The JMC-475 Hf standard was analyzed in alternation with the samples and the mass fractionation-corrected $^{176}\text{Hf}/^{177}\text{Hf}$ ratio gave 0.282156±0.000007 (2SD,
n=15) over the course of the analyses, which is identical within error to the accepted value of 0.282163±0.000009 (Blichert-Toft et al., 1997). Hence, no corrections were applied to the data. Total procedural blanks for Hf and Lu were less than 20 pg. Isochron calculations (ages and initial isotopic compositions) were performed using the ISOPLOT®.

4.3 Results

4.3.1 Lu-Hf isotope systematics in the Nuvvuagittuq supracrustal belt

The Lu-Hf isotope data for the NSB samples analyzed here are listed in Table A.4.1. For the gneiss samples, $^{176}\text{Lu}/^{177}\text{Hf}$ ratios show a broad range from very low (0.0018) to supra-chondritic (0.035). Likewise, $^{176}\text{Hf}/^{177}\text{Hf}$ ratios range from 0.280474 for the least radiogenic tonalitic gneiss, to 0.282912 for the most radiogenic amphibolite in the sample suite. The NSB gneisses form a positive correlation in $^{176}\text{Lu}/^{177}\text{Hf}$-$^{176}\text{Hf}/^{177}\text{Hf}$ space (Fig. 4.1) corresponding to an age of 3864±70 Ma and an initial $^{176}\text{Hf}/^{177}\text{Hf}$ of 0.280326±0.000026. This translates into an $\epsilon_{\text{Hf}}$ of +0.4±0.9 when normalized to CHUR (Bouvier et al., 2008). The fuchsitic quartzite sample plots on the trend defined by both felsic and mafic lithologies, which is consistent with its mixed sedimentary origin (Cates et al., 2012). Published data for the tonalite-trondhjemite-granodiorite (TTG) whole-rock samples and zircons from the NSB reported in Guitreau et al. (2012) are also in good agreement with the new data presented here, both for the regressed initial $^{176}\text{Hf}/^{177}\text{Hf}$ (0.280354±0.000035) and the oldest Pb-Pb zircon ages (3770-3840 Ma).

When considered separately, the cummingtonite-amphibolite samples documented to preserve low $^{142}\text{Nd}/^{144}\text{Nd}$ (Roth et al., 2013a) have a Lu-Hf age of 3911±32 Ma and an initial $^{176}\text{Hf}/^{177}\text{Hf}$ of 0.280295±0.00006. Hornblende-amphibolites yield an imprecise Lu-Hf age of 4016±1200 Ma with an initial $^{176}\text{Hf}/^{177}\text{Hf}$ of 0.28023±0.00075. The granitoid gneisses define a Lu-Hf age of 3139±360 Ma and an initial $^{176}\text{Hf}/^{177}\text{Hf}$ of 0.280369±0.000026. With the exception of the granitoid gneisses, the age determined by regression through all the samples, as well as the initial Hf isotopic composition determined herein, are consistent within analytical uncertainties with the separate age groups and initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios. The Lu/Hf spread and absolute values for the felsic rocks are small (0.0018 to 0.0083) and, therefore, the age determined for these rocks should not be considered robust. It should also be noted that samples IN05003, IN05012, IN05018, and IN05028 were previously reported by Guitreau et al. (2012), but on different sample powders, and that the initial $\epsilon_{\text{Hf}}$ value differences between TTGs analyzed in this study and by Guitreau et al. (2012) are less than 1 epsilon unit (except for sample IN05028 for which the difference is 4.3 epsilon units). Since the Lu/Hf ratios are similar and very low for the two analyses of sample IN05028, we ascribe this difference to sample heterogeneity exacerbated by the fact that different powder aliquots were used in the two studies. Aside from this sample, the other Nuvvuagittuq TTG gneisses (IN05003, IN05012 and IN05018) have highly consistent Hf isotope compositions between
4.3 Results

Fig. 4.1 Lu-Hf isochron diagram showing the distribution of felsic and mafic lithologies of the Nuvvuagittuq supracrustal belt from this study as well as from Guitreau et al. (2012). Analytical uncertainties on individual data points are smaller than the symbol size. Age, initial isotope composition, and uncertainties were determined using ISOPLOT® and data from this study only.

this study and Guitreau et al. (2012). Sample IN05028 is the least radiogenic granitoid gneiss measured here, and also plots slightly below the main errorchron compared to the Guitreau et al. (2012) data for the same sample (Fig. 4.1). The apparent Lu-Hf age of 3139 Ma for the TTG gneisses is at odds with the older ca. 3800 Ga U-Pb zircon ages for the same samples, which are interpreted as crystallization ages (Cates & Mojzsis, 2007, 2009). The lack of what is normally good agreement between Hf isotopes in TTGs and their U-Pb zircon ages (Guitreau et al., 2012) means that the determined whole-rock Lu-Hf age for this subgroup of samples has no geological meaning and merely results from the very small scatter in their Lu/Hf ratios.

Initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios calculated for an age of 3864 Ma range from 0.280250 to 0.280367 for the felsic gneisses, from 0.280293 to 0.280371 for the hornblende-amphibolites, and from 0.280302 to 0.280325 for the cummingtonite-amphibolites. Sample IN05028 has an initial Hf isotope composition of 0.280250, while in the study of Guitreau et al. (2012) the initial was 0.280371. The quartzite has an initial $^{176}\text{Hf}/^{177}\text{Hf}$ of 0.280361, which falls within the range defined by the other rock groups.

An age of 3800 Ma for the NSB was chosen to calculate the initial $\epsilon_{\text{Hf}}$ (relative to CHUR; Bouvier et al. (2008)). This age is used in the calculations hereafter, the reason being that it is consistent within the quoted analytical uncertainties for the long-lived chronometers applied to the same rocks (Lu-Hf, Sm-Nd, and U-Pb). In this manner, initial $\epsilon_{\text{Hf}}$ values for
4 Hadean silicate differentiation inferred from Hf isotopes in the NSB

the Nuvvuagittuq gneisses range from -1.9 to +3.5 (or from 0 to +3.5 using the Guitreau et al. (2012) value for sample IN05028) with an average value of +0.4±0.9. This corresponds to a $^{176}\text{Hf}^{177}\text{Hf}$ ratio of 0.280326±0.000026 as given by the global scatterchron of all the samples shown in Fig. 4.1. When calculating relative to the BSE parameters of Caro & Bourdon (2010), it is found that initial $\epsilon_{\text{Hf}}$ for the Nuvvuagittuq gneisses ranges from -4.0 to +1.4 (or from -2.2 to +1.4 using the Guitreau et al. (2012) value for sample IN05028) with an average value of -1.7±0.9.

4.3.2 Lu-Hf isotope systematics in an adjacent (unnamed) belt in the Inukjuak terrane

One of the hornblende-bearing amphibolites (IN08021) and one of the tonalitic gneisses (IN08023) analyzed in this study were sampled from a neighboring (unnamed) supracrustal belt that is part of the Inukjuak terrane and located approximately 5 kilometers northeast of the NSB. The two samples plot somewhat off the Lu-Hf correlation line defined by the NSB rocks and yield significantly different initial Hf isotope compositions when calculated using the age defined by this regression. Samples IN08021 and IN08023 have initial $^{176}\text{Hf}^{177}\text{Hf}$ calculated at 3800 Ma of 0.280219 and 0.280482, respectively, which translates into initial $\epsilon_{\text{Hf}}$ of -3.4 and +6.0. When re-calculated to the assumed age of 3660 Ma for the Voizel suite tonalites that surround the NSB (David et al., 2009), sample IN08023 yields an initial Hf isotope composition of 0.280490. This value is significantly different from the NSB samples analyzed in this study, but resembles that determined for sample IN05001 (0.280419) collected from a tonalite body in the center of the NSB and reported in Guitreau et al. (2012). Hence, IN08023 may be related to the tonalitic basement that surrounds the NSB. Sample IN08021 is petrographically and geochemically similar to common hornblende-amphibolites found in the NSB (Cates & Mojzsis, 2007; Cates et al., 2012) but its age is presently unconstrained. This sample (IN08021) is part a suite of rocks of great potential importance since it has the most negative initial $\epsilon_{\text{Hf}}$, $\epsilon^{143}\text{Nd}$, and $\mu^{142}\text{Nd}$ (Roth et al., 2013a) so far observed in the Inukjuak terrane.

4.4 Discussion

4.4.1 The age(s) of the Nuvvuagittuq supracrustal belt

The actual age(s) of the NSB rocks is currently a matter of debate because of the incongruity between the two Sm-Nd chronometers (O’Neil et al., 2008; Roth et al., 2013a), and debate over the interpretation of U-Pb zircon ages. However, combining the two independent long-lived isotope systems (U-Pb and Lu-Hf) can help establish a robust age estimate, and consequently pave the way towards understanding the observed $^{142}\text{Nd}$ anomalies.

Although the Lu-Hf age of 3864 Ma for the NSB determined in this study (Fig. 4.1) is
4.4 Discussion

Fig. 4.2 $^{147}$Sm-$^{143}$Nd isochron diagram showing the distribution of mafic and felsic lithologies of the Nuvvuagittuq supracrustal belt from previous studies (O’Neil et al., 2008; Roth et al., 2013a). Data from Roth et al. (2013a) are the average values of dynamic measurements. Age, initial isotope compositions, and uncertainties were calculated using ISOPLOT®. Black outline are results from Roth et al. (2013a), while no outline are results from O’Neil et al. (2008). Lithology names used in this figure are identical to those of the respective publications.

Consistent with the results of other long-lived chronometers (Cates & Mojzsis, 2007; Cates et al., 2012; David et al., 2009; O’Neil et al., 2008; Roth et al., 2013a), it is at variance with the $^{146}$Sm-$^{142}$Nd age of ca. 4400 Ma advocated by O’Neil et al. (2012). Figure 4.2 shows $^{143}$Nd/$^{144}$Nd as a function of $^{147}$Sm/$^{144}$Nd for the data from Roth et al. (2013a) and O’Neil et al. (2008, 2012). The Sm-Nd data for Nuvvuagittuq gneisses by David et al. (2009), that yielded an age of 3820 Ma, are not plotted in Fig. 4.2 but they fall exactly between the two data sets. The $^{147}$Sm-$^{143}$Nd ages determined by O’Neil et al. (2008), David et al. (2009), and Roth et al. (2013a) are, respectively, 3927±150 Ma, 3934±290 Ma, and 3869±130 Ma. The Sm-Nd age obtained by combining the three data sets is 3818±81 Ma, which together with the separate ages is identical within error to the Lu-Hf age obtained in this study as well as to U-Pb zircon ages.

Evidently, after nearly four billion years in the crust, the $^{176}$Hf and $^{143}$Nd isotope systematics of these gneisses have become sufficiently dominated by radiogenic in-growth for any initial source heterogeneities to have become overwhelmed. Alternatively, the dispersion of points about the alignment of the NSB samples could be due to later metamorphic disturbance(s). Whether one or the other is the cause of the observed scatter among NSB rocks will be discussed further below. This conclusion does not preclude the likelihood that some
of the Nuvvuagittuq rocks formed a few tens of millions of years before or after some others as hinted at by U-Pb chronology on detrital zircons (Cates et al., 2012). However, it does rule out the possibility that the NSB rocks could have formed hundreds of millions of years earlier (or later) because this would show up as significant deviations from the observed average scatterchron. The Hadean ages derived by O’Neil et al. (2008, 2012) are dependent on the interpretation of the positive correlation between $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$. So far, no evidence of crust older than about 3800 Ma has been found in the Nuvvuagittuq detrital zircon record (Cates et al., 2012), nor has any source of detrital zircons older than about 4000 Ma been found in North America (Maier et al., 2012). One can argue that because the NSB is dominated by amphibolites of mafic to ultramafic composition it would not be expected to contain substantial, if any, amounts of zircon. Furthermore, the apparent absence of Hadean zircons in the little-explored ancient North American detrital record is not a strong argument to refute a Hadean age for Nuvvuagittuq. Yet, as described earlier, if these rocks really were hundreds of millions of years older than the other units from the NSB, they would be expected to show real differences in the $^{176}\text{Lu-}^{176}\text{Hf}$ and $^{147}\text{Sm-}^{143}\text{Nd}$ isochron plots and would not align with the other samples.

Another line of argument may be that the $^{147}\text{Sm-}^{143}\text{Nd}$ chronometer was disturbed by metamorphism and that the 3800 Ma “age” derived from the positive correlation between $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ is merely a mixed age between ca. 4400 Ma and 2700 Ma isochrons (O’Neil et al., 2008). The latter (young) age corresponds to the formation of late zircon overgrowths (Cates & Mojzsis, 2009), and to the formation time of garnets (O’Neil et al., 2012; Sullivan et al., 2011) that are abundant in some NSB amphibolites. Garnet has a high affinity for Lu and a low partition coefficient for Hf, resulting in a mean $^{176}\text{Lu}/^{177}\text{Hf}$ ratio in crustal garnets $>1$ (Duchêne et al., 1997; Herwartz et al., 2011). If these garnets were formed from exogenous metamorphic fluids, which is not a trivial issue as both internal and external fluids can be involved in metamorphism (Kohn et al., 1997), the Lu-Hf chronometer should have been significantly disturbed compared to the Sm-Nd system. This is not seen in the data. Rare-earth element (REE) patterns also would show such a disturbance, which is not observed either, and indicates that garnet mostly formed in a closed system in response to metamorphism. O’Neil et al. (2008, 2012) have also argued that the 3800 Ma age given by the $^{147}\text{Sm-}^{143}\text{Nd}$ system may have been due to a small shift in the Sm/Nd ratios that did not affect the $^{146}\text{Sm-}^{142}\text{Nd}$ age. It seems fortuitous then that the Lu-Hf system, also disturbed by metamorphism, would yield exactly the same age. The explanations provided by O’Neil et al. (2008, 2012) for the discordance between $^{147}\text{Sm-}^{143}\text{Nd}$ and $^{146}\text{Sm-}^{142}\text{Nd}$ are in contradiction with the Lu-Hf isotope results.

Recently, O’Neil et al. (2012) reported on a group of Nuvvuagittuq amphibolites that give a $^{147}\text{Sm-}^{143}\text{Nd}$ isochron age of 4272±150 Ma and a $^{146}\text{Sm-}^{142}\text{Nd}$ age of 4403 Ma; the two ages are consistent within analytical uncertainties. However, the sole criterion used to select the best preserved rocks that define these ages is depleted mantle model ages with $T_{DM}$
between 4200 and 4400 Ma. A sample described by the authors as “the least disturbed” was actually rejected in their analysis because it was not isochronous between the two Sm-Nd chronometers. Without this sample an even better agreement is obtained between the $^{147}\text{Sm}$-$^{143}\text{Nd}$ and $^{146}\text{Sm}$-$^{142}\text{Nd}$ systems with ages now of, respectively, $4321 \pm 160$ Ma and $4406^{+14}_{-17}$ Ma. It is noteworthy that these ages are defined by only nine samples selected from the pool of 56 amphibolites that form the overall correlation between $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ for the NSB. Taking all the evidence together, we consider the filtering approach of O’Neil et al. (2012) to be problematic and that 3800 Ma is the best age estimate for the emplacement time of the NSB rocks. This is because of its consistency with the Sm-Nd, Lu-Hf and U-Pb isotope systematics cited above. In the following sections, we explore how the varying age results for the NSB derived from the different short- and long-lived chronometers can be reconciled.

### 4.4.2 Significance of the $^{142}\text{Nd}$ anomalies in light of U-Pb and Lu-Hf chronology

If 3800 Ma is taken as the emplacement age for the NSB, interesting implications arise for the significance of anomalous $^{142}\text{Nd}/^{144}\text{Nd}$ signatures. By this late time in Earth history, such anomalies could not have formed by radiogenic ingrowth within the rocks themselves because the parent $^{146}\text{Sm}$ was already extinct well before 4200 Ma. In this case the anomalous ratios must have been inherited from a Hadean source or contaminant (Roth et al., 2013a). As discussed by O’Neil et al. (2008, 2012), the central argument in favor of a Hadean age for the NSB has been the correlation between $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$. This correlation can, however, be interpreted as a mixing line instead of an isochron. Like the positive anomalies reported for rocks in the ISB, the negative anomalies in the NSB could have been inherited from their mantle sources or derived from a crustal source. It is also possible that they originate from mantle-derived material that defines a mantle isochron; this seems to be the case for samples from the ISB (Caro, 2011) even though $^{142}\text{Nd}/^{144}\text{Nd}$ and Sm/Nd are not as well correlated there as in Nuvvuagittuq (Roth et al., 2013a).

There are compelling reasons to assume that the $^{146}\text{Sm}$-$^{142}\text{Nd}$ system records a mixing event. Although $^{146}\text{Sm}$ was already extinct well before NSB emplacement in the Eoarchean, the long-lived $^{147}\text{Sm}$-$^{143}\text{Nd}$ and $^{176}\text{Lu}$-$^{176}\text{Hf}$ chronometers could still form a positive correlation and therefore provide an age close to the true crystallization age because their present-day Hf and Nd isotope variations are dominated by radiogenic ingrowth. The short-lived $^{146}\text{Sm}$-$^{142}\text{Nd}$ chronometer evolved so rapidly while it was alive that the Hadean crust contaminant would have had a $\mu^{142}\text{Nd}$ value well below that of the BSE. In such a case it would be highly resolvable in the mixture. This would not necessarily be the case for the long-lived Sm-Nd and Lu-Hf chronometers, especially after billions of years of radiogenic accumulation subsequent to the mixing event. To explore this further, we examined the relationships between the Lu-Hf and Sm-Nd couples, as well as their relationships with
other high-field-strength elements (HFSE) and REE. The latter are relatively insensitive to alteration and metamorphism and are good tracers of both magmatic and mixing processes.

**Relationship between the Lu-Hf and Sm-Nd isotope systems**

When present-day Hf isotope compositions and \(^{176}\text{Lu}/^{177}\text{Hf}\) ratios of all NSB rocks are plotted against Zr content (used here as an indicator of enrichment), it appears that the Lu-Hf distribution vs. Zr content follows the parent/daughter ratio with Hf isotope variations being fully controlled by radiogenic ingrowth (Fig. 4.3). This relationship also holds true for the \(^{147}\text{Sm}-^{143}\text{Nd}\) system. Another observation is that when \(\epsilon_{\text{Hf}}\) is plotted as a function of \(\epsilon_{\text{Nd}}\) at 3800 Ma (considered as initial values) for the amphibolite samples only, a mixing hyperbola emerges from the data (Fig. 4.4a). The samples plot along a mixing curve and amphibolite sample IN08023 coherently plots on the hyperbola with a composition that corresponds to the unradiogenic end-member. The same hyperbola also exists between Hf isotopes and \(^{142}\text{Nd}/^{144}\text{Nd}\) (Fig. 4.4b). As a consequence, we can infer that these relationships reflect initial source heterogeneities from likely non-cogenetic rocks.

**A mixing model for the NSB source**

The well-defined hyperbola that appears from the data in Hf-Nd isotope space in Fig. 4.4 favors the hypothesis that the \(^{142}\text{Nd}\) anomalies were inherited from the mixing of two distinct reservoirs which gave rise to the protoliths of the NSB amphibolites. One was an enriched reservoir that carried the low \(^{142}\text{Nd}/^{144}\text{Nd}\) anomalies, and the other was a normal BSE-like reservoir. To identify likely geological candidates for the end-member reservoirs, both isotopic and elemental parameters must be considered. Two plausible geological scenarios that can account for the data are considered here: (1) interaction of two NSB magmas, with one originating from an enriched mantle reservoir with low \(^{142}\text{Nd}/^{144}\text{Nd}\); and (2) assimilation of ancient preserved enriched felsic Hadean crust or sub-continental lithospheric mantle. The question is whether the Nuvvuagittuq rocks were sourced from a normal BSE mantle without a \(^{142}\text{Nd}\) anomaly and then subsequently experienced contamination by an enriched reservoir carrying a low \(^{142}\text{Nd}/^{144}\text{Nd}\) signature, or whether they tapped two distinct mantle domains (including one with a negative \(^{142}\text{Nd}\) anomaly) which then subsequently commingled? The enriched end-member \(^{143}\text{Nd}/^{144}\text{Nd}\) value on the mixing hyperbola is close to 0.50773 (Fig. 4.4a), which is not only the asymptote on the x-axis of the covariant plot but also the initial composition deduced from the regression line through the Roth *et al.* (2013a) data in \(^{143}\text{Nd}/^{144}\text{Nd}-^{147}\text{Sm}/^{144}\text{Nd}\) space. Although the \(^{176}\text{Hf}/^{177}\text{Hf}\) composition of this contaminant is undefined, the compositions of the amphibolite groups provide some clues.

O’Neil *et al.* (2011) and Cates *et al.* (2012) defined different cummingtonite-amphibolite groups (“low-” and “high-TiO\(_2\)”) based on their bulk major element compositions. The
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Fig. 4.3 Diagrams showing the distribution of mafic and felsic lithologies as a function of Zr contents in ppm for (a) $^{176}\text{Lu}/^{177}\text{Hf}$ (b) $^{176}\text{Hf}/^{177}\text{Hf}$ (c) $^{147}\text{Sm}/^{144}\text{Nd}$ (d) $^{143}\text{Nd}/^{144}\text{Nd}$. The Lu-Hf data are from this study and the Sm-Nd data are from Roth et al. (2013a). Note the similar data distribution between diagrams (a) and (b) and diagrams (c) and (d), which indicates that the present-day Hf and Nd isotope compositions are dominated by radiogenic ingrowth.

Mafic protoliths of these populations were necessarily sourced in two distinct mantle domains and the least and the most radiogenic of the amphibolite samples reported here belong to the “low-” and the “high-TiO$_2$” groups, respectively. End-members of the Hf-Nd mixing hyperbola could correspond to these two magma series. When the mixing hypothesis is tested, it is found that the calculated mixing hyperbola follows the data (Fig. 4.4). The curvature of the hyperbola is determined by dividing the ratios of the respective denominators of each end-member (Langmuir et al., 1978), i.e., $(^{177}\text{Hf}/^{144}\text{Nd})_2 / (^{177}\text{Hf}/^{144}\text{Nd})_1$ and thus, $(\text{Hf/Nd})_2 / (\text{Hf/Nd})_1$.

Accordingly, the absolute concentrations of Hf and Nd in the samples strongly affect the curvature of the mixing hyperbola. The “low-TiO$_2$” amphibolites IN08023 and IN08012, which are also the least radiogenic in our sample set, have approximately five times more Nd and four times more Sm, respectively, than the other amphibolites. The Lu and Hf concentrations are not very different among the various amphibolites, and taken together this
Fig. 4.4 Hafnium and $^{143}{\text{Nd}}/^{144}{\text{Nd}}$ isotope plots for initial compositions of Nuvvuagittuq amphibolites calculated at 3800 Ma (black diamonds). Panel (a) shows a well-defined mixing hyperbola between $^{176}{\text{Hf}}/^{177}{\text{Hf}}$ and $^{143}{\text{Nd}}/^{144}{\text{Nd}}$ also seen in panel (b) showing a less well-defined hyperbola between $^{176}{\text{Hf}}/^{177}{\text{Hf}}$ and $^{142}{\text{Nd}}/^{144}{\text{Nd}}$. The Nd isotope data are from Roth et al. (2013a). Also shown are the calculated results for variable degrees of theoretical mixing between the two extreme amphibolite compositions (grey squares) assuming they represent the two end-members.
4.4 Discussion

\[ \mu_{142}^{\text{Nd}} \] (ppm)

Fig. 4.5 $^{142}\text{Nd}$ anomalies as a function of (a, b) HFSE and (c) REE contents. Data are from O’Neil et al. (2008) and correspond to the low-TiO$_2$ groups (depleted and enriched) only. Note the relatively good correlation between anomalies and element concentrations indicative of a continuum between these two low-TiO$_2$ sub-groups. Also reported in panel b is the range of likely Hf and Zr concentrations for the most pristine (uncontaminated) BSE-like rock group. In this same panel, the Zr and Hf scales have been set so that any vertical line has the chondritic value of 37 (Jochum et al., 1986).

Such compositions resemble ultramafic magmas such as komatiites (Arndt, 2008). Ultramafic rocks with flat REE patterns (similar to the “high-TiO$_2$” group) have been documented in the NSB (Cates & Mojzsis, 2007) and the few samples of this kind analyzed for $\mu^{142}\text{Nd}$ (O’Neil et al., 2008, 2012) have the closest-to-BSE, or slightly supra-BSE, compositions among the NSB rocks in both $^{142}\text{Nd}/^{144}\text{Nd}$ ($\mu^{142}\text{Nd} = 0$) and $^{147}\text{Sm}/^{144}\text{Nd}$.

The “low-TiO$_2$” group NSB amphibolites that carry negative $^{142}\text{Nd}$ anomalies have REE patterns which resemble depleted peridotite that was later re-fertilized to yield subchondritic Sm/Nd ratios (O’Neil et al., 2011) (Fig. 4.6). Even a “low-TiO$_2$” amphibolite sample with the least re-fertilized REE pattern (sample PC-230 in O’Neil et al. (2008)) has a $^{142}\text{Nd}$ deficit of -6.8 ppm, which is consistent with its subchondritic Sm/Nd ratio. Data in Fig. 4.6 show that
**Fig. 4.6** Panel (a) shows chondrite-normalized (Sun & McDonough, 1989) REE patterns for the low-TiO$_2$ amphibolite samples of O’Neil *et al.* (2008). Panel (b) shows the relationship (positive correlation) between $^{142}$Nd anomalies and $^{147}$Sm/$^{144}$Nd for the samples of O’Neil *et al.* (2008) also presented in panel (a), and the samples of Roth *et al.* (2013a). Panel (c) shows chondrite-normalized REE patterns, from Cates *et al.* (2012), which correspond to amphibolite samples analyzed for Sm-Nd isotopes by Roth *et al.* (2013a). Note the large range of spectra in panel (a) ranging from light to middle REE depletion (black diamonds) to enrichment of light to heavy REE (white diamonds). This spectrum is also reflected in panel (b) where the global enrichment in REE (translated into the Sm/Nd ratio) seems to correlate with the size of $^{142}$Nd anomalies. Also shown is the field of isotopic compositions displayed by the felsic units in the NSB described as either TTG intrusive sheets Cates & Mojzsis (2007) or felsic bands (O’Neil *et al.*, 2008). Figure (c) illustrates the difference between high-TiO$_2$ relatively flat (grey shaded circles) and low-TiO$_2$ fractionated (white circles) REE patterns for rocks analyzed in this study.

An increase of LREE compared to HREE (translated into an increase in La/Yb) is associated with larger $^{142}$Nd deficits, decreasing Sm/Nd, and an increase in total REE content. It is likely then that the $^{142}$Nd anomalies developed in the “low-TiO$_2$” mantle source of these amphibolites after re-fertilization rather than being acquired through contamination with an enriched reservoir. The “low-TiO$_2$” source was already enriched, and even the least enriched amphibolites have Sm/Nd ratios below BSE. This episode of re-fertilization necessarily has to have occurred early in Earth history to be recorded in the form of $^{142}$Nd anomalies. Therefore, the conclusion is that the positive correlation between $^{142}$Nd/$^{144}$Nd and $^{147}$Sm/$^{144}$Nd stems from the combined effect of Hadean mantle re-fertilization and mixing between the “low-”
(negative anomalies) and “high-TiO$_2$” (BSE composition) amphibolite sources at the time the NSB was formed at ca. 3800 Ma. Later metamorphic events modified the apparent slope of Sm-Nd and Lu-Hf isochrons as detailed in Roth et al. (2013a), while still preserving the mixing hyperbola (Fig. 4.4).

The inferred proportions of mixing between the hypothesized end-members are too substantial to match a scenario of straightforward contamination by later assimilation of one group by the other because the allowable limit of $\sim$20% (Bohrson & Spera, 2001; Reiners et al., 1995) is exceeded (Fig. 4.4). This means that the two groups were contemporaneous magmas able to mix in high proportions, which in turn justifies the use of the scatterchron to determine an average age for the NSB rocks. The magma mixing processes assumed for the Nuvvuagittuq rocks are similar to those commonly seen in recent magmatic provinces (Cantagrel et al., 1984), and also discussed in detail by Perugini & Poli (2012).

4.4.3 Age of the re-fertilization event

An important parameter for understanding Earth’s early history is the age of the fractionation event that must have occurred in the Hadean in order to allow for the development of the observed $^{142}$Nd anomalies. The age derived from the correlation between $^{142}$Nd/$^{144}$Nd and $^{147}$Sm/$^{144}$Nd cannot date this event because it has been shifted towards a younger age (Roth et al., 2013a). Therefore, a solution must be found to a two-stage model that simultaneously solves for the initial $^{143}$Nd/$^{144}$Nd, $^{142}$Nd/$^{144}$Nd, and $^{176}$Hf/$^{177}$Hf ratios, which corresponds to three unknowns (Sm/Nd, Lu/Hf, and the time of fractionation, $T_f$). A least-squares equation was used to minimize the differences between the target and calculated values such that these differences do not exceed the analytical uncertainties and iteratively converge to the solution. In this model, it was assumed that the time spent between the depletion and later re-fertilization episodes corresponds to a single fractionation event to match a simple two-stage model. It was further assumed that the silicate mantle before fractionation at $T_f$ had a composition equivalent to that of the non-chondritic BSE of Caro & Bourdon (2010); this corresponds to the composition of the mantle after formation of a hidden reservoir or via collisional erosion (O’Neill & Palme, 2008). The decay constant of Kinoshita et al. (2012) was used for these new $^{146}$Sm-$^{142}$Nd isotope system calculations. The best solution obtained by iteration gave 4510 Ma as the time of the fractionation event, while the derived result for $^{147}$Sm/$^{144}$Nd (≈0.20) was only slightly lower than BSE, and $^{176}$Lu/$^{177}$Hf was equal to 0.0268 (see Fig. 4.7). This latter value is significantly below BSE.

4.4.4 Early history of the enriched reservoir and possible link with worldwide $^{142}$Nd anomalies

Although the exact re-fertilization protagonist(s) cannot be identified based on the present data, some useful observations can still be made. Prior to the re-fertilization event (estimated
Fig. 4.7 Schematic $^{176}\text{Lu}/^{177}\text{Hf}$ (a) and $^{147}\text{Sm}/^{144}\text{Nd}$ (b) evolution diagrams showing the enriched mantle source history before the actual formation of the NSB at ca. 3800 Ma. In this model, the NSB mantle source first evolved with a BSE composition until it was fractionated during crystallization of a terrestrial magma ocean in the presence of Ca- and Mg-perovskite (event 1). It was then re-fertilized at $T_f$ (4510 Ma corresponding to event 2) and subsequently evolved in a closed system to develop $^{142}\text{Nd}$ anomalies until NSB formation. Also shown are the $^{176}\text{Lu}/^{177}\text{Hf}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ values of the NSB high-TiO$_2$ amphibolite source together with the same parameters for the source of the Isua amphibolites (see text for more details). The BSE values were taken from Caro & Bourdon (2010). Note that the slopes of parent/daughter evolution through time are not to scale for the sake of clarity.

to take place around 4510 Ma), the mantle source that hosted $^{142}\text{Nd}$ anomalies must have been significantly fractionated. Yet, the exact cause for fractionation remains unclear and probably corresponds to partial melting of a primitive mantle-like source.

As both positive and negative $^{142}\text{Nd}$ anomalies have been reported for ancient terrestrial
rocks that counterbalance each other to yield the BSE composition, it is legitimate to ask whether the two types of anomalies are genetically related or complementary. An interesting outcome of the model is that the fractionation followed by a re-fertilization event changed the mantle $^{176}\text{Lu}/^{177}\text{Hf}$ ratio by 29% relative to BSE (0.0268), while the $^{147}\text{Sm}/^{144}\text{Nd}$ ratio was changed by only 4% compared to BSE (0.200) as illustrated in Fig. 4.7. This incongruence between Lu/Hf and Sm/Nd cannot simply be explained by melt extraction or re-fertilization involving mineral assemblages that fractionate elements in ways similar to those of the ambient upper mantle. Therefore, as suggested by Caro et al. (2005); Hoffmann et al. (2011); Rizo et al. (2011), the observed decoupling between the Sm-Nd and Lu-Hf isotope systems could instead originate from an earlier event of Ca- and Mg-perovskite fractionation in the lower mantle (note that the actual mode of Ca-perovskite would not need to be large, e.g. Caro et al. (2005)), which would be consistent with the direction and amplitude of the observed Hf-Nd decoupling. To account for the decoupling in the NSB enriched source, it is assumed here that the mantle source prior to re-fertilization already had fractionated Lu/Hf and Sm/Nd ratios similarly to what is observed for the source of Isua amphibolites. The re-fertilization event hence would not have actually fractionated Sm/Nd relative to Lu/Hf but only lowered these ratios from the initially supra-BSE $^{147}\text{Sm}/^{144}\text{Nd}$ and sub-BSE $^{176}\text{Lu}/^{177}\text{Hf}$ ratios (Fig. 4.7). As a result, when calculating the time-integrated $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ ratios for the Isua amphibolite source (using the data of Rizo et al. (2011) for consistency between the two isotope systems) we find, respectively, 0.215 and 0.0311. If these ratios are compared to those inferred from the NSB enriched source, it follows that the re-fertilization event further fractionated the $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ ratios relative to the Isua amphibolite source by, respectively, 7 and 14%. These results are in accord with what would be expected as the outcome of a re-fertilization process. It seems that the Isua and Nuvvuagittuq amphibolites sources shared a common early history that may be linked to the consequences of crystallization of an early deep magma ocean, which is also consistent with the old age obtained for the value of $T_f$ (Fig. 4.7). The NSB source possibly was located at shallower depths within the mantle and was affected by re-fertilization at ca. 4510 Ma; as a consequence, the histories of Isua and Nuvvuagittuq subsequently diverged.

4.5 Conclusions

This study presents new Lu-Hf isotope data for Eoarchean rocks from the Nuvvuagittuq supracrustal belt that integrates the data with other radiogenic systems (Sm-Nd, U-Pb) and trace element compositions of metavolcanic and metasedimentary rocks. Results indicate an emplacement age of 3864±70 Ma for the Nuvvuagittuq supracrustal belt (both mafic and felsic lithologies) that is in agreement with $^{147}\text{Sm}/^{143}\text{Nd}$ (David et al., 2009; O’Neil et al., 2008; Roth et al., 2013a) and zircon U-Pb ages (Cates & Mojzsis, 2007, 2009; Cates et al., 2012; David et al., 2009). This age is best interpreted as the mean age of the different samples
analyzed and not as a strict isochron because it is recognized that the analyzed samples are likely not co-genetic. The Nuvvuagittuq supracrustal belt, however, is old enough for its isotope compositions to be dominated by radiogenic ingrowth, which is sensitive to significant age variations. Hafnium and Nd isotope systematics calculated at 3800 Ma reveal a well-defined mixing hyperbola. This mixing event possibly took place between the protoliths of the two NSB amphibolite groups identified by O’Neil et al. (2011) (cf. Cates et al. (2012)).

Owing to a clear difference and some variability in the REE patterns of each group, one cannot derive one group from the other by simple assimilation of evolved Hadean crust. Such a scenario fails to explain the existence of $^{142}$Nd anomalies nor can it reconcile the correlation between these anomalies and the Sm/Nd ratios of NSB rocks. Furthermore, we conclude that the $^{142}$Nd anomalies were not acquired through contamination of each amphibolite group by the same enriched Hadean crust, but instead the anomalies are endemic to one of the two sources. The “low-TiO$_2$” amphibolites (O’Neil et al., 2011) have the most pronounced $^{142}$Nd anomalies and always have Sm/Nd ratios lower than BSE. In addition, they have typical REE patterns of depleted mantle later re-fertilized in LREE with a large range of depletion and replenishment. We propose that the $^{142}$Nd anomalies developed in response to a re-fertilization process that happened in an already fractionated Hadean mantle source at 4510 Ma.
Table 1: Lu-Hf isotope data for samples from the Nuvvuagittuq supracrustal belt.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Sample name</th>
<th>Age (Ma)</th>
<th>[Hf]</th>
<th>[Lu]</th>
<th>176Lu/177Hf</th>
<th>176Hf/177Hf</th>
<th>ɛHf</th>
<th>ɛHf (3.8 Ga)</th>
<th>CHUR BSE</th>
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<tr>
<td>Amphibolite (Cummingtonite)</td>
<td>INO8012 3864</td>
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<td>0.28033</td>
<td>-0.3</td>
<td>0.05</td>
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<td>0.0739</td>
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<td>0.28033</td>
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<td>0.28034</td>
<td>-59.4</td>
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<td>0.28037</td>
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New $^{147,146}$Sm-$^{143,142}$Nd constraints on the lifetime of early terrestrial crust

Abstract

Primordial planetary differentiation may have played a critical role in determining the composition of the oldest crustal rocks. Inherited $^{142}$Nd anomalies in Archean rocks are vestiges of early mantle-crust differentiation during Hadean times. Here, we report new whole-rock $^{147,146}$Sm-$^{143,142}$Nd data for the ancient Acasta Gneiss Complex in the Slave Province (Canada). Our $^{147}$Sm-$^{143}$Nd data combined with those of Bowring & Housh (1995) and Moorbath et al. (1997) define an age of $3371 \pm 141$ Ma (2 SD) and yield initial $\epsilon^{143}$Nd of $-5.6 \pm 2.1$. This is at odds with older zircon U-Pb ages of up to ca. 3960 Ma. Ten of our thirteen samples show $^{142}$Nd deficits of $-9.6 \pm 4.8$ ppm (2 SD) relative to modern terrestrial value. This age discrepancy can be reconciled by Nd isotope equilibration of rocks in closed system (Roth et al., 2013a) during metamorphic perturbations of Acasta at ca. 3400 Ma (Moorbath et al., 1997; Whitehouse et al., 2001). A model age of ca. 4310 Ma is derived for the early enrichment of the oldest ca. 3960 Ma Acasta rocks. Two compositional end-members can be identified in Acasta: a felsic composition with $^{142}$Nd/$^{144}$Nd identical to the modern terrestrial value, and a mafic one with $^{142}$Nd/$^{144}$Nd as low as $-14.1$ ppm. The ca. 4310 Ma Hadean crustal source of Acasta is 190 Ma younger than those observed in Nuvvuagtituq (Roth et al., 2013a) and Isua (Rizo et al., 2012) and did not show decoupled Nd-Hf patterns that were attributed to the crystallization of an early magma ocean. The Acasta signature can be attributed to the formation of an early crust during Hadean times and shows that early crust could be preserved for at least 350 Ma.

5.1 Introduction

The last vestiges of Hadean silicate differentiation are preserved in Archean rocks, notably in the form of anomalies in the abundance of radiogenic $^{142}$Nd due to the decay of the short-lived $^{146}$Sm [half-life $T_{1/2} = 68$ million years (Ma) (Kinoshita et al., 2012)]. Small variations in $^{142}$Nd resulted from limited fractionation of Sm-Nd during magmatic processes that happened prior to about 4100 Ma and from the initially low abundance of $^{146}$Sm. Yet, A version of this chapter will be published in Earth and Planetary Science Letters as: Roth, A.S.G., Bourdon, B., Mojzsis, S.J., Guitreau, M. & Blichert-Toft, J. New $^{147,146}$Sm-$^{143,142}$Nd constraints on the lifetime of early terrestrial crust.
the $^{146}\text{Sm}-^{142}\text{Nd}$ chronometer is a unique and sensitive tracer of early silicate Earth differentiation and it is often assumed that this system is less affected by later events, unlike the $^{147}\text{Sm}-^{143}\text{Nd}$ system. Modeling of the combined $^{146}\text{Sm}-^{142}\text{Nd}$ and $^{147}\text{Sm}-^{143}\text{Nd}$ systematics in the Nuvvuagittuq Supracrustal Belt in Québec (Canada) has shown that later perturbations could have disturbed early radiogenic signatures preserved in the oldest rocks (Roth et al., 2013a) and thus cause interpretational issues. One possible approach to overcome this problem is to combine several radiochronometers, such as the long-lived $^{176}\text{Lu}-^{176}\text{Hf}$ systems together with U-Pb zircon geochronology. The ancient Acasta Gneiss Complex is a key Eoarchean locality where such an integrated approach could help to resolve possible Hadean processes. Unresolved issues concerning Acasta are the discrepancy between old ca. 4000 Ma U-Pb zircon ages and the younger ca. 3400 Ma $^{147}\text{Sm}-^{143}\text{Nd}$ record, and the implication of the very enriched (unradiogenic) $^{143}\text{Nd}$ composition of the protoliths.

The Acasta Gneiss Complex in the westernmost Slave Province (Canada) is the oldest outcrop of continental crust discovered so far. Acasta is the remnant of a late-Hadean/Eoarchean terrane, consisting of a complex assemblage of geological units with different igneous protolith ages (Bowring et al., 1989b; Bowring & Housh, 1995; Bleeker & Stern, 1997; Stern & Bleeker, 1998; Bowring & Williams, 1999; Sano, 1999). Acasta gneisses have zircon U-Pb crystallization ages that fall into three groups: 4030-3940 Ma, 3740-3720 Ma, and 3600 Ma for the granitoid gneisses; and 4000 Ma and 3600 Ma for the plagioclase-hornblende schists (Iizuka et al., 2007). Remarkably, the oldest rocks preserved zircon xenocrysts with ages of up to 4200 Ma (Bowring & Williams, 1999; Iizuka et al., 2006).

Based on their $^{147}\text{Sm}-^{143}\text{Nd}$ study of two Acasta samples, Bowring et al. (1989a) reported a CHUR (chondritic uniform reservoir) model age of 4100 Ma and an initial $\epsilon^{143}\text{Nd}$ at 3700 Ma of -4.8. This age was the oldest chondritic model age reported for a terrestrial sample and it provided evidence for the preservation of an early strongly-enriched crust. Comprehensive whole-rock $^{147}\text{Sm}-^{143}\text{Nd}$ systematics for Acasta, however, yielded a much younger age of ca. 3300 Ma (Bowring & Housh, 1995; Moorbath et al., 1997). This errorchron was interpreted as either the age of resetting of the $^{147}\text{Sm}-^{143}\text{Nd}$ chronometer, corresponding to a large scale Nd-isotope homogenization of Acasta at ca. 3300 Ma (Moorbath et al., 1997; Whitehouse et al., 2001), or a mixing line with no age significance (Bowring & Housh, 1995). Bowring et al. (1990) and Bowring & Housh (1995) attributed the large range in initial $\epsilon^{143}\text{Nd}$ from -4.8 to +3.6 (calculated using the ages given by zircon U-Pb geochronology) to major Hadean mantle heterogeneities. In contrast, Moorbath et al. (1997) and Whitehouse et al. (2001) argued that the resetting of the Sm-Nd system makes the calculation of initial $\epsilon^{143}\text{Nd}$ based on zircon U-Pb ages geologically meaningless. They interpreted the negative initial $\epsilon^{143}\text{Nd}$ value of -5.7±0.7 calculated with the age given by the $^{147}\text{Sm}-^{143}\text{Nd}$ errorchron as an independent support for an early enrichment of Acasta protoliths.

The first $^{146}\text{Sm}-^{142}\text{Nd}$ studies of Acasta showed no evidence for early differentiation. McCulloch & Bennett (1993) and Caro et al. (2006) conducted $^{142}\text{Nd}$ measurements on three
5.2 Geological setting and sample description

Acasta samples, 92-179, SP-405, and SM/Ac/18 and reported $^{142}\text{Nd}/^{144}\text{Nd}$ identical to the modern terrestrial composition. Samples 92-179 and SP-405 were two granitoid gneisses with zircon U-Pb age of 3962±3 Ma (Bowring et al., 1989a; Williams et al., 1992) and with $\epsilon^{143}\text{Nd}$ at 3962 Ma of +2.5 and +0.8, respectively (Bowring et al., 1990). SM/Ac/18 was a hornblende-plagioclase schist with $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.1212 and 0.510721, respectively (Moorbath et al., 1997).

Iizuka et al. (2009) subsequently reported in situ Lu-Hf isotope analyses of zircons from five granitoid gneisses with ages between ca. 3590 to 3970 Ma. Magmatic zircons yielded negative initial $\epsilon^{176}\text{Hf}$ of -6.1 to -1.2. This was consistent with the presence of zircon xenocrysts in these rocks (Iizuka et al., 2006, 2007), and suggested that some of them were formed from Hadean crust that had been reworked during the Eoarchean.

To better understand the formation history of the Acasta Gneiss Complex and thereby the significance of discordant $^{147}\text{Sm}-^{143}\text{Nd}$ and zircon U-Pb ages of these rocks, high-precision whole-rock $^{147},^{146}\text{Sm}-^{143},^{142}\text{Nd}$ were obtained on samples that had already been studied in detail for Hf isotopes in zircons and whole-rocks by Guitreau (2013). The new $^{147},^{146}\text{Sm}-^{143},^{142}\text{Nd}$ systematics were compared to literature $^{147}\text{Sm}-^{143}\text{Nd}$ (Bowring & Housh, 1995; Moorbath et al., 1997) and $^{146}\text{Sm}-^{142}\text{Nd}$ (McCulloch & Bennett, 1993; Caro et al., 2006) data for Acasta and to the new Lu-Hf isotope data (Guitreau, 2013). The principal goals of our study were 1) to assess if Acasta rocks preserved $^{142}\text{Nd}$ evidence for early differentiation, 2) to trace the Acasta source using $^{147},^{146}\text{Sm}-^{143},^{142}\text{Nd}$ systematics in light of the new Lu-Hf isotope data, and 3) to reassess the lifetime of early terrestrial crust during the Eoarchean and Archean periods.

5.2 Geological setting and sample description

The Acasta Gneiss Complex was discovered in the early 1980s during regional mapping by the Geological Survey of Canada (King, 1985; St-Onge et al., 1988). It is located at the western margin of the Slave Province approximately 300 km north of Yellowknife in the Northwest Territories of Canada. The extent of Acasta is unknown but probably far exceeds 25 km$^2$ across several domal basement antiforms. Only small areas of one of these domes have been investigated in fine detail (Cates et al., 2013).

Our sample set comprises eleven granitoid gneisses and two hornblende-plagioclase schists. We selected these rocks for their old Eoarchan U-Pb zircon age (Cates et al., 2013; Guitreau, 2013) or low negative initial $\epsilon^{176}\text{Hf}$ (Guitreau, 2013), which suggested that they might have preserved $^{142}\text{Nd}$ evidence for early differentiation. Granitoid gneisses are quartz-, hornblende- and biotite-bearing rocks and can be separated into (i) “silica-poor” tonalitic series with SiO$_2$ \leq 60 wt.% (AG09008 and AG09017), (ii) “intermediate” tonalitic with 65-70 wt.% SiO$_2$ (AG09014 and AG09016), and (iii) granitic with SiO$_2$ \geq 70 wt.% (AG09009). Our samples have typical tonalite-trondhjemite-granodiorite compositions with LREE enrichments and
HREE depletions (normalized to chondrite), small negative Eu anomalies and negative Nb and Ti anomalies relative to the primitive mantle. Hornblende-plagioclase schists are silica poor (∼44 wt.% SiO₂) and have comparatively flat LREE/HREE patterns, positive Eu anomalies, small positive Nb and large positive Ti anomalies relative to primitive mantle. This indicates that the protolith of these rocks was a cumulate. More detailed lithological descriptions of the samples are given in Cates et al. (2013) and Guitreau (2013).

U-Pb zircon ages of our samples (Cates et al., 2013; Guitreau, 2013) fall into the three age groups, as defined by Iizuka et al. (2007). The oldest granitoid gneisses AG09005, AG09006, AG09017, AG09030, AG09031, AG09016, and AG09008g have an age of ca. 3960 Ma; the granitoid gneisses AG09001 and AG09008 an intermediate age of ca. 3750 Ma; and the youngest granitoid gneisses AG09014 and AG09022 an age of ca. 3600 Ma. The plagioclase-hornblende schists AG09017N and AG09020 have an age of ca. 3960 Ma similar to the oldest granitoid gneisses.

5.3 Methods

5.3.1 Chemical separation of Sm and Nd

Samarium and Nd were separated from bulk rock samples by ion-exchange chromatography (Caro et al., 2006; Roth et al., 2013a). About 100-250 mg of powdered rocks (equivalent to about 1 µg of Nd) were digested in concentrated HF-HNO₃ and then taken up in HNO₃-HClO₄ to redissolve insoluble fluorides. The residues were subsequently completely dissolved in 6M HCl. Iron was reduced with ascorbic acid to avoid later competition between the REE and trivalent Fe on the ion exchange columns. The REE were first 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 (heptane). The organic solvent was pipetted out from the Ce-free aqueous phase and discarded. The Nd fraction was then cleaned on a AG50W-X8 cation exchange column that was 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.

5.3.2 Neodymium mass spectrometry

Neodymium was measured as a positive metal ion (Nd⁺) with the Thermo Triton (TIMS) at ETH Zurich (Roth et al., 2013a). About 500 ng of Nd per sample were ionized on double rhenium filaments with a ¹⁴²Nd ion beam intensity of about 7.5 volts (using 10¹¹ Ω feedback resistors). Instrumental mass bias was corrected for with an exponential law using ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219. Isobaric interferences of ¹⁴⁴,¹⁴⁸,¹⁵⁰Sm and ¹⁴²Ce were monitored with
147Sm and 140Ce, respectively, and corrected for online. The 142Ce/142Nd and 144Sm/144Nd ratios never exceeded 1.98 \times 10^{-6} and 1.05 \times 10^{-6}, respectively. A dynamic acquisition scheme using two magnet settings (corresponding to 145Nd and 143Nd in the central detector) allowed gain biases caused by the wearing out of Faraday detectors to cancel out. A more detailed description of the dynamic acquisition scheme is given in Roth et al. (2013b). The repeated 142Nd/144Nd measurements of the JNdi-1 standard over a period of three years (n = 94) yielded an external precision for the of ±5.1 ppm (2 SD) with a mean 142Nd/144Nd value of 1.1418351 ± 0.0000042 (Roth et al., 2013a). Over the course of this study, the external precision was ±4.3 ppm (2 SD, n = 13), with a mean 142Nd/144Nd value of 1.1418370 ± 0.0000049 for the JNdi-1 standard. The Nd isotopic compositions of Acasta samples and the JNdi-1 standards are reported in Table A.5.1.

5.3.3 Samarium and Nd concentrations

Samarium and Nd concentrations were determined by isotope dilution mass spectrometry. Aliquots of completely dissolved samples in 6 M HCl were spiked with an enriched, mixed 150Nd-149Sm 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 (Roth et al., 2013a). The concentrations of Sm and Nd in Acasta samples are reported in Table A.5.1.

5.4 Results

The new Acasta 147,146Sm-143,142Nd whole-rock data obtained for the eleven granitoid gneisses and two plagioclase-hornblende schists are reported in Table A.5.1.

In a 147Sm-143Nd isochron diagram (Fig. 5.1) our Acasta samples fall on the same array reported in Bowring & Housh (1995) and Moorbath et al. (1997). The 147Sm/144Nd ratios of our samples also show a broad range from very low (0.0741) to subchondritic values (0.1810). Likewise, 143Nd/144Nd ratios range from 0.509611 for the least radiogenic granitoid gneiss, to 0.512256 for the most radiogenic plagioclase-hornblende schist. The combined datasets define an errorchron with an age of 3371 ± 141 Ma and yield an initial 143Nd/144Nd value of 0.507976 ± 0.000106. This translates into an \((\epsilon_{143}^{143}Nd)\) of -5.6 ± 2.1 when normalized to CHUR (Bouvier et al., 2008) and -7.3 ± 2.1 using a superchondritic terrestrial composition as in Caro & Bourdon (2010).

In contrast to previous reports (McCulloch & Bennett, 1993; Caro et al., 2006), ten out of our thirteen Acasta samples have 142Nd anomalies. Figure 5.2 shows the 142Nd/144Nd ratios of our samples expressed as ppm deviations from the JNdi-1 standard (assumed to be equal to the modern terrestrial value). The three granitoid gneisses AG09001, AG09014, and AG09022 have 142Nd/144Nd identical within errors to the terrestrial standard. All other
Fig. 5.1 Long-lived $^{147}$Sm-$^{143}$Nd isochron diagram for the Acasta samples. The Acasta samples from this study (black symbols) were combined with those of Bowring et al. (1990), Bowring & Housh (1995) and Moorbath et al. (1997) (grey symbols). Data points have uncertainties about as large as the symbol size. The solid line represents the best fit to the combined datasets.

analyzed Acasta samples show resolvable $^{142}$Nd deficits from -6.0 to -14.1 ppm. When pooled together they have a $^{142}$Nd/$^{144}$Nd average of -9.6±4.8 ppm (2 SD).

In contrast to the $^{147}$Sm/$^{143}$Nd chronometer, the $^{142}$Nd/$^{144}$Nd data plotted against $^{147}$Sm/$^{144}$Nd (Fig. 5.3) for our Acasta samples do not define an errorchron. The three granitoid gneisses AG09001, AG09014, and AG09022 with $^{142}$Nd/$^{144}$Nd identical to the standard have very low $^{147}$Sm/$^{144}$Nd from 0.0741 to 0.0802. Acasta samples with $^{142}$Nd deficits have higher $^{147}$Sm/$^{144}$Nd from 0.0890 to 0.1810, corresponding to more mafic lithologies. When the Acasta samples are combined together they yield a $^{142}$Nd/$^{144}$Nd average of 1.141826±0.000006 (2 SD).

The $^{142}$Nd/$^{144}$Nd data plotted against major and trace element concentrations (Fig. 5.4) show systematic trends. The $^{142}$Nd/$^{144}$Nd data correlate positively with Nd, SiO$_2$, and Na$_2$O concentrations and negatively with Fe$_2$O$_3$, MgO and TiO$_2$ concentrations. The ca. 3960 Ma granitoid gneiss AG09016 with a low $^{142}$Nd/$^{144}$Nd of -12.4 ppm falls off all trends.
5.5 Discussion

5.5.1 $^{147}$Sm-$^{143}$Nd systematics

As shown by Moorbath et al. (1997), it cannot be fortuitous for undisturbed Acasta rocks with differences in U-Pb zircon ages of up to 400 Ma and differences in initial $\varepsilon^{143}$Nd of up to 8 (Bowring & Housh, 1995) to define a correlation in a $^{147}$Sm-$^{143}$Nd isochron diagram with the narrow spread of only 140 MSWD. Thus, we interpret the age of 3371±141 Ma defined by the $^{147}$Sm-$^{143}$Nd system (Fig. 5.1) as an errorchron that records the time of the last metamorphic event that homogenized Nd isotopes (Moorbath et al., 1997; Whitehouse et al., 2001). This age is similar to those of few zircon overgrowths that date high-grade...
New $^{147,146}\text{Sm-}^{143,142}\text{Nd}$ constraints on the lifetime of early terrestrial crust

Fig. 5.3 Short-lived $^{146}\text{Sm-}^{142}\text{Nd}$ isochron diagram for Acasta samples. The shaded area defines the external error of ±4.3 ppm (2 SD) of repeated measurements of the JNd1-1 standard (n = 13). Error bars are either the 2 SEM of multiple analyses or the 2 SD of the individual mass spectrometer run. The values of the super-chondritic bulk silicate Earth (BSE; Caro & Bourdon, 2010) and the chondritic uniform reservoir (CHUR; Bouvier et al., 2008) are shown for reference.

metamorphism and Pb loss from magmatic zircons (Bleeker & Stern, 1997). It also roughly agrees within uncertainties with the Lu-Hf age of 3681±352 Ma reported by Guitreau (2013) for the same samples. Negative initial $\epsilon^{143}\text{Nd}$ (Fig. 5.1) and $\epsilon^{176}\text{Hf}$ of -5.6±2.1 and -4.8±3.4 (Guitreau, 2013), respectively, indicate that $^{147}\text{Sm-}^{143}\text{Nd}$ and $^{176}\text{Lu-}^{176}\text{Hf}$ are coupled and record an early enrichment of the Acasta protoliths, although the $^{147}\text{Sm-}^{143}\text{Nd}$ system shows evidence for resetting.

5.5.2 $^{146}\text{Sm-}^{142}\text{Nd}$ systematics

Ten Acasta samples have $^{142}\text{Nd}$ deficits from -6.0 to -14.1 ppm and only three samples (AG09001, AG09014, and AG09022) have $^{142}\text{Nd}/^{144}\text{Nd}$ identical to the terrestrial standard, representing the bulk silicate Earth composition (Fig. 5.2). Notably, these three samples show the lowest $^{147}\text{Sm}/^{144}\text{Nd}$ ratios and thus correspond to the most felsic rocks we analyzed (Fig. 5.3). This more felsic character is also exemplified by the correlation of $^{142}\text{Nd}/^{144}\text{Nd}$ with major element concentrations (Fig. 5.4). Samples AG09014 and AG09022 have young zircon U-Pb ages of ca. 3600 Ma while sample AG09001 has an intermediate age of ca. 3750 Ma. All Acasta samples with $^{142}\text{Nd}$ deficits however show old ages of ca. 3960 Ma, except for sample AG09008 with an age of ca. 3750 Ma (Cates et al., 2013; Guitreau, 2013). Samples
5.5 Discussion

Fig. 5.4 $^{142}$Nd/$^{144}$Nd data plotted against Nd and major element concentrations. Only samples AG09008, AG09014, AG09016, AG09017, AG09017N, and AG09020 are plotted in $^{142}$Nd/$^{144}$Nd versus major element concentrations because chemical composition data for the other Acasta samples are not yet available. The labels correspond to the last figures of the sample names.
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AG09001, AG09014, and AG09022 were thus likely derived from a younger geological unit that inherited $^{142}$Nd/$^{144}$Nd ratios identical to the bulk silicate Earth.

The $^{146}$Sm-$^{142}$Nd systematic shows that the oldest Acasta rocks with an age of ca. 3960 Ma have a mean $^{142}$Nd deficit of -9.6±4.8 ppm (2 SD). These rocks likely inherited low $^{142}$Nd/$^{144}$Nd from an enriched Hadean source because the radioactive $^{146}$Sm was already extinct when they formed. The early enrichment of Acasta was already evidenced by $^{147}$Sm-$^{143}$Nd (Bowring et al., 1989a; Moorbath et al., 1997; Whitehouse et al., 2001) and $^{176}$Lu-$^{176}$Hf (Guitreau, 2013) in whole rock, $^{176}$Lu-$^{176}$Hf in zircons (Iizuka et al., 2009), and by the occurrence of up to ca. 4200 Ma zircon xenocrysts in the oldest rocks (Bowring & Williams, 1999; Iizuka et al., 2006). One should note that it was difficult to precisely define the age of enrichment corresponding to Sm/Nd fractionation simply based on the $^{147}$Sm-$^{143}$Nd chronometer because the Sm-Nd systematics of Acasta rocks are disturbed. Combining the $^{147}$Sm-$^{143}$Nd with $^{146}$Sm-$^{142}$Nd systems can now help to reassess this issue.

5.5.3 Coupled $^{147,146}$Sm-$^{143,142}$Nd systematics

The $^{147}$Sm-$^{143}$Nd systematics for Acasta rocks suggests that a metamorphic event homogenized at least partially the $^{143}$Nd/$^{144}$Nd ratios at ca. 3371 Ma. It is likely that the $^{142}$Nd/$^{144}$Nd ratios were also affected by this event. Our younger Acasta samples are characterized by the most felsic composition and the absence of $^{142}$Nd deficits. In contrast, our older Acasta samples all have more mafic compositions and show $^{142}$Nd deficits in a restricted range of -9.6±4.8 ppm (2 SD). This indicates that the partial resetting of $^{143}$Nd also possibly modified the $^{142}$Nd systematics. It is possible to numerically model these effects. For this purpose we used the numerical model of partial isotope equilibration for coupled $^{147,146}$Sm-$^{143,142}$Nd systematics described in Roth et al. (2013a). This model assumes that the rate of isotope exchange between several interacting phases depends on the difference in their isotope compositions. Solids interact with an aqueous fluid phase in a closed system. The metamorphic fluid is assumed to have a composition equal to that of the mean composition of the solids. 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 isotope exchange for phase i. The phase f
5.5 Discussion

represents the fluid phase that facilitates isotope exchange at grain boundaries. Two sets of such equations can be written for the $^{147}\text{Sm}-^{143}\text{Nd}$ and $^{146}\text{Sm}-^{142}\text{Nd}$ systems and solved simultaneously using a MATLAB™ script. The rocks were assumed to form at an arbitrary age $T_f$ and then were partially reset at ca. 3371 Ma. The age $T_f$ and the parameters $k_i$ were determined by iteration until the $^{147}\text{Sm}-^{143}\text{Nd}$ and $^{146}\text{Sm}-^{142}\text{Nd}$ model outputs (Fig. 5.5) matched the observations in Figures 5.1 and 5.3. An approximate formation age of ca. 4350 Ma was obtained for the Acasta protoliths. In this model, the metamorphic event that reset the $^{147}\text{Sm}-^{143}\text{Nd}$ at ca. 3371 Ma also strongly affected the $^{146}\text{Sm}-^{142}\text{Nd}$ system. Figure 5.5 shows that after partial reset, the $^{143}\text{Nd}$ age became ca. 3410 Ma and the $^{142}\text{Nd}$ age decreased to about 4100 Ma with an average $^{142}\text{Nd}$ composition of about -11 ppm. However, this age is only theoretical as the maximum relative difference in $^{142}\text{Nd}/^{144}\text{Nd}$ ratios between the samples with extreme Sm/Nd is up to 3 ppm, a difference that is analytically indistinguishable with current instrumentation. Initial $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{142}\text{Nd}/^{144}\text{Nd}$ ratios calculated at ca. 3371 Ma therefore represent the average isotopic compositions of Acasta after Nd-isotope homogenization.

Based on the calculated initial $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{142}\text{Nd}/^{144}\text{Nd}$ ratios at 3371 Ma, it is also possible to determine a model age of Sm-Nd fractionation starting from a BSE composition using a simple two-stage model for the Nd isotope evolution. For this purpose, we assume that the precursor material of Acasta evolved until the age of fractionation ($T_f$) with a BSE composition. At $T_f$, the formation of crust yields a new Sm/Nd ratio lower than that of the BSE. A model age of 4310 Ma and a $^{147}\text{Sm}/^{144}\text{Nd}$ fractionation of 0.1461 are obtained for the Acasta source by coupling the $^{147}\text{Sm}-^{143}\text{Nd}-^{142}\text{Nd}$ systematics and using initials $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.507958 and $^{142}\text{Nd}/^{144}\text{Nd}$ of 1.141826 for rocks with $^{142}\text{Nd}$ deficits. This corresponds to a $^{176}\text{Lu}/^{177}\text{Hf}$ ratio of 0.0144 when using an initial $^{176}\text{Lu}/^{177}\text{Hf}$ of 0.280260 for Acasta (Guitreau, 2013). One should note that the $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ fractionation values obtained for the Acasta source fall in the range of those measured in these rocks.

In summary, our modeling shows that the Sm-Nd systematics of the Acasta rocks can be explained by an early fractionation at 4310-4350 Ma followed by a later thermal event that has homogenized the Nd isotopes at ca. 3400 Ma. Similarly to the Nuvvuagittuq Supracrustal Belt (Roth et al., 2013a), the negative $^{142}\text{Nd}$ anomalies were inherited from the Hadean period and preserved within the crust.

5.5.4 A scenario for the formation of Acasta

Trends in $^{142}\text{Nd}/^{144}\text{Nd}$ data plotted against Nd and major element concentrations (Fig. 5.4) reveal that the Acasta protoliths consist of two end-members. One is felsic in composition and has a $^{142}\text{Nd}/^{144}\text{Nd}$ value identical to the modern BSE value. The other is mafic and characterized by lower SiO$_2$, Al$_2$O$_3$ and higher MgO and shows $^{142}\text{Nd}/^{144}\text{Nd}$ with a mean value of -9.6±4.8 ppm. Sample AG09016 with low $^{142}\text{Nd}/^{144}\text{Nd}$ of -12.4 ppm falls off all
5 New $^{147,146}$Sm-$^{143,142}$Nd constraints on the lifetime of early terrestrial crust

![Graph A]

![Graph B]

**Fig. 5.5** (A) Synthetic $^{147}$Sm-$^{143}$Nd isochron diagram showing (i) a closed system formed at ca. 4350 Ma (solid circles) and (ii) a system formed at ca. 4350 Ma and disturbed by a thermal event at ca. 3371 Ma (solid squares). The thermal event produces almost total isotope equilibration (see text for details) that shifts the slope of the isochron to yield a slope with an age of ca. 3410 Ma. (B) Synthetic $^{146}$Sm-$^{142}$Nd isochron diagram showing (i) a closed system formed at ca. 4350 Ma (solid circles) and (ii) a system formed at ca. 4350 Ma and disturbed by a thermal event at ca. 3371 Ma (solid squares). In the case of $^{146}$Sm-$^{142}$Nd, the age of the disturbed system becomes insignificant with an average $^{142}$Nd composition of -11 ppm.

trends and possibly represents an Eoarchean partial melt of the mafic end-member. In what follows, we focus on the origin of the mafic end-member.

Figure 5.6 represents $^{143}$Nd/$^{144}$Nd and $^{142}$Nd/$^{144}$Nd versus time diagrams corresponding to the isotope evolution of the Acasta protoliths. The early-enriched Hadean source of Acasta differentiated at 4310 Ma (see above for the model age estimate) from the BSE that had an $\epsilon^{143}$Nd of -25.3 and $^{142}$Nd/$^{144}$Nd of -27 ppm. The Acasta source evolved with lower
5.6 Implications

$^{143}\text{Nd}/^{144}\text{Nd}$ and $^{142}\text{Nd}/^{144}\text{Nd}$ ratios than those of the BSE owing to its low $^{147}\text{Sm}/^{144}\text{Nd}$ of 0.1461. Eoarchean Acasta rocks formed at 3960 Ma (zircon U-Pb age) from the enriched Hadean source that had $\epsilon^{143}\text{Nd}$ of -18.7 and a $^{142}\text{Nd}/^{144}\text{Nd}$ ratio of -10 ppm and evolved with $^{147}\text{Sm}/^{144}\text{Nd}$ ratios ranging from 0.0900 to 0.1800. This range in $^{147}\text{Sm}/^{144}\text{Nd}$ corresponds to measured values in our Acasta sample suite. The low $^{142}\text{Nd}/^{144}\text{Nd}$ of -10±5 ppm inherited by the mafic Acasta rocks did not further evolve because $^{146}\text{Sm}-^{142}\text{Nd}$ was already extinct at 3960 Ma. Acasta rocks were partially reset due to a metamorphic event at 3371 Ma (age of the $^{147}\text{Sm}-^{143}\text{Nd}$ errorchron, see Fig. 5.1) in a closed system. Their Nd-isotope compositions were homogenized to a mean value of $\epsilon^{143}\text{Nd}$ of -7.7±4.6 and $^{142}\text{Nd}/^{144}\text{Nd}$ of -10±5 ppm. Acasta rocks eventually evolved with the same $^{147}\text{Sm}/^{144}\text{Nd}$ range until today. Sample AG09008 with a $^{142}\text{Nd}$ deficit of -7.4 ppm and estimated zircon U-Pb age of ca. 3750 Ma possibly formed from the same source as the 3960 Ma Acasta rocks but 210 Ma later. The felsic Acasta rocks with no resolvable $^{142}\text{Nd}$ deficits likely formed at 3600 Ma (zircon U-Pb age) from the Archean BSE and evolved with a low $^{147}\text{Sm}/^{144}\text{Nd}$ of ca. 0.0750. They were intermixed with the older protoliths and also partially reset at 3371 Ma in a closed system, while their U-Pb zircon ages and $^{142}\text{Nd}$ compositions were preserved.

5.6 Implications

Coupled $^{147,146}\text{Sm},^{143,142}\text{Nd}$ and $^{176}\text{Lu}-^{176}\text{Hf}$ systematics (Guitreau, 2013) for Acasta show that oldest Eoarchean ca. 3960 Ma protoliths were derived from ca. 4310 Ma early-enriched Hadean crust characterized by low Nd and Hf isotope compositions. Younger Paleoarchean protoliths with an age of ca. 3600 Ma derived from an Archean BSE source and were intermixed with the Hadean source. This indicates that the Hadean crustal source of Acasta persisted for at least 350 Ma but that this older enriched material was ultimately recycled. Zircon xenocrysts with ages of up to ca. 4200 Ma (Bowring & Williams, 1999; Iizuka et al., 2006) crystallized from the early-enriched source during its crustal evolution in the Hadean period. Magmatic zircons inherited low $\epsilon^{176}\text{Hf}$ (Iizuka et al., 2009) from the Hadean source when the Acasta mafic protolith formed. Recycling of ca. 4310 Ma Hadean crust thus played a critical role in determining isotope compositions of Eoarchean Acasta protoliths.

The recycling of old Hadean crust to form new Archean crust was not restricted to Acasta. Early-enriched Hadean sources were also reported by O’Neil et al. (2008) and later confirmed by Roth et al. (2013a) for the ca. 3750 Ma Nuvvuagittuq Supracrustal Belt in Québec (Canada) and for younger ca. 3400 Ma rocks from Isua in southwest Greenland (Rizo et al., 2012). In contrast to Acasta, Nuvvuagittuq (Roth et al., 2013a) and Isua (Rizo et al., 2012) have older model ages of ca. 4500 Ma; Nuvvuagittuq (Guitreau et al., 2013) and Isua (e.g. Caro et al., 2005; Rizo et al., 2011) have decoupled Nd-Hf systematics that possibly record the differentiation of an early magma ocean implying crystallization in the presence of Ca-perovskite. Nuvvuagittuq (Cates & Mojzsis, 2009; Cates et al., 2012) and Isua (e.g.
New $^{147,146}\text{Sm}^{143,142}\text{Nd}$ constraints on the lifetime of early terrestrial crust

![Diagram](image)

**Fig. 5.6** $^{143}\text{Nd}/^{144}\text{Nd}$ (upper panel) and $^{142}\text{Nd}/^{144}\text{Nd}$ (lower panel) evolution diagrams that explain the Nd isotope evolution of Acasta. BSE and Acasta evolutions are shown in black and grey, respectively. The BSE corresponds to the superchondritic composition defined in Caro & Bourdon (2010).

1. Extraction at ca. 4310 Ma of the early-enriched Acasta source from the BSE.
2. Formation at ca. 3960 Ma of Acasta rocks from the early-enriched source.
3. Nd-isotope equilibration at ca. 3371 Ma of Acasta rocks (red arrows).

Felsic Acasta rocks with $^{142}\text{Nd}/^{144}\text{Nd}$ identical to BSE formed at ca. 3600 Ma (zircon U-Pb age) from the BSE and evolved with low $^{147}\text{Sm}/^{144}\text{Nd}$ of 0.0750 (dashed arrow).

Compston et al., 1986) did not preserve Hadean zircons. The early-enriched source found in Acasta is thus different from those reported so far. It may represent a second generation of early-formed Hadean crust that formed late and did not preserve primitive geochemical evidence for deep magma ocean differentiation.
5.7 Conclusions

The study of the Acasta gneiss complex with the $^{147,146}\text{Sm}-^{143,142}\text{Nd}$ in light of $^{176}\text{Lu}-^{176}\text{Hf}$ systematics and U-Pb zircon geochronology revealed that Acasta rocks formed from the recycling of ca. 4310 Ma Hadean crust. Oldest Acasta rocks have preserved low $^{142}\text{Nd}/^{144}\text{Nd}$ value of $-9.6\pm4.8$ ppm (2 SD). Acasta gneisses inherited low $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ compositions from this early-enriched source. A thermal event at ca. 3400 Ma, however, partially reset both the $^{147}\text{Sm}-^{143}\text{Nd}$ and $^{146}\text{Sm}-^{142}\text{Nd}$ systematics. Remarkably, the Hadean crustal source of Acasta is ca. 190 Ma younger than those observed in Nuvvuagittuq (Roth et al., 2013a) and Isua (Rizo et al., 2012), and does not show decoupled Nd-Hf pattern that can be attributed to the crystallization of deep early magma ocean. This early crust persisted at least 350 Ma and was eventually all recycled. Thus, the Acasta crustal source may represent a second generation of early-formed Hadean crust. This suggests that formation and recycling of early crust happened over short timescales and that the model for early mantle-crust evolution can be revised.
Appendix

Table A.5.1 Nd isotope compositions and Sm and Nd concentrations of the Acasta samples. The table shows the Nd isotope ratios measured for the static line 1 and the dynamic $^{143}\text{Nd} / ^{144}\text{Nd}$ ratio. All Nd isotope ratios are mass-fractionation corrected using $^{146}\text{Nd} / ^{144}\text{Nd} = 0.7219$. Isobaric interferences are expressed in ppm. Errors are 2 SD. Also listed are 13 measurements of the JNd-1 Nd standard (continued table).
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<td>0.5121043 ± 11</td>
<td>0.3483788 ± 7</td>
<td>0.2415878 ± 8</td>
<td>0.2364634 ± 11</td>
<td>0.9</td>
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<tr>
<td>9</td>
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<td>0.5120920 ± 9</td>
<td>0.3483557 ± 5</td>
<td>0.2415922 ± 6</td>
<td>0.2364715 ± 9</td>
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<td>0.8</td>
</tr>
<tr>
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<td>2.9</td>
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<td>0.3483742 ± 9</td>
<td>0.2415854 ± 10</td>
<td>0.2364589 ± 14</td>
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<td>1.1</td>
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Error 2SD ppm  

4.3 26.1 69.9 36.9 36.9

Table A.5.1: Continued.
6 Revisiting the $^{142}\text{Nd}$ deficits in the 1.48 Ga Khariar alkaline rocks (India)*

Abstract

The $^{146}\text{Sm}-^{142}\text{Nd}$ system plays a central role in tracing the silicate differentiation of the Earth before 4.1 Ga. Upadhyay et al. (2009) reported negative $^{142}\text{Nd}$ anomalies in 1.48 Ga rocks of the Khariar nepheline syenite complex (India). The authors inferred that an early enriched low-Sm/Nd reservoir must have contributed to the mantle source of these rocks. Because $^{146}\text{Sm}$ had been extinct for about 2.7 Ga before their crystallization, this Nd isotope signature must have remained isolated for at least that long. The authors suggested that the Nd had been sequestered in the lithospheric roots of craton. Using a different chemical separation method and Thermal Ionization Mass Spectrometry (TIMS) analysis protocol, this study attempted to replicate the finding of negative $^{142}\text{Nd}$ anomalies, but none were found. To determine which data set was correct, we investigated three possible sources of analytical bias: (1) imperfect cancelation of Faraday collector efficiencies during multidynamic TIMS analysis, (2) rapid sample fractionation between the sequential measurement of $^{146}\text{Nd}/^{144}\text{Nd}$ and $^{142}\text{Nd}/^{144}\text{Nd}$, and (3) non-exponential law behavior resulting from so-called “domain mixing”. Incomplete correction of collector efficiencies was found unlikely to cause resolvable biases. Although domain mixing may explain apparent “reverse” fractionation trends observed in some TIMS analyses, it cannot be the cause of the apparent negative $^{142}\text{Nd}$ anomalies in the study of Upadhyay et al. (2009). It was determined that rapid fractionation during multidynamic TIMS analysis can bias all measured Nd isotope ratios. After applying an approximate correction for this effect, only one rock retained a small negative $^{142}\text{Nd}$ anomaly. This, in conjunction with our new, anomaly-free data set measured at fractionation rates too low to cause bias, leads to the conclusion that the earlier reported negative $^{142}\text{Nd}$ anomalies are a subtle and reproducible analytical artefact. The absence of negative $^{142}\text{Nd}$ anomalies in the Khariar rocks relaxes the need for a mechanism (other than crust formation) that can isolate a Nd reservoir from the convective mantle for billions of years.

*A version of this chapter will be published in Chemical Geology as: Roth, A.S.G., Scherer, E.E., Maden, C. & Bourdon, B. Revisiting the $^{142}\text{Nd}$ deficits in the 1.48 Ga Khariar alkaline rocks (India).
Revisiting the $^{142}$Nd deficits in the 1.48 Ga Khariar alkaline rocks (India)

6.1 Introduction

The short-lived $^{146}$Sm-$^{142}$Nd chronometer [half-life $T_{1/2} = 68$ million years (Ma) (Kinoshita et al., 2012)] is a sensitive tracer of early silicate differentiation. Variations in $^{142}$Nd/$^{144}$Nd in planetary materials and meteorites are small and below 100 parts per million (ppm) in most cases. This is to be expected owing to the low initial $^{146}$Sm/$^{144}$Sm value 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 similarity between Sm and Nd mineral-liquid partition coefficients, which results in limited Sm/Nd fractionation. The detection of $^{142}$Nd anomalies thus requires very clean separation of Nd from its matrix and in particular from Sm and Ce to lower isobaric interferences to negligible levels, and a dynamic acquisition scheme during Thermal Ionization Mass Spectrometry (TIMS) measurements to correct for efficiency differences among the detectors and amplifiers (e.g. Caro et al., 2006; Brandon et al., 2009; Roth et al., 2013a). Resolving the small variations in $^{142}$Nd/$^{144}$Nd among terrestrial samples is analytically demanding because it requires achieving a long-term standard reproducibility of 5 ppm (2 SD) or better. The detection of positive or negative $^{142}$Nd anomalies may also be hampered by inappropriate mass bias correction if Nd evaporates from multiple domains within the sample load that have fractionated to different degrees (Upadhyay et al., 2008; Andreasen & Sharma, 2009).

Early mantle depletion is well documented by $^{142}$Nd excesses of up to 15 ppm relative to the modern terrestrial value in the ca. 3770 Ma Itsaq Gneiss Complex of West Greenland (Caro et al., 2003, 2006; Rizo et al., 2011) as well as the Narryer Gneiss Complex in Western Australia (Bennett et al., 2007). The first evidence for a complementary early-enriched reservoir characterized by $^{142}$Nd deficits of as much as -15 ppm was discovered (O’Neil et al., 2008) and later confirmed (Roth et al., 2013a) for the ca. 3750 Ma Nuvvuagittuq Supracrustal Belt in Québec (Canada). Deficits in $^{142}$Nd of as much as -13 ppm were also reported for the 1480 Ma alkaline rocks from the Khariar nepheline syenite complex in southeastern India (Upadhyay et al., 2009). Because the Khariar rocks formed long after the parent nuclide $^{146}$Sm was effectively extinct, these authors concluded that the rocks had inherited the $^{142}$Nd signature of an early-formed, low-Sm/Nd reservoir that had escaped mixing back into the convective mantle for at least 2.7 Ga. This was proposed by Upadhyay et al. (2009) to have occurred by the incorporation of early mantle heterogeneities into the lithospheric roots of continents. Alternatively, such a signature may have been preserved within ancient crust for much of the 2.7 Ga before being subducted and contributing to the mantle source of the Khariar rocks. A more recent study by Rizo et al. (2012) reported resolvable $^{142}$Nd deficits as low as -11 ppm for three 3400 Ma samples from Isua (southwest Greenland). This latter study suggests that the mantle would have preserved early-enriched reservoirs until at least the Early Archean.

Here, we report the results of replicate analyses performed at ETH Zurich on four of the Khariar rocks, for which two had been reported to have negative $^{142}$Nd anomalies (DU-36,
DU-1/4) and two had been found to have no anomaly (DU-1/2, DU-9/2). To avoid any operator bias during the TIMS analyses and subsequent data comparison, the identities of the samples were not revealed to the analysts (ASGR and EES) until all analyses were complete. The replicate analyses obtained for these rocks during this blind experiment show no resolvable $^{142}$Nd anomalies, contradicting the -12.3 ppm and -10.9 ppm anomalies previously reported by Upadhyay et al. (2009) for the samples DU-1/4 and DU-36, respectively. In the following, we evaluate the potential reasons for the discrepancy between the two data sets. We show that most of the $^{142}$Nd deficits reported by Upadhyay et al. (2009) for the Khariar rocks can be explained by a subtle, yet reproducible analytical artefact that has not been previously described. Further, we suggest data quality metrics that could be reported along with future $^{142}$Nd studies and other studies attempting to resolve <10 ppm differences between isotope ratios.

6.2 Methods

For this blind experiment, the four Khariar rocks were chemically processed for the separation of Nd along with the BCR-2 USGS standard and one sample from the Isua Supracrustal Belt (SM/GR/97/31) previously analyzed by Caro et al. (2006) and Roth et al. (2013a). Each Nd cut was then split into two aliquots and measured by TIMS for isotopic composition in addition to seven JNdI-1 Nd standards.

6.2.1 Chemical separation of Nd

Neodymium was separated from bulk rock samples by ion-exchange chromatography using the methods described in Caro et al. (2006) and Roth et al. (2013a). For each sample, about 50-70 mg of powdered rock (containing about 1 µg of Nd) were digested first in concentrated HF-HNO$_3$ and then taken up in HNO$_3$-HClO$_4$ to re-dissolve fluoride precipitates. Subsequently, the residues were completely dissolved in 6 M HCl. Iron was reduced with ascorbic acid to avoid competition between the REE and trivalent Fe on the ion exchange columns. The REE were separated from the rock matrix using TRU-Spec chromatographic columns. To lower the isobaric interferences to negligible levels, Ce was removed from Nd using an efficient two-phase solvent extraction technique (Rehkämper et al., 1996). To this end, Ce was oxidized with sodium bromate and the tetravalent Ce was then complexed by an organic solvent (heptane). This solvent was pipetted out from the Ce-free aqueous phase and discarded. Cation exchange columns (AG50W-X8) were then used to remove the large amounts of Na previously added as sodium bromate. Neodymium was finally separated from the remaining REE and collected using Ln-Spec chromatographic columns.
Neodymium was measured as a positive metal ion (Nd\textsuperscript{+}) with the Thermo Triton (TIMS) at ETH Zurich. About 500 ng of Nd per sample and 1 µl of 0.01% phosphoric acid were loaded onto one filament of a double rhenium filament assembly. During TIMS analysis, the ionization filament was heated to 5500 mA at a rate of 200 mA per minute. The evaporation filament was then heated at the same rate to typically 1600 mA until a \textsuperscript{142}Nd ion beam of about 7.5 V was obtained (using 10\textsuperscript{11} ohm feedback resistors). The evaporation filament was automatically reheated when signal intensity dropped below 80% of the initial signal intensity. Mass fractionation was corrected with the exponential law using \textsuperscript{146}Nd/\textsuperscript{144}Nd = 0.7219 as the reference. Isobaric interferences from \textsuperscript{144,148,150}Sm and \textsuperscript{142}Ce were monitored by measuring \textsuperscript{147}Sm and \textsuperscript{140}Ce, respectively, and corrected online. The \textsuperscript{142}Ce/\textsuperscript{142}Nd and \textsuperscript{144}Sm/\textsuperscript{144}Nd mean values for the analyses never exceeded 1.56 \times 10\textsuperscript{-6} and 2.55 \times 10\textsuperscript{-7}, respectively. As there are variations in efficiency among the Faraday collectors and their associated amplifiers, a dynamic acquisition scheme using two magnet settings (corresponding to \textsuperscript{145}Nd and \textsuperscript{143}Nd in the axial detector) was used to reduce the effects of these variations on measured isotope ratios to negligible levels. The amplifier rotation feature on the Triton can cancel variation among amplifier gains even for static analyses, but it cannot cancel differences in cup efficiencies. Table 6.1 shows the cup configuration and measurement conditions for the dynamic Nd isotope analyses. The integration time was 8.4 seconds for each magnet setting. The two magnet settings were separated with an idle time of 4.0 seconds. The coincidences of each mass with its appropriate Faraday collector were optimized for the first magnet setting. To precisely align the beams into the detectors for the second magnet setting, the dispersion quadrupole was set to a value of 7.5 to 8.5 V. A measurement consisted of 24 to 80 blocks with 20 cycles per block, and lasted 4 to 14 hours. Amplifiers were rotated to the left every block. The peaks were centered in the central detector every three blocks using the \textsuperscript{145}Nd- (magnet setting 1) and \textsuperscript{143}Nd- (magnet setting 2) beams. Lens focusing using \textsuperscript{145}Nd in central detector was done every three blocks. Baselines were measured every block (30 integrations of 1 second). Over the course of this study, the means of individual baseline measurements for each individual cup did not vary by more than 90 µV (i.e., 12 ppm for a signal intensity of 7.5 V). On average, the difference between two consecutive means of individual baseline measurements for each individual cup did not vary by more than 12 µV (i.e. 1.6 ppm for a signal intensity of 7.5 V). The repeated \textsuperscript{142}Nd/\textsuperscript{144}Nd measurements of the JNdi-1 Nd standard over a period of three years (n = 94) yielded an external precision of 5.1 ppm (2 SD), with a mean \textsuperscript{142}Nd/\textsuperscript{144}Nd value of 1.1418351±0.0000042 (Roth et al. 2013). Over the course of this study, the external precision of the JNdi-1 Nd standard was 5.0 ppm (n = 7), with a mean \textsuperscript{142}Nd/\textsuperscript{144}Nd value of 1.1418361±0.0000057. The Nd isotope compositions of the four Khariar samples, two replicates of the BCR-2 USGS standard, one replicate of sample SM/GR/97/31 from the Isua Supracrustal Belt, and seven repeated measurements
6.3 Results

The BCR-2 USGS standard yielded a $^{142}\text{Nd}/^{144}\text{Nd}$ value identical to that of the terrestrial JNdi-1 Nd standard (Table A.6.1). Sample SM/GR/97/31 from the Isua Supracrustal Belt showed an excess in $^{142}\text{Nd}$ of 8±3 ppm relative to the terrestrial standard. This is identical to the value of 8±2 (n = 3) published by Roth et al. (2013a), but lower than the value of 14±2 (n = 1) reported in Caro et al. (2006). Moreover, the measurement protocol described here was also used in Roth et al. (2013a) to replicate negative $^{142}\text{Nd}$ anomalies reported by O’Neil et al. (2008) for the Nuvvuagittuq Supracrustal Belt. Thus, our measurement protocol is capable of resolving both positive and negative $^{142}\text{Nd}/^{144}\text{Nd}$ anomalies and provides a useful reference frame for considering the Khariar data set. Figure 6.1 shows the measured $^{142}\text{Nd}/^{144}\text{Nd}$ values for the Khariar samples expressed as ppm deviation from the modern terrestrial composition (JNdi-1 Nd standard). Our analyses of samples DU-1/2 and DU-9/2 show normal terrestrial compositions in agreement with the Upadhyay et al. (2009) results. However, in contrast to their results for DU-1/4 and DU-36 ($^{142}\text{Nd}$ deficits of -13.6 ppm and

Table 6.1 Collector configurations and measurement conditions for this study and the study of Upadhyay et al. (2009).

of the JNdi-1 Nd standard are reported in Table A.6.1.

<table>
<thead>
<tr>
<th>Magnet setting</th>
<th>Faraday collectors</th>
<th>Integration time [s]</th>
<th>Number of integrations</th>
<th>Idle time [s]</th>
<th>Peak centre focus</th>
<th>Lens focus</th>
<th>Zoom optics</th>
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<td>14$^{142}\text{Nd}$</td>
</tr>
</tbody>
</table>

Measurement conditions:
- 20 cycles per block
- Peak centre every 3 blocks
- Lens focus every 3 blocks
- Amplifier rotation left every block
- Baseline every block, 30 integrations of 1 second

Upadhyay et al. (2009):

<table>
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<th>Magnet setting</th>
<th>Faraday collectors</th>
<th>Integration time [s]</th>
<th>Number of integrations*</th>
<th>Idle time [s]**</th>
<th>Peak centre focus</th>
<th>Lens focus</th>
<th>Zoom optics</th>
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</tr>
</tbody>
</table>

Measurement conditions:
- 10 cycles per block
- Peak centre every 4 blocks
- Lens focus every 4 blocks, turret optimized at start
- Amplifier rotation left every block
- Baseline every block, 30 integrations of 1 second
- Magnet removed from ion source
* Number of integrations was changed over course of study: 16 (n=1), 8 (n=20), 6 (n=28)
** 4s magnet settling time before signal measurements. An additional ca. 3 seconds delay occurred between measurement cycles
Approximate total time [s] required for each measurement cycle is: 3x idle time + 3x integration time x integrations + 3

Table 6.1 Collector configurations and measurement conditions for this study and the study of Upadhyay et al. (2009).
6 Revisiting the $^{142}$Nd deficits in the 1.48 Ga Khariar alkaline rocks (India)

![Diagram of $^{142}$Nd/144Nd data for the Khariar rocks. Red symbols are the original data of Upadhyay et al. (2009) and green symbols are the replicate analyses from this study. Each symbol represents a single TIMS analysis. The vertical grey bar represents the 5-ppm external reproducibility (2 SD) of the JNd-1 Nd standard. DU-36 and DU-1/4 were reported by Upadhyay et al. (2009) to possess negative $^{142}$Nd anomalies. No anomalous Nd isotope compositions were observed in the present study.]

-14.4 ppm, respectively), we found no resolvable $^{142}$Nd anomalies outside of our 5.0-ppm external reproducibility (given as 2 SD).

6.4 Discussion

In principle, there are numerous theoretical and experimental limitations on the accuracy and precision of dynamic Nd isotope analyses by TIMS. First, when using the exponential law to correct for mass fractionation, the efficiencies of the Faraday collectors do not completely cancel out, as is the case when using the power law in a dynamic acquisition scheme (Thirlwall, 1991). As shown below, a threshold value for the relative Faraday collector efficiency can be estimated, above which the propagated error due to variations in detector efficiencies would exceed the 5-ppm external precision obtained with dynamic $^{142}$Nd/144Nd measurements. Second, given that the evaporating sample undergoes continuous mass fractionation and that there is a time gap between the measurements of $^{146}$Nd/144Nd at one magnet setting and $^{142}$Nd/144Nd at another, the mass fractionation correction of $^{142}$Nd/144Nd using $^{146}$Nd/144Nd can be biased by a factor that depends on the rate (and sign) of change in...
146\textsuperscript{Nd}/144\textsuperscript{Nd}. In general, a faster fractionation would be expected to result in greater analytical biases. A threshold value for the rate of fractionation may be estimated, above which this bias would exceed the 5-ppm external precision on the dynamic 142\textsuperscript{Nd}/144\textsuperscript{Nd} measurements. Third, the detection of 142\textsuperscript{Nd} anomalies may also be hampered by inappropriate mass bias correction if Nd evaporates from multiple domains that have fractionated to different degrees (e.g. Upadhyay et al., 2008; Andreasen & Sharma, 2009).

6.4.1 Faraday collector efficiencies

Using the exponential law and measured isotope ratios that have already been corrected for amplifier gains, baselines and isobaric interferences, the equation for the dynamic 142\textsuperscript{Nd}/144\textsuperscript{Nd} value corrected for mass fractionation can be written as follows:

\[
\left(\frac{142\text{Nd}}{144\text{Nd}}\right)_{\text{dyn}} = \left(\frac{142\text{Nd}}{144\text{Nd}}\right)_{S2} \times \left(\frac{m_{142}}{m_{144}}\right) \ln\left(\frac{\text{(146Nd/144Nd)}_{\text{nat}}}{\left(\frac{146\text{Nd}}{144\text{Nd}}\right)_{S1}}\right)
\]

where \(\left(\frac{142\text{Nd}}{144\text{Nd}}\right)_{\text{dyn}}\) is the corrected dynamic 142\textsuperscript{Nd}/144\textsuperscript{Nd} value, \(\left(\frac{142\text{Nd}}{144\text{Nd}}\right)_{S2}\) is the 142\textsuperscript{Nd}/144\textsuperscript{Nd} measured in magnet setting 2, \(\left(\frac{146\text{Nd}}{144\text{Nd}}\right)_{\text{nat}}\) is the natural 146\textsuperscript{Nd}/144\textsuperscript{Nd} value used for normalization, \(\left(\frac{146\text{Nd}}{144\text{Nd}}\right)_{S1}\) is the 146\textsuperscript{Nd}/144\textsuperscript{Nd} ratio measured in magnet setting 1 and m is the exact mass of the specified Nd isotope. The collector settings used in this study are given in Table 6.1 for reference. Again, note that Faraday collector efficiencies do not completely cancel when using the exponential law in equation (6.1), but the true 142\textsuperscript{Nd}/144\textsuperscript{Nd} value can be written with the following equation:

\[
\left(\frac{142\text{Nd}}{144\text{Nd}}\right)_{\text{true}} = \frac{cL_1}{cH_1} \times \left(\frac{142\text{Nd}}{144\text{Nd}}\right)_{S2} \times \left(\frac{m_{142}}{m_{144}}\right) \ln\left(\frac{\left(\frac{146\text{Nd}}{144\text{Nd}}\right)_{\text{nat}}}{\left(\frac{146\text{Nd}}{144\text{Nd}}\right)_{S1}}\right)
\]

where \(\left(\frac{142\text{Nd}}{144\text{Nd}}\right)_{\text{true}}\) is the true 142\textsuperscript{Nd}/144\textsuperscript{Nd} of the unfractionated sample, and c is the correction factor that accounts for the efficiency of the Faraday collectors L1 and H1 (see Table 6.1; note that c = 1/[cup efficiency]). Combining equations (6.1) and (6.2), a third equation can then be derived, which expresses the dynamic and true 142\textsuperscript{Nd}/144\textsuperscript{Nd} values as a function of C, the relative correction factor defined as \(C = \frac{cL_1}{cH_1}\):

\[
\left(\frac{142\text{Nd}}{144\text{Nd}}\right)_{\text{true}} = \left(\frac{142\text{Nd}}{144\text{Nd}}\right)_{\text{dyn}} \times \frac{\ln\left(\frac{\left(\frac{146\text{Nd}}{144\text{Nd}}\right)_{\text{nat}}}{\left(\frac{146\text{Nd}}{144\text{Nd}}\right)_{S1}}\right)}{\ln\left(\frac{m_{142}}{m_{144}}\right)} + 1
\]
Equation (6.3) shows that above a difference of $\sim 370$ ppm in relative detector efficiency, the dynamic $^{142}\text{Nd}/^{144}\text{Nd}$ deviates from the true $^{142}\text{Nd}/^{144}\text{Nd}$ value by more than 5 ppm. However, the maximum difference between the static $^{142}\text{Nd}/^{144}\text{Nd}$ values measured at magnet settings 1 and 2 for 94 JNd-1 Nd standard measurements was only about 124 ppm (Roth et al., 2013a). In this study, the maximum difference for the 7 static standard measurements was only about 110 ppm. If differences between the static $^{142}\text{Nd}/^{144}\text{Nd}$ values measured at magnet settings 1 and 2 may be taken as an indicator of the variation of efficiency among Faraday collectors, in spite of additional collectors involved, then the relative variation is about three times lower than the threshold value defined above. This demonstrates that even though Faraday collector efficiencies do not completely cancel when using the exponential law during dynamic measurements, the relative Faraday collector efficiencies probably cause only a 1-ppm deviation during dynamic $^{142}\text{Nd}/^{144}\text{Nd}$ measurements in the conditions of this study.

### 6.4.2 Rate of change in mass fractionation

As mentioned above, if the rate of change in mass fractionation is fast over the timescale used to switch the magnetic field between the two measurement lines, there can be a bias introduced during dynamic measurements. One can determine a threshold value for the rate of change in mass fractionation in $^{146}\text{Nd}/^{144}\text{Nd}$ above which the bias on $^{142}\text{Nd}/^{144}\text{Nd}$ values would exceed 5 ppm. The true $^{142}\text{Nd}/^{144}\text{Nd}$ ratio can be rewritten as:

$$
\left( \frac{^{142}\text{Nd}}{^{144}\text{Nd}} \right)_{\text{true}} = \left( \frac{^{142}\text{Nd}}{^{144}\text{Nd}} \right)_{S2} \times \left( \frac{m_{142}}{m_{144}} \right)_{S2} \left( \frac{m_{146}}{m_{144}} \right)_{S1} = \frac{\ln \left( \frac{^{146}\text{Nd}}{^{144}\text{Nd}} \right)_{\text{nat}}}{\ln \left( \frac{m_{146}}{m_{144}} \right)} (6.4)
$$

where $F$ is the factor needed to adjust the $^{146}\text{Nd}/^{144}\text{Nd}$ actually measured at the time of S1 to what it should be at the time of S2 after fractionating slightly. For example, $F = 1.000005$ indicates a 5 ppm increase in $^{146}\text{Nd}/^{144}\text{Nd}$ between its measurement in S1 and when $^{142}\text{Nd}/^{144}\text{Nd}$ is measured in S2. Combining equations (6.1) and (6.4) gives:

$$
\left( \frac{^{142}\text{Nd}}{^{144}\text{Nd}} \right)_{\text{dyn}} = F^{-\epsilon_1/\epsilon_2} \approx F^{-1} = \frac{1}{1 + \Delta} (6.5)
$$

where $\epsilon_1 = (m_{144}-m_{142})/m_{144}$, $\epsilon_2 = (m_{146}-m_{144})/m_{144}$, $\ln(1+\epsilon) \approx \epsilon$, $\epsilon_1 \approx \epsilon_2$ and $F \equiv 1+\Delta$. Equation (6.5) shows that a 5 ppm increase ($\Delta$) in $^{146}\text{Nd}/^{144}\text{Nd}$ between its measurement in
6.4 Discussion

S1 and when $^{142}\text{Nd}/^{144}\text{Nd}$ is measured in S2 will lower the dynamic $^{142}\text{Nd}/^{144}\text{Nd}$ value relative to its true value by approximately 5 ppm. Given the calculated time gap of 12.4 seconds between the midpoints of S1 and S2 intervals of our measurement scheme (see parameters reported in Table 6.1), the threshold value for the rate of change in mass fractionation between the two sequences is about $0.40 \text{ ppm s}^{-1}$. However, for the seven JNd-1 Nd standards and the eight replicates of the four Khariar rocks measured in this study, the average fractionation rate determined from $(^{146}\text{Nd}/^{144}\text{Nd})_{S1}$ versus time never exceeded $0.34 \text{ ppm s}^{-1}$ and the mean rate for all measurements was $0.18 \pm 0.14$ (2 SD) $\text{ppm s}^{-1}$.

The $^{146}\text{Nd}/^{144}\text{Nd}$ did not always increase constantly over the course of measurements (as it would be expected from a normal fractionation path) and sometimes even momentarily decreased ("reverse" fractionation). Such changes in the sign of fractionation rate will change the sign of the bias and will thus partially cancel biases on $^{142}\text{Nd}/^{144}\text{Nd}$ (and other isotope ratios) caused by mass fractionation between the two magnet settings. They also provide a simple explanation for the sudden jumps to higher $^{142}\text{Nd}/^{144}\text{Nd}$ that were associated with the onset of "reverse" fractionation marked by a peak in $^{146}\text{Nd}/^{144}\text{Nd}$ vs. time or cycle number (sample 17 in Fig. 3 of Upadhyay et al., 2008). Despite local sign reversals, the average fractionation rate offers a first-order means of approximating the speed at which a sample was consumed. As shown later, it allows detection of possible biases. The averaged rates of mass fractionation during our measurements never exceeded the threshold value that would cause a resolvable bias in measured $^{142}\text{Nd}/^{144}\text{Nd}$, i.e., any bias due to this effect was smaller than the 5-ppm external precision (2 SD).

A major difference between the dynamic acquisition scheme of this study and that of Upadhyay et al. (2008, 2009) is the time gap between the centers of the measurement intervals for $^{146}\text{Nd}/^{144}\text{Nd}$ and $^{142}\text{Nd}/^{144}\text{Nd}$ values. Their measurement scheme had three magnet settings with total integration times (integration time $\times$ number of integrations) of generally either 6 or 8 seconds (one analysis, however, employed 16-second measurements at each mass setting). The $^{146}\text{Nd}/^{144}\text{Nd}$ value was measured in magnet setting 1 (S1) and the $^{142}\text{Nd}/^{144}\text{Nd}$ on magnet setting 3 (S3), see Table 6.1. The average S1-S3 time gap of 22 seconds and the ca. 5-ppm external precision they reported correspond to a threshold value of only $0.21 \text{ ppm s}^{-1}$ for the rate of change in mass fractionation. The averaged rates of mass fractionation of all their measurements are above this threshold value, with a mean value of $0.34 \pm 0.27 \text{ ppm s}^{-1}$ and maximum value of $0.46 \text{ ppm s}^{-1}$. Thus, the rates of mass fractionation of their measurements were higher than the threshold value that would cause a 5-ppm shift in corrected $^{142}\text{Nd}/^{144}\text{Nd}$ values. As the $^{146}\text{Nd}/^{144}\text{Nd}$ generally increased over the course of the measurement (as expected for normal mass fractionation) and this ratio was measured before $^{142}\text{Nd}/^{144}\text{Nd}$, one can predict that some of their dynamic $^{142}\text{Nd}/^{144}\text{Nd}$ data were possibly biased towards lower values. This is can be seen in Figure 6.2, which shows $\mu^{142}\text{Nd}$ values plotted against the observed fractionation rate / threshold fractionation rate (i.e., the relative fractionation rate, $r_f$). The predicted trend on the plot has a slope of -5.
Revisiting the $^{142}$Nd deficits in the 1.48 Ga Khariar alkaline rocks (India)

Fig. 6.2 (A) $^{142}$Nd vs. ratio of observed- to threshold fractionation rate ($r_f$) for the data of Upadhyay et al. (2009). Yellow points indicate individual analyses with purported negative anomaly. The middle solid line passes through the mean of La Jolla analyses (black circle, $r_f = 1.1$ at $^{142}$Nd = 0) and has a slope of -5. A sample with a $r_f$ of 1 will have 5 ppm of negative systematic bias in $^{142}$Nd (see text). The dotted lines represent the 5-ppm external reproducibility of $^{142}$Nd. The majority of analyses are compatible with the predicted trend. (B) $^{142}$Nd vs. $r_f$ for the data from the present study. The middle solid line passes through the mean of JNdi-1 analyses (black circle, $r_f = 0.37$, at $^{142}$Nd = 0). Note the smaller $r_f$ values, smaller range of $r_f$ values, and lack of negative anomalies as compared to the Upadhyay et al. (2009) data.

because every increment of 1 unit in $r_f$ brings about another ca. -5 ppm bias in $^{142}$Nd. The trend passes through the point (1.1, 0), which corresponds to the mean value for the La Jolla standard (Table 6.2). Most analyses lie within 5 ppm of the predicted trend and thus can be explained by our model. Three of the points plotting below the trend are from DU-1/4, possibly suggesting that there is an additional source of systematic error for this sample, that the external reproducibility of that sample is poorer than the 7.8 ppm (2 SD) suggests, or that some of its $r_f$ values were underestimated. In contrast, the analyses made in the current study do not spread out along the excessive fractionation rate trend (Fig. 6.2).

Table 6.2 lists the S1-S3 time delays, together with the average- and threshold fractionation rates for the pooled analyses of each standard and sample measured by Upadhyay et al. (2009). In that work, the static $^{150}$Nd/$^{144}$Nd was subject to a long-term drift of 160 ppm over the course of that 33-month study. Here, we used the method outlined in Thirlwall (1991) to calculate a multidynamic $^{150}$Nd/$^{144}$Nd from the original data set, thereby largely eliminating the effects of the evolving Faraday collector efficiencies. Also included in this table are $^{142,145,148,150}$Nd values that have been corrected for the effects of fractionation between sequential magnet settings. For these corrections, it is important to use the instantaneous fractionation rate and not an average for the entire measurement. In this context, we used moving averages (i.e., the slope of isotope ratio vs. time) from every group of 11 consecutive
measurement cycles to establish the “local” fractionation rate at any given time during the analysis. For each ratio of interest (i.e., $^{142}\text{Nd}/^{144}\text{Nd}$, $^{145}\text{Nd}/^{144}\text{Nd}$, $^{146}\text{Nd}/^{144}\text{Nd}$, and $^{150}\text{Nd}/^{144}\text{Nd}$), the mass fractionation monitor (i.e., $^{146}\text{Nd}/^{144}\text{Nd}$, $^{145}\text{Nd}/^{146}\text{Nd}$, $^{144}\text{Nd}/^{146}\text{Nd}$, $^{148}\text{Nd}/^{150}\text{Nd}$, respectively), which was measured in the same collectors at a different magnet setting, was corrected to the time at which the ratio of interest was measured. This was done by interpolation of the “local” fractionation rate by the number of seconds between the centers of the two measurement intervals. The multidynamic measurement of $^{143}\text{Nd}/^{144}\text{Nd}$ is more complex because it involves three magnet settings and three Faraday cups (see Table 1 of Upadhyay et al., 2008). In that case, the $^{146}\text{Nd}/^{144}\text{Nd}$ from magnet setting 1 was simply extrapolated to the midpoint between the two measurements of $^{143}\text{Nd}/^{144}\text{Nd}$ in magnet settings 2 and 3. We did not use $^{143}\text{Nd}/^{144}\text{Nd}$ for evaluating fractionation rate effects here because of the large variability in radiogenic component among natural samples.

Owing to the different timing relationships between measurements of isotope ratios of interest and their normalization ratios, the magnitude and sign of bias will vary by isotope ratio. This can be seen in the differences between multidynamic and time-corrected multidynamic analyses in Table 6.2 and in Figure 6.3. For all isotope ratios, the differences are generally small relative to the external reproducibility. Exceptions are the differences in $\mu^{142}\text{Nd}$ values of the four samples thought by Upadhyay et al. (2009) to have negative anomalies. For these samples, the modeled shift in $\mu^{142}\text{Nd}$ that occurred as a result of mass fractionation between S1 and S3 measurements is on the same order as—or greater than—the external reproducibility. This happens even though $r_f$ values of these samples overlap with the higher values of the control samples (normal rocks and La Jolla standard). Although $r_f$ values negatively correlate with $\mu^{142}\text{Nd}$ (Fig. 6.2), averages of $r_f$ values of samples such as used in Table 6.2 do not obviously single out the four samples with the purported negative anomaly. Only one sample, DU-1/4 still shows a resolvable negative anomaly at the 95% confidence level, albeit smaller. If one instead takes the 2 SD value of 6.8 ppm reported for this sample in Table 6.2 then the corrected $\mu^{142}\text{Nd}$ value of DU-1/4 overlaps within error with that of the standard. As a group, the anomalous samples still yield a negative anomaly with a mean value of -4.6 ppm that is again smaller than for the uncorrected data (-11.8 ppm).

We do not consider these to be robust anomalies because our correction uses a moving average of the fractionation rate, i.e., it performs a linear fit through an isotope ratio measured 11 times over ca. 6-7 minutes. Changes in fractionation rate on shorter timescales will be smoothed out, potentially leading to an under-correction. Rate of fractionation differed between the two labs possibly as function of amounts of Nd and phosphoric acid loaded onto the filament, time taken to ramp up the ionization current, and signal intensity. What we propose here provides a reasonable explanation for the negative $\mu^{142}\text{Nd}$ anomalies initially reported for the Khariar rocks. For these samples, the rate of fractionation has led to a reproducible analytical artefact that has shifted the $\mu^{142}\text{Nd}$ to negative values.
6 Revisiting the $^{142}$Nd deficits in the 1.48 Ga Khariar alkaline rocks (India)

<table>
<thead>
<tr>
<th>Table 6.2</th>
<th>Shifts in Nd isotope compositions caused by the S1-S3 time delay in the Upadhyay et al. (2009) data set (see explanation in text).</th>
</tr>
</thead>
<tbody>
<tr>
<td>avg. melt</td>
<td>observed / change in Nd fractionation factor (%)</td>
</tr>
</tbody>
</table>
| interval  | Nd
| ppm s$^{-1}$ | ppm s$^{-1}$ | 2 s.d. | $^{142}$ | 2 s.d. | $^{145}$ | 2 s.d. | $^{148}$ | 2 s.d. | $^{150}$ | 2 s.d. |
| La Jolla Nd standard set ($n = 10$) | MO only | 21 | 0.26 | 0.24 | 1.1 | 0.8 | 0.0 | 4.0 | 1.1 | 0.0 | 3.2 | 0.8 | 0.0 | 12.8 | 3.4 | 0.0 | 8.6 | 2.3 |
| MO, time-corrected | 0.0 | 4.3 | 1.1 | 0.0 | 3.5 | 0.9 | 0.0 | 7.7 | 2.0 | 0.0 | 7.9 | 2.1 |
| "Normal" terrestrial rocks | MO only | 21 | 0.32 | 0.24 | 1.3 | 0.9 | 3.9 | 6.4 | 4.0 | 1.7 | 2.0 | 1.2 | -10.3 | 14.9 | 8.3 | -4.1 | 18.8 | 11.7 |
| MO, time-corrected difference | -1.9 | 8.4 | 5.2 | 2.9 | 3.1 | 1.3 | -8.7 | 9.7 | 6.0 | -4.5 | 14.2 | 8.6 |
| BHVO-2 Basalt (International rock standard; $n = 2$) | MO only | 24 | 0.44 | 0.21 | 2.1 | -5.1 | 7.2 | 3.7 | 5.8 | -4.7 | 11.7 | -9.0 | 12.2 |
| MO, time-corrected difference | -1.9 | 6.7 | 4.0 | 4.2 | -2.8 | 11.5 | -3.7 | 9.8 |
| DU-17 Gaboro (Internal rock standard; $n = 7$) | MO only | 20 | 0.42 | 0.25 | 1.7 | 0.7 | 4.4 | 5.3 | 2.4 | 2.3 | 5.2 | 2.4 | -12.0 | 13.7 | 6.3 | -8.8 | 11.5 | 5.3 |
| MO, time-corrected difference | -1.8 | 7.6 | 3.5 | 3.4 | 5.3 | 2.4 | -4.6 | 13.1 | 6.1 | -4.5 | 8.3 | 3.8 |
| DU-3/1 Ns-yenite (Khariar; $n = 1$) | MO only | 24 | 0.28 | 0.21 | 1.3 | -1.8 | 7.2 | 6.9 | 6.8 | -6.2 | 11.7 | -5.0 | 12.2 |
| MO, time-corrected difference | -6.9 | 37.2 | 7.2 | 5.3 | -9.9 | 17.2 | -3.4 | 11.7 |
| DU-3/2 Ns-yenite (Khariar; $n = 2$) | MO only | 24 | 0.25 | 0.21 | 1.2 | 1.5 | 7.2 | 5.2 | 6.9 | -11.2 | 11.7 | -5.5 | 12.2 |
| MO, time-corrected difference | 2.8 | 7.7 | 4.8 | 4.3 | -12.9 | 12.5 | -4.6 | 12.8 |
| DU-82 Ns-yenite (Khariar; $n = 2$) | MO only | 22 | 0.28 | 0.23 | 1.2 | 1.4 | 7.2 | 2.0 | 6.0 | -6.0 | 11.7 | -4.5 | 12.2 |
| MO, time-corrected difference | 0.8 | 7.7 | 2.4 | 4.3 | -2.7 | 11.5 | -1.0 | 8.6 |
| Pooled analyses of the six "normal" terrestrial rocks above ($n = 19$) | MO only | 21 | 0.38 | 0.23 | 1.5 | 0.4 | 0.8 | 7.2 | 1.7 | 2.9 | 4.8 | 1.2 | -10.0 | 11.7 | 2.8 | -8.8 | 12.2 | 2.9 |
| MO, time-corrected difference | 1.4 | 6.7 | 1.6 | 3.5 | 4.3 | 1.0 | -5.9 | 11.5 | 2.8 | -4.0 | 8.6 | 2.1 |
| Kharar samples with purported negative $^{142}$Nd anomaly | MO only | 26 | 0.41 | 0.20 | 2.0 | 2.2 | -12.3 | 7.8 | 3.6 | 7.7 | 10.0 | 4.7 | -12.0 | 25.3 | 11.7 | -15.5 | 20.3 | 9.4 |
| MO, time-corrected difference | -8.0 | 6.8 | 3.1 | 6.3 | 10.2 | 4.7 | -12.3 | 15.7 | 7.7 | -10.5 | 16.1 | 7.5 |
| DU-1/4 Mes-syenite (Khariar; $n = 7$) | MO only | 24 | 0.46 | 0.21 | 2.2 | -4.1 | 7.2 | 6.0 | 6.8 | -9.1 | 11.7 | -13.0 | 12.2 |
| MO, time-corrected difference | -0.3 | 6.7 | 5.4 | 4.3 | -4.1 | 11.5 | -7.6 | 8.6 |
| DU-1/5 fette (Khariar; $n = 1$) | MO only | 24 | 0.31 | 0.21 | 1.5 | -13.4 | 7.2 | 6.6 | 6.6 | -3.7 | 11.7 | -15.3 | 12.2 |
| MO, time-corrected difference | -7.0 | 7.7 | 3.7 | 5.3 | -6.3 | 11.5 | -11.0 | 11.5 |
| DU-13/2 Ns-yenite (Khariar; $n = 2$) | MO only | 24 | 0.40 | 0.22 | 1.9 | 1.2 | -15.9 | 2.5 | 1.9 | 1.7 | 4.3 | 3.4 | -3.3 | 24.4 | 19.4 | -11.8 | 9.0 | 7.2 |
| MO, time-corrected difference | -5.4 | 4.9 | 3.9 | 1.1 | 5.1 | 6.1 | -1.8 | 10.4 | 9.2 | -7.8 | 11.3 | 9.0 |
| DU-36 (Khariar; $n = 4$) | MO only | 23 | 0.40 | 0.22 | 1.9 | 1.2 | -15.9 | 2.5 | 1.9 | 1.7 | 4.3 | 3.4 | -3.3 | 24.4 | 19.4 | -11.8 | 9.0 | 7.2 |
| MO, time-corrected difference | -5.4 | 4.9 | 3.9 | 1.1 | 5.1 | 6.1 | -1.8 | 10.4 | 9.2 | -7.8 | 11.3 | 9.0 |
| Pooled analyses of all 4 "anomalous" rocks above ($n = 14$) | MO only | 25 | 0.40 | 0.21 | 1.9 | 1.6 | -11.8 | 6.1 | 1.8 | 5.8 | 8.9 | 2.6 | -8.2 | 22.5 | 8.5 | -13.8 | 15.1 | 4.3 |
| MO, time-corrected difference | -4.6 | 7.2 | 2.1 | 4.4 | 8.6 | 2.5 | -7.7 | 15.8 | 4.6 | -8.5 | 12.8 | 3.7 |

All data are from Upadhyay et al., 2009. Their static $^{142}$Nd/$^{144}$Nd values have been replaced here with dynamic values calculated using the method of Thornhill (1991). MD = multiply dynamic analysis, wherein collector blases are largely cancelled. "MO, time-corrected" indicates that multiply dynamic measurements have been corrected for the change in mass fractionation state of the normalisation ratio (e.g., $^{143}$Nd/$^{144}$Nd) between the time it is measured at one magnet setting and the time the ratio of interest (e.g., $^{142}$Nd/$^{144}$Nd) is measured at another magnet setting. This correction was performed offline using the raw data of Upadhyay et al. (2009).

For samples that were analyzed more than 3 times, the 2 s.d. and 0.95 confidence limits of these analyses are shown.

For samples only analyzed 1-2 times, the 2 s.d. of the "normal" terrestrial samples was used as an estimator of external reproducibility (underlined 2 s.d. values).

"Differences" reflect the approximate shift in measured values (i.e., error) to be expected from the observed degree of fractionation between the measurement of the normalisation ratio and the ratio of interest.

Table 6.2 Shifts in Nd isotope compositions caused by the S1-S3 time delay in the Upadhyay et al. (2009) data set (see explanation in text).
6.4 Discussion

Fig. 6.3 Summary of Nd isotope data for the Khariar samples and standards analyzed by Upadhyay et al. (2009). The red data points reflect the data as originally published, except that the original static $^{150}$Nd/$^{144}$Nd values were converted to dynamic values (to cancel collector efficiencies) using the original raw data and the method described in Thirlwall (1991). Data in blue have been approximately corrected for the effects of rapid mass fractionation, which leads to differing fractionation states of the sample between the measurement of $^{146}$Nd/$^{144}$Nd at magnet setting 1, and the measurement of $^{142}$Nd/$^{144}$Nd at magnet setting 3, see Table 6.1. For samples analyzed more than 3 times, the error bars show 95% confidence limits. For samples that were measured only once or twice, the 2 SD of the population of normal rocks (n = 19) was used to estimate external reproducibility. The $\mu$-units are referenced to the La Jolla Nd standard. The vertical black line is the mean of the 19 analyses of 6 normal rocks, with dashed lines indicating 95% confidence limits. Normal rocks are used as the reference here because they have gone through the same chemical procedure as the four samples that have a purported negative anomaly, and La Jolla might have an anomalous isotope composition as seen here and noted by others (O’Neil et al., 2008). For the time-corrected data, none of the individual rocks deviate significantly from the mean of normal samples for $\mu^{145}$Nd, $\mu^{148}$Nd, and $\mu^{150}$Nd. This is also the case for all but one of the rocks with respect to $\mu^{142}$Nd. Only sample DU-1/4 still retains a small apparent $^{142}$Nd anomaly after the data have been time-corrected. The colored vertical bars show the 95% confidence limits for the four samples that were previously reported to have $^{142}$Nd anomalies.
6 Revisiting the $^{142}$Nd deficits in the 1.48 Ga Khariar alkaline rocks (India)

6.4.3 Domain mixing

On the basis of early work on Mg and Ca isotope analyses (Esat et al., 1986; Papanastassiou & Wasserburg, 1987; Hart & Zindler, 1989), it was suggested that different domains of a sample load on a filament might become fractionated to different degrees during TIMS analysis. The formation of such domains may occur due to cracking of the sample as it is dried down out of solution on the filament after loading. During measurement, a difference in surface emissivity of the sample compared to the rhenium filament surrounding it may cause temperature gradients across the sample, while a clean filament—or a filament loaded with a sample of the same surface emissivity as the filament—would maintain a fairly homogeneous temperature distribution. If two or more differently fractionated domains are evaporating, ionizing, and thus contributing to the measured ion beam, the resulting beam will consist of an isotope mixture that does not lie on an exponential fractionation curve but off to its concave side (see Fig. 1 of Upadhyay et al., 2008). In contrast, isotopic composition of the domains themselves should lie on a mass fractionation curve going through the true ratios. Upadhyay et al. (2008) and Andreasen & Sharma (2009) have investigated the potential effects of such “domain mixing” for dynamic Nd measurements by TIMS and have concluded that it would bias $^{142}$Nd/$^{144}$Nd, $^{148}$Nd/$^{144}$Nd, and $^{150}$Nd/$^{144}$Nd to higher- and $^{145}$Nd/$^{144}$Nd to lower values than the true values.

We examined the Khariar data after it was corrected for the mass fractionation rate effects as explained above and using dynamic $^{150}$Nd/$^{144}$Nd instead of the originally published static data (the static data exhibited a long-term drift of 160 ppm over the course of that 33-month study). To test for domain mixing trends in $\mu^{142}$Nd vs. $\mu^{150}$Nd and $\mu^{142}$Nd vs. $\mu^{148}$Nd space (Fig. 6.4), we considered four population means: the 19 pooled analyses of all six “normal” rocks, the 16 analyses of the La Jolla Nd standard, the 14 analyses of four supposedly “negative anomaly”-bearing rocks, and the seven analyses of one rock that still shows a slight negative anomaly after the time-correction was applied. Domain mixing trends have fixed slopes in these diagrams (Upadhyay et al., 2008; Andreasen & Sharma, 2009). In Figure 6.4, intercepts were arbitrarily chosen such that trends having these domain-mixing slopes pass through all population means. Domain mixing trends originating from an initial composition will follow the slopes only toward increasing $\mu^{142}$Nd, $\mu^{148}$Nd, and $\mu^{150}$Nd. Because of the concavity of the fractionation curves, domain mixing can never result in a decrease in these values (Upadhyay et al., 2008; Andreasen & Sharma, 2009). Thus, domain mixing away from the normal rocks would proceed toward the upper right in both diagrams, and not towards the “anomalous” samples. Hypothetical domain mixing starting from the “anomalous” population and proceeding toward “normal” rocks and the La Jolla Nd population is also untenable: this would require that the 19 analyses of normal rocks and 16 analyses of La Jolla underwent strikingly similar degrees of domain mixing, such that they all stopped at the same relatively elevated $^{142}$Nd/$^{144}$Nd. At the same time,
6.4 Discussion

Fig. 6.4 $\mu^{142}\text{Nd}$ vs. $\mu^{150}\text{Nd}$ and $\mu^{142}\text{Nd}$ vs $\mu^{148}\text{Nd}$. The time-corrected Khariar and standard data are shown. The ellipses represent 95% confidence intervals. Black ellipses represent the 16 pooled analyses of the La Jolla Nd standard. Blue ellipses are the 19 pooled analyses from six “normal” rocks, including three from Khariar. Orange ellipses are all 14 analyses of the four “anomalous” Khariar rocks pooled together. Pale orange ellipses are seven pooled analyses of sample DU-1/4, the only rock that still consistently yields a negative $^{142}\text{Nd}$ after the multidynamic analysis has been time-corrected. Trends having the theoretical slopes resulting from domain mixing processes described by Upadhyay et al. (2008) and Andreasen & Sharma (2009) are shown. For illustrative purposes, the trends have been arbitrarily placed to pass through the bulk of analyses. Because domain mixing effects can only result in positive shifts in $\mu^{142}\text{Nd}$, $\mu^{148}\text{Nd}$, and $\mu^{150}\text{Nd}$, the “anomalous” analyses cannot be a result of “domain mixing” away from a “normal” rock composition, which would result in compositions trending to the upper right of both diagrams. Also note that for a given population, the error correlations have opposite signs (related to slopes of long axes of ellipses) between the two diagrams. This would not be the case if domain mixing occurred and was the dominant source of scatter among samples in each population.

The four remaining rocks would have to reproducibly exhibit no domain mixing in all 14 analyses, and thus plot, relative to the terrestrial standards at negative $\mu^{142}\text{Nd}$. We consider this a highly unlikely scenario.

As a final point, the sign of the correlation among all individual analyses within each population switches between $\mu^{142}\text{Nd}$ vs. $\mu^{150}\text{Nd}$ and $\mu^{142}\text{Nd}$ vs $\mu^{148}\text{Nd}$ diagrams. This feature would not be expected if the spread among samples within populations were produced mainly by domain mixing. The expected pattern would be a positive correlation for all populations on both plots in Figure 6.4. Although domain mixing may be able to explain apparent reverse-fractionation trends in $^{146}\text{Nd}/^{144}\text{Nd}$ with associated jumps in $^{142}\text{Nd}/^{144}\text{Nd}$ to higher values (e.g., Fig. 3 in Upadhyay et al., 2008), it cannot explain the relative positions of the population means in Figure 6.4, or the occurrence of apparent negative anomalies in the Upadhyay et al. (2009) data. We stress that it is necessary to use dynamic (not static)
Revisiting the $^{142}$Nd deficits in the 1.48 Ga Khariar alkaline rocks (India)

$^{150}$Nd/$^{144}$Nd and $^{148}$Nd/$^{144}$Nd measurements and to avoid a high fractionation rate (or correct its effects) before the evaluation of purported domain mixing trends.

6.5 Implications and conclusions

Most of the $^{142}$Nd deficits reported by Upadhyay et al. (2009) for the Khariar rocks can be explained by anomalously high fractionation rates, which reproducibly biased the $^{142}$Nd/$^{144}$Nd values of four samples (DU-1/4, DU-1-5, DU-13/2, DU-36) downward. After approximately correcting for the effect of differences in fractionation state between the magnet settings, only one of the Upadhyay et al. (2009) samples (DU-1/4) still showed an apparent, slightly negative $^{142}$Nd anomaly of $-6.0 \pm 3.1$ ppm (95% confidence limits). In contrast, our present replicate analyses of the four Khariar rocks were all performed below the threshold fractionation level and none showed resolvable $^{142}$Nd anomalies. In light of the demonstrable effect of elevated fractionation rates on multidynamic Nd analyses, the elevated $r_f$ values of the Upadhyay et al. (2009) data set, and the lack of anomalies in our new, low-$r_f$ data set, we conclude that the negative $^{142}$Nd anomalies reported earlier are analytical artifacts. The effects were reproducible, being limited to the same four rocks for the length of the study. The effects were also subtle: the ranges of average fractionation rates for normal and “anomalous” rocks overlapped significantly at 0.25-0.44 and 0.31-0.46 ppm s$^{-1}$, with only 0.04 ppm s$^{-1}$ between the pooled group means (Table 6.2). Clearly, problematic analyses cannot be identified by fractionation rate alone. The absence of negative $^{142}$Nd anomalies in the Khariar rocks obviates the need for a geological process (other than formation of a stable crust) that could preserve a low-Sm/Nd reservoir for about 2.7 Ga and prevent it from mixing back into the convective mantle.

Dynamic acquisition schemes during TIMS measurements correct for efficiency differences among the detectors and amplifiers. Such acquisition schemes use different magnet settings to reduce the effects of variable collector efficiencies on measured isotope ratios to negligible levels. We recommend minimizing the time interval between the measurements of $^{146}$Nd/$^{144}$Nd at one magnet setting and $^{142}$Nd/$^{144}$Nd ratio at another, since even our corrections do not completely account for the difference in mass fractionation between magnet settings. Special care should also be taken to keep fractionation rates as low as possible and to minimize fractionation rate differences among samples and standards. This may be accomplished in part by carefully controlling the sample loading process (amount and purity of Nd, amount of phosphoric acid, consistency of loading method, etc.). Filament heating rate, filament temperature, and the target ion beam intensity most likely also influence fractionation rate. Even if great care is taken in all of these areas, fractionation rates should still be monitored. We recommend reporting $r_f$ values as described here with every $\mu^{142}$Nd analysis done by TIMS as a simple quality control. Anomalies in $^{142}$Nd associated with $r_f$ values greater than 1 should be considered suspect.
6.5 Implications and conclusions

The method of correcting for the effects of high fractionation rate described here was meant only to estimate the effects on measured $\mu^{142}\text{Nd}$ and other Nd isotope ratios. It is not meant to compensate for less-than-ideal analyses in general. It may however provide a means of improving the precision of low-$r_f$ analyses by removing the component of scatter that arises from fluctuations in fractionation rate or a reversal in its sign. Such an application would require minimizing noise contributions to the interpolated fractionation trends, while retaining the ability to track fractionation closely. Thus the number of cycles included in the moving average would have to be optimized. Alternatively, the fractionation rate may perhaps be smoothly tracked simply by making efficient use of the several isotope ratios (also with denominators other than $^{144}\text{Nd}$) that are measured statically at each magnet setting.
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Appendix Table A.6.1: $^{142}$Nd isotope compositions of the Khariar samples, two replicates of the BCR-2 USGS standard, one replicate of sample SM/GR/97/31 from the Isua Supracrustal Belt and seven repeated measurements of the JNdi-1 Nd standard. The table shows the $^{142}$Nd isotope ratios measured for the static line 1 and the dynamic $^{142}$Nd/$^{144}$Nd ratio. All Nd isotope ratios are mass-fractionation corrected using $^{146}$Nd/$^{144}$Nd = 0.7219. Isobaric interferences are expressed in ppm. Internal errors are 2 SEM.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{142}$Nd/$^{144}$Nd</th>
<th>$^{148}$Nd/$^{144}$Nd</th>
<th>$^{150}$Nd/$^{144}$Nd</th>
<th>$^{152}$Nd/$^{144}$Nd</th>
<th>$^{154}$Nd/$^{144}$Nd</th>
<th>$^{156}$Nd/$^{144}$Nd</th>
<th>$^{158}$Nd/$^{144}$Nd</th>
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</thead>
<tbody>
<tr>
<td>KH1</td>
<td>0.7219</td>
<td>-</td>
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Table A.6.1: $^{142}$Nd isotope compositions of the Khariar samples, two replicates of the BCR-2 USGS standard, one replicate of sample SM/GR/97/31 from the Isua Supracrustal Belt and seven repeated measurements of the JNdi-1 Nd standard. The table shows the $^{142}$Nd isotope ratios measured for the static line 1 and the dynamic $^{142}$Nd/$^{144}$Nd ratio. All Nd isotope ratios are mass-fractionation corrected using $^{146}$Nd/$^{144}$Nd = 0.7219. Isobaric interferences are expressed in ppm. Internal errors are 2 SEM.

6 Revisiting the $^{142}$Nd deficits in the 1.48 Ga Khariar alkaline rocks (India)
Concluding remarks

The study of the early differentiation of the Earth using the coupled $^{147,146}$Sm-$^{143,142}$Nd systems started in the 1990s. It was established by several research groups that the oldest rocks have preserved the vestiges of early-depletion of the Hadean mantle in the form of positive $^{142}$Nd anomalies of about 15 ppm relative to the modern terrestrial composition. The complementary early-enriched crust was first discovered by O’Neil et al. (2008) and Upadhyay et al. (2009). They have reported negative $^{142}$Nd anomalies of about -15 ppm in the Nuvvuagittuq Supracrustal Belt (Canada) and the Khariar Alkaline Complex (India), respectively. The accuracy of these new findings was however questioned (e.g. Andreasen & Sharma, 2009) and their implications for the evolution of the early Earth gave rise to debates, especially about a new possible Hadean age of ca. 4300 Ma for the oldest terrestrial rocks. This dissertation started in 2009 within this scientific context with the study of the coupled $^{147,146}$Sm-$^{143,142}$Nd systems in Nuvvuagittuq, Khariar and Acasta rocks.

The results of this dissertation clarified some of these issues and showed that (1) the negative $^{142}$Nd anomalies reported in Khariar resulted from an analytical artifact, (2) the $^{146}$Sm-$^{142}$Nd apparent “age” of ca. 4300 Ma proposed for Nuvvuagittuq is in disagreement with the younger ca. 3800 Ma $^{147}$Sm-$^{143}$Nd and $^{176}$Lu-$^{176}$Hf records and represents the inheritance of up to ca. 4500 Ma early terrestrial crust, and (3) negative $^{142}$Nd anomalies of about -10 ppm were found in Acasta and, like in Nuvvuagittuq, were inherited from Hadean crust. The outcomes of this dissertation thus firmly established that Hadean vestiges of early terrestrial crust are preserved in Archean rocks.

The interpretation of the $^{142}$Nd anomalies required an integrated approach using several chronometers such as the $^{147}$Sm-$^{143}$Nd and $^{176}$Lu-$^{176}$Hf systems, and the U-Pb zircon geochronology. This helped to resolve the age of metamorphic events that disturbed the systematics of the rocks. The development of a new numerical model of partial isotope equilibration for the coupled $^{147,146}$Sm-$^{143,142}$Nd systematics showed the sensitivity of the $^{146}$Sm-$^{142}$Nd system to resetting and the importance of considering isotope homogenization for interpreting isochron ages.

The measurement of Nd isotope compositions by TIMS with a precision of about ±5 ppm for the $^{142}$Nd/$^{144}$Nd ratio was analytically demanding. Examination of the Upadhyay et al. (2009) data showed that rapid sample fractionation during dynamic TIMS analysis can bias $^{142}$Nd/$^{144}$Nd to lower values. This limitation was not reported so far and could potentially help to improve future analytical protocols and data reduction schemes.
Concluding remarks

Further studies using the coupled $^{147,146}$Sm-$^{143,142}$Nd systems may focus on the prospection of new Archean terranes that potentially exhibit $^{142}$Nd anomalies (e.g., enclaves in the vicinity of the Nuvvuagittuq Supracrustal Belt). Numerical modeling using positive and negative $^{142}$Nd anomalies to constrain crustal recycling may help to better understand the Hadean evolution of the mantle-crust system.

An important aspect in tying to reconstruct the early events of Earth’s differentiation with radiogenic isotopes is the accurate estimate of the BSE composition. This estimate is used as reference value for the calculation of model ages. Chondritic vs. super-chondritic models are still debated. However, this issue was not addressed in this dissertation and was beyond its scope. Further studies of meteorites using $^{147,146}$Sm-$^{143,142}$Nd and other combined systems may clarify this problematic.
Bibliography


Bibliography


Bibliography


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Bibliography


Acknowledgments

I would like to express my gratitude to the following people with whom I have had the pleasure of working with for the past four years:

⋆ my supervisor and “doctor father” Prof. Dr. Bernard Bourdon who offered me to undertake these research projects and helped me to complete my doctoral studies,

⋆ my supervisor Prof. Dr. Rainer Wieler who advised me after the departure of Prof. Dr. Bernard Bourdon for the Ecole Normale Supérieure in Lyon,

⋆ my examiners Prof. Dr. Maria Schönbächler and Prof. Dr. Bernard Marty who expressed strong interest in my research,

⋆ my chairman Prof. Dr. Jean-Pierre Burg who has a great sense of humour,

⋆ my co-workers Prof. Dr. Stephen Mojzsis, Prof. Dr. Janne Blichert-Toft, Prof. Dr. Erik Scherer, Dr. Colin Maden, Dr. Mathieu Touboul, Dr. Peter Sprung, and Dr. Martin Guiterau who taught me lab work and/or helped me with writing articles,

⋆ my guides Prof. Dr. Stephen Mojzsis and Dr. Nicole Cates who showed me the Nuvvuagittuq supracrustal belt,

⋆ the technicians who maintain labs and instruments of the Institute of Geochemistry and Petrology, and

⋆ my colleagues and friends from ETH Zurich who supported me.

And none of this would have been possible without my family that I love so much — thank you all for your precious help and encouragements!

P.-S. Un grand merci aux “Bellevistes” pour avoir été toujours là!