Chemical Geology 386 (2014) 238–248

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Revisiting the ^{142}Nd deficits in the 1.48 Ga Khariar alkaline rocks, India

Antoine S.G. Roth [a,*], Erik E. Scherer [b], Colin Maden [a], Klaus Mezger [c], Bernard Bourdon [d]

[a] Institute of Geochemistry and Petrology, ETH Zurich, 8092 Zurich, Switzerland
[b] Institut für Mineralogie, Universität Münster, 48149 Münster, Germany
[c] Institute of Geological Sciences, University of Bern, 3012 Bern, Switzerland
[d] Laboratoire de Géologie de Lyon, ENS Lyon and UCBL, UMR 5276, CNRS, France

ARTICLE INFO

Article history:
Received 10 December 2013
Received in revised form 19 June 2014
Accepted 24 June 2014
Available online 2 July 2014

Editor: L. Reisberg

Keywords:
Neodymium-142
Hadean differentiation
Khariar alkaline rocks
Thermal ionization mass spectrometry
Multidynamic analysis

ABSTRACT

The ^{146}Sm–^{142}Nd system plays a central role in tracing the silicate differentiation of the Earth prior to 4.1 Ga. After this time, given its initial abundance, the ^{146}Sm can be considered to be extinct. Upadhyay et al. (2009) reported unexpected negative ^{142}Nd anomalies in 1.48 Ga rocks of the Khariar nepheline syenite complex (India) and inferred that an early enriched, low-Sm/Nd reservoir must have contributed to the mantle source rocks of the Khariar complex. As ^{146}Sm had been effectively extinct for about 2.6 billion years before the crystallisation of the Khariar samples, this Nd signature should have remained isolated from the convective mantle for at least that long. It was thus suggested that the source rock of Khariar samples had been sequestered in the lithospheric root of the Indian craton. Using a different chemical separation method, and a different Thermal Ionization Mass Spectrometry (TIMS) analysis protocol, the present study attempted to replicate these negative ^{142}Nd anomalies, but none were found. To determine which data set is correct, we investigated three possible sources of bias between them: imperfect cancellation of Faraday collector efficiencies during multidynamic TIMS analysis, rapid sample fractionation between the sequential measurement of ^{146}Nd/^{144}Nd and ^{142}Nd/^{144}Nd, and non-exponential law behaviour resulting from so-called "domain mixing." Incomplete cancellation of collector efficiencies was found unlikely to cause resolvable biases at the estimated level of variation among collector efficiencies. Even in the case of highly variable efficiency and resolvable biases, there is no reason to suspect that they would reproducibly affect only four rocks out of 10 analysed by Upadhyay et al. (2009). Although domain mixing may explain apparent "reverse" fractionation trends observed in some TIMS analyses, it cannot be the cause of the apparent negative anomalies in the study of Upadhyay et al. (2009). It was determined that rapid mass fractionation during the course of a multidynamic TIMS analysis can bias all measured Nd ratios. After applying an approximate correction for this effect, only one rock from Upadhyay et al. (2009) retained an apparent negative ^{142}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 anomalies reported by Upadhyay et al. (2009) are a subtle and reproducible analytical artefact. 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.

1. Introduction

The short-lived ^{146}Sm–^{142}Nd chronometer (half-life $t_{1/2}$ = 68 Ma; Kinoshita et al., 2012) is a sensitive tracer of early silicate Earth 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 of the solar system (0.0094 ± 0.0005; Kinoshita et al., 2012, based on the data of Boyet et al., 2010) and the similarity between Sm and Nd mineral-liquid partition coefficients, which results in limited Sm/Nd fractionation. The detection of ^{142}Nd anomalies requires a very clean separation of Nd from its matrix, and in particular from Sm and Ce, to lower isobaric interferences to negligible levels. Furthermore, a dynamic acquisition scheme is often applied 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., 2013). 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 relative standard deviations, RSD) 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 and Sharma, 2009).

* Corresponding author at: Institute of Physics, University of Bern, 3012 Bern, Switzerland. Tel.: +41 31 631 84 34.
E-mail address: antoine.roth@space.unibe.ch (A.S.G. Roth).

http://dx.doi.org/10.1016/j.chemgeo.2014.06.022
0009-2541/

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 recently discovered (O'Neil et al., 2008) and later confirmed (Roth et al., 2013) for the ca. 3750 Ma Nuvvuagittuq supracrustal belt in Québec (Canada). Deficits in ^{142}Nd as large 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). As 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 billion years. According to Upadhyay et al. (2009), this may 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 more than 2.6 billion years 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. More recent work by Debaille et al. (2013) also showed that positive ^{142}Nd anomalies could be preserved in 2.7 Ga mantle-derived rocks.

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 anonymized by a laboratory assistant and not revealed to the analysts (ASGR, EES and BB) until all analyses and the initial data interpretation 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 had 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 differences smaller than 10 ppm between isotope ratios.

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 a sample from the Isua Supracrustal Belt (SM/GR/97/31) previously analysed by Caro et al. (2006) and Roth et al. (2013). Each Nd cut was then split into two aliquots and measured by TIMS for isotopic composition in addition to seven JNdi-1 Nd standards.

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. (2013, 2014). 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 were 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 resulting tetravalent Ce was complexed by an organic solvent (heptane). This solvent was pipetted away and discarded, leaving behind the Ce-free aqueous phase. The overall extraction technique was repeated twice. 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 chemistry yields were >80% and total procedural blank was about 150 pg.

2.2. Neodymium mass spectrometry

Neodymium was measured as a positive metal ion (Nd^+) with a Thermo Triton (TIMS) at ETH Zurich. About 500 ng of Nd per sample dissolved in 1 μl of 6 M HCl and 1 μl of 0.01% phosphoric acid were loaded onto one filament of a double rhenium filament assembly (filament dimensions: 0.04 mm thick by 0.76 mm wide zone refined Re ribbon from H. Cross Company, Moonachie, USA). During TIMS analysis, the ionisation filament current was increased to 5500 mA at a rate of 200 mA per minute. The evaporation filament current was then increased at the same rate to typically 1600 mA until a $^{142}Nd^+$ ion current corresponding to about 7.5 V over a 10^{11} Ω feedback resistor was obtained. The evaporation filament was automatically reheated between measurement blocks when signal intensity dropped below 80% of its initial intensity. Mass fractionation was corrected with the exponential law using $^{146}Nd/^{144}Nd = 0.7219$ as the reference. Isobaric interferences from ^{144,148,150}Sm and ^{142}Ce were monitored by measuring ^{147}Sm and ^{140}Ce, respectively, and corrected online. The $^{142}Ce/^{142}Nd$ and $^{144}Sm/^{144}Nd$ mean values for the analyses never exceeded 1.56×10^{-6} and 2.55×10^{-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 ^{145}Nd and ^{143}Nd in the axial detector) was used to reduce the effects of these variations on measured isotope ratios as much as possible. The amplifier rotation feature on the Triton can cancel variations among amplifier gains even for static analyses, but it cannot cancel differences in cup efficiencies. Table 1 shows the cup configuration and measurement conditions for the dynamic Nd isotope analyses. The integration time was 8.4 s for each magnet setting. The two magnet settings were separated by an idle time of 4.0 s. The coincidences of each beam with its corresponding Faraday collector were optimized for the first magnet setting by physically moving the cups to the correct positions. To precisely align the beams into the detectors for the second magnet setting, the dispersion quadrupole setting was changed from 0 V to a value between 7.5 and 8.5 V. A measurement consisted of 24 to 80 blocks with 20 cycles per block, and lasted 4 to 14 h. Amplifiers were rotated "to the left" every block. Previous tests indicated that no systematic biases occur between data sets collected during left rotation and those collected during right rotation. The peaks were centered in the axial detector every three blocks using the ^{145}Nd- (magnet setting 1) and ^{143}Nd- (magnet setting 2) beams. An iterative automatic lens focusing routine involving the Condenser, Extraction Left, Right, and Symmetry, X-Symmetry, and Z-Focus electrodes was done every three blocks using ^{145}Nd in the axial detector. The turret position was set to the center position and never changed to optimize ion beam intensity. Baselines were measured every block (30 integrations of 1 s). 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