Sm–Nd Isotopic Systematics of Continental Igneous Rocks of India: Implications for the Early Evolution of the Silicate Earth

Thesis submitted to The Maharaja Sayajirao University Of Baroda Vadodara, India

> For the degree of Doctor of Philosophy in Geology by

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October, 2017



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Certificate

I certify that the thesis entitled "*Sm–Nd Isotopic Systematics of Continental Igneous Rocks of India: Implications for the Early Evolution of the Silicate Earth*" by Ms. Ikshu Gautam was prepared under my guidance. She has completed all requirements as per Ph. D. regulations of the University. I am satisfied with the analysis of data, interpretation of results and conclusions drawn. I recommend the submission of the thesis.

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Declaration

I, Ikshu Gautam, hereby declare that the research work incorporated in the present thesis entitled "*Sm-Nd Isotopic Systematics of Continental Igneous Rocks of India: Implications for the Early Evolution of the Silicate Earth*" is my own work and is original. This work (in part or in full) has not been submitted to any university or institute for the award of a Degree or a Diploma. I have properly acknowledged the material collected from secondary sources wherever required. I solely own the responsibility for the originality of the entire content.

Date:

Ikshu Gautam (Author)

Dedicated to

My Family

and

Well-wishers

Acknowledgements

'If we'd known we were going to make it, the challenge would not have been the same – we might not have gone. If we'd known what lay ahead, we *certainly* would not have gone.' (Starkell, D., 1994. *Paddle to the Amazon- the ultimate 12,000 mile canoe adventure*, A Douglas Gibson book).

These lines caught my attention five years ago when my supervisor gave me the referred book to read as a motivation exercise. These lines perfectly summarize my journey as a PhD student in PRL. A perfectionist that my supervisor (Prof. J. S. Ray) is, has helped me, to develop a better thought process and presentation skills, to carry out scientific research. Under his guidance, I have learned the importance of ethics in science and quality of work, which one needs to maintain. I thank him for his patience while correcting my manuscripts and thesis. I must confess that those were the most difficult times for both of us. The research work carried out by me would not have been possible in a way that I have, if it was not for him. He gave me freedom to carry out my own experiments, even though we didn't agree on the setups and results some of the times. I thank him for motivating me and tolerating my mistakes. I express my sincere gratitude to him.

I would like thank my co-guide, Prof. L.S. Chamyal of the M.S. University of Baroda for his advice and help. A special thanks to Balaji for the help extended during every single visit to the university. I thank my Doctoral Supervising Committee members at PRL, Prof. R. Ramesh and Dr. Sanjeev Kumar for their critical comments and good suggestions during the course of my research. This work would not have been possible without the help of my collaborators at the Department of Earth Sciences, Pondicherry University. I thank Prof. S. Balakrishanan for providing me access to TIMS facility. Prof. Rajneesh Bhutani was not only my collaborator, but also a mentor and a friend during my stays at the Pondicherry University. Thanks are dues to the Head of department and other faculty members of Pondicherry University.

My research journey in PRL has been incredible. The understanding of the concepts, the discussions, re-evaluations of the existing interpretations, has been supported with the Tuesday divisional seminars. I thank all the members of the Geosciences Division and others who attended my talks. I would like to thank all the faculty members who taught me during the course work. The focus on work could be maintained as the other issues were always taken care of by PRL. I thank the Director (present and then) for providing the facilities. Without the help extended by members from administrative staff, library, computer centre, workshop, maintenance, purchase,

stores, accounts, medical, housekeeping, canteen and office, life would not have been as convenient here.

If I start writing names of the people who have helped me in one way or the other during these last six years, I would probably be able to write an equivalent volume of my thesis. With due regards, I thank everyone who has been a support during this journey, not only in PRL but at Pondicherry University as well.

However, I would like to mention names of my batch-mates, without whom, the life at PRL would have been very difficult. Manu, Abhaya and Anirban are family, and Shraddha is an integral part of it. The extended part of this family (in alphabetical order) are – Alok, Arun, Chithra, Gaurava, Girish, Guru, Kuldeep, Sanjay, Saweeta, Swapana and Tanmoy. The second extension of this family belongs to my jade palace buddies – Alok, Neeraj, Souvik, Shrema, Bivin and Anirban. I thank all my friends in other batches who motivated and helped me.

Oscillating between Ahmedabad and Puducherry for research work, I became a migratory bird who used to travel south in winter. I have been lucky to meet some wonderful people in this exchange, and gained some important experiences. I thank Shimla, Maya, Rekha, Sathya, Aswathy, Deepana, Jisha, Kingson, Dash bhaiya, Chandru, Vishnu, Madhu, Sminto and Nizam. Sincere thanks to *the akka* in the department, who used to feed me sometimes with her food. I must thank all the security akkas at the Madame Curie Hostel and Saraswathy Hostel, Pondicherry University, for opening hostel gates for me, late at night.

This journey would be impossible without the constant motivation and support from my family. I thank my family – papa, mumma, shailu, subu, jiju and the little ones. Whenever in doubt, they have guided me through my lowest of times. I am fortunate to have a strong family back-up. With this thesis, I am fulfilling a dream of many. I feel happy to be able to do it.

Thank you everyone for everything.

Ikshu

Abstract

Earth as we know today, externally as well as internally, is a consequence of the planetary evolution subsequent to its formation from the solar nebula at 4.56 Ga. The first five hundred million years of the Earth's history have been critical to this, during which, it differentiated into different density layers forming the core, mantle, crust, and atmosphere. Evidence for these differentiation events and their timings come from short-lived radionuclide systematics such as: 182 Hf- 182 W (T_{1/2} = 9 Ma); 146 Sm- 142 Nd (T_{1/2} = 103 Ma); 129 L- 129 Xe (T_{1/2} = 16 Ma). The timing of core formation has been constrained to within first 30-50 Ma of the formation of Solar System, however, the early differentiation of the remaining Bulk Silicate Earth still remains enigmatic. Refractory Lithophile Elements (RLEs) like Sm and Nd are tracers of Silicate Earth Differentiation and by using ¹⁴⁶Sm-¹⁴²Nd short-lived isotopic systematics information about early differentiation events can be obtained. Using this tracer, important insights have been gained on the silicate differentiation that took place early in the history of Earth for which there are very few rock records. The signatures of these event(s) are preserved as anomalous ¹⁴²Nd/¹⁴⁴Nd isotopic compositions with respect to terrestrial standard that is assumed to possess the same ¹⁴²Nd isotopic composition as the accessible mantle of Earth. As known to us today, most of these signatures are limited in space to Greenland and Canada, and in time to Hadean-Archean Eons. Questions pertaining to the size of the early formed reservoirs: the EDR (Early Depleted Reservoir) and EER (Early Enriched Reservoir), remains unanswered and so are those on their preservation in time. In an effort to unravel some of these mysteries of the early differentiation of silicate Earth, I worked towards finding ¹⁴²Nd anomalies in various mantle reservoirs, focusing on rocks from the Indian Shield. In particular, Archean mantle and the non-convective mantle domains were of my interest. I studied several Archean granitoids and alkaline rocks including carbonatites of varying ages for their ¹⁴²Nd isotope composition. Since the anomalous composition (if present) vary in the sixth decimal for 142 Nd/ 144 Nd isotopic ratio (defined as μ^{142} Nd), obtaining accurate and precise data is analytically challenging. The analytical procedures developed and adapted for this study reveal important information on the role of analytical methods in the possible generation of artefacts/bias in the measurements. In

addition, commonly used terrestrial standards, Ames Nd and JNdi-1, were found to have dissimilar ¹⁴²Nd/¹⁴⁴Nd ratio. This has an important implication to the value of μ^{142} Nd calculated, as depending on the choice of standard, anomalies may appear or disappear. Through this study I provide a cross-calibration of the two standards, which can be used for comparison of existing and future data. For future studies, I strongly recommend use of a homogeneous standard like JNdi-1. Using the information obtained from the analytical procedures, accurate and precise data were obtained for the TTGs and alkaline rocks of India. My study finds that the nonconvecting mantle domains may not be the sites for preservation of the signatures of the EER. However, ¹⁴²Nd data from Singhbhum suggests that this oldest Archean Craton of India may have preserved evidence of the EDR.

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References

Chapter 1 Introduction One of the most fascinating questions which has caught the attention of the humans is: How did the planet that we live come into existence? This question is intricately related to the origin of the solar system and the two cannot be isolated and understood separately. Since our planet forms a part of the solar system, understanding its evolution can in principle provide insights into the formation of other planets as well. As for the questions about the timings and processes of formations of the early solar system objects, a lot have been inferred with the help of extinct radioactivity in some of the first solids that formed out of the solar nebula. The long-lived radionuclides have helped provide ages of the oldest solar system materials and the age of the Earth, which is 4.568 Ga (Amelin et al. 2002; Bouvier and Wadhwa, 2010; Jacobsen et al. 2008). The commonly used short-lived radionuclide systematics to study the early solar system processes are: ¹²⁹I-¹²⁹Xe (T_{1/2} = 16 Ma); ²⁴⁷Cm-²³⁵U (T_{1/2} = 15.6 Ma); ¹⁰⁷Pd-¹⁰⁷Ag (T_{1/2} = 6.5 Ma); ⁵³Mn-⁵³Cr (T_{1/2} = 3.7 Ma); ⁶⁰Fe-⁶⁰Ni (T_{1/2} = 1.5 Ma); ²⁶Al-²⁶Mg (T_{1/2} = 0.7 Ma); ⁴¹Ca-⁴¹K (T_{1/2} = 0.1 Ma). The values of half-lives are as reported in (Dickin, 2005).

The Chondrite meteorites are considered to be the best representatives of the chemical compositions of the parent material of terrestrial planets, including Earth (Anders and Grevesse, 1989; Kargel and Lewis, 1993; Lodders, 2003; Palme and O'Neil, 2014). There exist numerous hypotheses on the formation of the terrestrial planets as well as the gas giants and the way these are positioned in the solar system. Some of the important models that best explains the observations are the Nice model, Truncated Disk model etc. (e.g. Jacobsen and Walsh, 2015). Among these, the Grand Tack model best explains the mechanisms by which our planets and their planetary embryos could have formed from the cloud of gas and dust at high temperature and low pressure conditions, which led to the arrangement of the solar system bodies the way we observe them today (Jacobsen and Walsh, 2015). Earth was not the same during its early history as we know it today, both externally as well as internally. The inner terrestrial planets had essentially formed by the processes in the order: dust sedimentation and growth, planetesimal growth, planetary embryo growth, planet growth and finally the giant impact phase (Jacobsen and Walsh, 2015). The last giant impact on Earth was Moon forming event and it is estimated to have happened within the first 95 Myr, the timing being constrained from highly siderophile element record for Earth (Jacobson et al. 2014). During these formation processes, planetary scale melting took place leading to magma ocean stages, during which, the planets rearranged themselves into different density layers (core-mantle-crust) - resulting into layered or differentiated planets. All these major differentiation events took place during the early history of the solar system, within the first 500 Ma (Carlson et al. 2015). Evidence for these events and their timings come from shortlived radionuclide systematics such as: ¹⁸²Hf-¹⁸²W (T_{1/2} = 9 Ma); ¹⁴⁶Sm-¹⁴²Nd (T_{1/2} = 103 Ma); ¹²⁹I-¹²⁹Xe (T_{1/2} = 16 Ma).

1.1 The Early Earth

1.1.1 Core Formation

The estimates about the composition of the Earth's core can be made by studying undifferentiated (chondrite) and differentiated (iron) meteorites and terrestrial rocks. Chemically, core is essentially an alloy of Fe and Ni. There are many models available to explain the segregation of the core (Rubie et al. 2015). The understanding is still evolving, which is largely hinged on assumption of the type of the starting composition of the Earth. However, the age of formation has been constrained with some confidence. With the help of the extinct radioactivity of 182 Hf- 182 W (T_{1/2} = 9 Ma), the timing of the core segregation has been constrained to be within the first 30-50 Ma of the formation of the solar system (Jacobsen, 2005; Kleine et al. 2009; Nimmo and Kleine, 2015). This estimate depends upon the initial abundance of ¹⁸²Hf of the Solar System as well as the isotopic composition of W in chondritic meteorites, the starting material (Kleine et al. 2009; Nimmo and Kleine 2015). Hf is a lithophile element whereas W is siderophile. This means that all the W present in Earth during the formation of the core would have gone to the core along with the iron, while Hf had remained in the silicate mantle. If this event took place during the time when ¹⁸²Hf was extant, no anomalous composition of the radiogenic daughter ¹⁸²W should be observed in the mantle. Interestingly, however, ¹⁸²W anomalies are observed in the terrestrial mantle, which indicate that the core segregation process happened before all the ¹⁸²Hf had completely decayed to ¹⁸²W, thus constraining the age of the core formation.

1.1.2 Early Silicate Earth Differentiation

The crust is a product of differentiation of the terrestrial mantle. With the help of trace elements and isotopes, much information has been derived on how mantle dynamics operates and differentiation happens. Unfortunately, because of near absence of rock record we know very little about such processes that happened during the early history of Earth. The oldest Earth rock known today is ~ 4 Ga (Bowring and Williams, 1999; O'Neil et al. 2008), and hence, direct records of the first 500 Ma are missing, particularly of the early silicate differentiation process. Fortunately, however, we have access to indirect evidence about the

early silicate differentiation from the oldest zircons (Cavosie et al., 2005; Harrison et al., 2008; Valley et al., 2014; Valley et al., 2005; Wilde et al., 2001). The Hf isotopic study of these zircons from Jack Hills, Australia, provided valuable insights about the earliest crust (Blichert-Toft and Albaréde, 2008). The first assured evidence for the early differentiation of the silicate Earth was obtained with the help of ¹⁴⁶Sm-¹⁴²Nd systematics. The ¹⁴²Nd isotopic investigations of one of the oldest rocks preserved on Earth, the 3.8 Ga metasediments from Isua Supracrustals Belt in Greenland, showed an excess of ¹⁴²Nd radiogenic daughter, indicating the formation of its mantle source at a time when ¹⁴⁶Sm was still decaying (Harper and Jacobsen, 1992; Boyet et al. 2003; Caro et al. 2003, 2006; Bennett et al. 2007).

1.2 Tracers of Early Silicate Earth Differentiation

Refractory Lithophile Elements (RLEs) are some of the best tracers of the silicate differentiation processes. Refractory elements were present in the first solids that condensed from the solar nebula at around 50 % condensation temperatures, which is a function of pressure, oxygen fugacity etc. The elemental ratios of such elements in the chondritic meteorites are similar to those in the terrestrial planets (Lodders et al. 2009; Lodders, 2010; Palme et al. 2013). This helps in defining a (geo) chemical reference for Earth. These ratios get modified during differentiation processes thereby recording their effects. In order to be useful as tracers of differentiation of the silicate Earth, these refractory elements need to be present in the silica rich rocks, implying that they must also be lithophile. To be a good tracer an element should be incompatible so as to record a differentiation event such as the partial melting or fractional crystallization. Of all RLEs, Sm and Nd are two of the best available tracers for differentiation. Both Sm and Nd are Rare Earth Elements (REEs) and are incompatible. A small difference between their ionic radii, 1.08 Å for Nd⁺³ and 1.04 Å for Sm⁺³, makes Nd more incompatible than Sm. During any differentiation event, both Sm and Nd move out the solid source, however, since Nd is more incompatible it gets enriched in the melt. The melt also gets enriched in other incompatible elements like Large Ion Lithophile Elements – LILEs and hence in the rocks which form from this melt. This change in Sm/Nd ratio during a differentiation event is reflected in the isotopic composition of these elements over time. By studying their isotopes information about the differentiation process(s) and its timings can be obtained.

1.2.1¹⁴⁶Sm-¹⁴²Nd Systematics and Early Silicate Differentiation

Sm and Nd both have seven isotopes each, out of which two isotopes of Sm are radioactive and decay by alpha emissions to produce two radiogenic stable isotopes of Nd. The longlived ¹⁴⁷Sm-¹⁴³Nd systematics is a tracer of silicate differentiation over geologic history, it, however, fails to differentiate between early events that happened within a few hundreds of millions of years. Because of the long half-life of parent nuclide ¹⁴⁷Sm (T_{1/2} = 106 Ga) there is very little change in the isotope composition of daughter ¹⁴³Nd isotope during the timescales the early events. Any measureable change of this ratio is generally in the fourth decimal place and is often expressed as ε^{143} Nd = [((¹⁴³Nd/¹⁴⁴Nd)_{rock}/ (¹⁴³Nd/¹⁴⁴Nd)_{CHUR})-1)×10⁴]. This systematics is very useful to find the date of the event and is one of the robust chronometers to date very old rocks.

To extract information about early events, fortunately, a short-lived isotopic systematics of Sm-Nd is also available. ¹⁴⁶Sm is now extinct because it had decayed quickly with a short half-life of 103 Ma (Marks et al. 2014) or 68 Ma (Kinoshita et al. 2012) to produce ¹⁴²Nd. The events that took place within the first few hundreds of millions of years can be easily distinguished using the change in the ¹⁴²Nd/¹⁴⁴Nd isotopic ratios. Early formed reservoirs due to this differentiation can be understood as Early Depleted Reservoir (EDR) and Early Enriched Reservoir (EER). Using long-lived ¹⁴⁷Sm-¹⁴³Nd systematics, the early differentiation events cannot be resolved within first 500Ma. This is explained in Figure 1.1. Since the initial abundance of ¹⁴⁶Sm/¹⁴⁴Sm was low (0.0085±0.0007;



Figure 1.1 A schematic illustration showing how short-lived ¹⁴⁶Sm-¹⁴²Nd isotopic systematics helps in differentiating early events (events 1 and 2, closely spaced in time) as compared to the long-lived ¹⁴⁷Sm-¹⁴³Nd isotopic systematics (after Caro, 2011). The event no. 3 is a late differentiation event. Using ε^{142} Nd the early events can be distinguished which are not resolvable in time using ε^{132} Nd. The slope of the lines showing evolution of EDR and EER (or any other mantle reservoir) depends upon Sm/Nd ratio: EDR = Early Depleted Reservoir; EER = Early Enriched Reservoir. ε^{142} Nd defined as ε^{142} Nd = [((¹⁴³Nd/¹⁴⁴Nd)_{rock}/ (¹⁴³Nd/¹⁴⁴Nd)_{terrest std})-1)×10⁴].

Boyet et al. 2010), the change in ¹⁴²Nd/¹⁴⁴Nd isotopic composition is very small and is usually expressed as $\mu^{142}Nd = [(({}^{142}Nd/{}^{144}Nd)_{rock}/({}^{142}Nd/{}^{144}Nd)_{terrestrial standard}) - 1] \times 10^6$, to magnify the variations in the sixth decimal place. Any deviation in the ¹⁴²Nd/¹⁴⁴Nd isotopic composition of a rock from that of terrestrial standard shows that the Sm/Nd ratio of the rock at the time of its formation was different from that of the accessible mantle, which is represented by terrestrial standard, in μ notation, and this change took place when ¹⁴⁶Sm was still extant (i.e., during the first five hundred million years). This deviation is known as anomaly and represents a signature of early differentiation of silicate Earth. Table 1 summarizes all the μ^{142} Nd anomalies reported till date. A positive anomaly represents a mantle source which had more Sm than Nd and hence, possesses higher amount of radiogenic ¹⁴²Nd compared to that of the undifferentiated mantle. Since this mantle reservoir is depleted in incompatible elements like Nd (and LILEs), and had formed during the early differentiation, it is called Early Depleted Reservoir (EDR). Principles of mass balance suggests that a complimentary mantle reservoir with higher amounts of incompatible elements like Nd (and LILEs) should also have formed during this event, which is generally termed as an Early Enriched Reservoir (EER). Because this enriched reservoir had less Sm to begin with, the production of radiogenic ¹⁴²Nd would have been lower than that in the undifferentiated source, thus leading to a negative μ^{142} Nd. Whereas in the case of EDR, a positive value for μ^{142} Nd would be acquired over time.

Figure 1.2 shows most important results of the μ^{142} Nd studies plotted using La-Jolla/Ames Nd/JNdi-1 as the terrestrial standard (assuming all have identical ¹⁴²Nd/¹⁴⁴Nd compositions). It plots all anomalous values except the negative anomalies of 1.48 Ga alkaline rocks from Khariar, India (Upadhyay et al. 2009). A detailed discussion of these values is given in Chapter 4. Since anomalous μ^{142} Nd compositions represent signatures of the early silicate differentiation processes, it is necessary that such values are reproduced independently by different laboratories in order to rule out any bias/error generating from experimental methods and/or data handling protocols. The important information that has been derived from the earlier studies is discussed in the following paragraphs.



Figure 1.2 The plot shows ¹⁴²Nd/⁴⁴Nd in ppm, defined as $\mu^{142}Nd = [((^{142}Nd/^{144}Nd)_{rock} / (^{142}Nd/^{144}Nd)_{terrestrial standard})-1] \times 10^6$, of mantle derived rocks of varying ages and from different tectonic settings (Andreasen et al., 2008; Bennett et al., 2007; Boyet and Carlson, 2006; Burkhardt et al., 2016; Caro et al., 2006; Murphy et al., 2010; O'Neil et al., 2008a; Rizo et al., 2012, 2011; Roth et al., 2013, 2014a). Rock standard BHVO-2, and an in-house gabbro standard (Upadhyay et al. 2009) are also shown. Grey shaded area represents variability (2-standard deviation) in the measurement of the terrestrial standard (assuming all the commonly used terrestrial standards are isotopically same) over time, which is 6 ppm in this plot. Ordinary chondrites plot at -18.3 ppm (Burkhardt et al. 2016).

1.2.2 Chondritic Versus Non-Chondritic Earth

In the definition of μ^{142} Nd, ¹⁴²Nd/¹⁴⁴Nd of terrestrial standard (i.e. that of the Earth) is used for normalization. This is in contrast to the use of Chondritic Uniform Reservoir (CHUR) for the calculation of ε^{143} Nd. This is done to make the present day value of μ^{142} Nd = 0 for Earth's crust and present-day mantle (Caro, 2011). However, initially it was believed that the ¹⁴²Nd/¹⁴⁴Nd isotopic composition of the chondrites (Ordinary Chondrites-OC) is equivalent to that of the terrestrial standard, which represents ¹⁴²Nd/¹⁴⁴Nd isotopic composition of the accessible mantle. This assumption was proved wrong in 2005, when Boyet and Carlson (2005) showed that the OCs have μ^{142} Nd value of -20 ppm with respect to the terrestrial standard. This means that all the terrestrial rocks, except a few, have +20 ppm excess ¹⁴²Nd as compared to that of the chondrites. This important discovery has implications for our overall understanding of the geochemical evolution of the planet Earth. In the following paragraphs I discuss various evolutionary scenarios that could have resulted in a nonchondritic μ^{142} Nd composition of the Earth's accessible mantle (or terrestrial rocks).

Scenario I: Chondritic Earth undergoing a very early global scale differentiation

As proposed by Boyet & Carlson (2005), the non-chondritic ¹⁴²Nd/¹⁴⁴Nd for terrestrial rocks can be explained by an early global differentiation event which formed an Early Depleted Reservoir (EDR) that has been sampled by all the terrestrial rocks analyzed so far (Figure 1.3). In this model, mass balance requires formation of a complimentary Early Enriched Reservoir (EER). However, till date, this reservoir has remained elusive. Some believe that the EER is located either deep in the mantle and may not ever be sampled; or represented the earliest formed crust that got lost to space due to collisional erosion (O'Neill and Palme, 2008). The value of Sm/Nd of the EDR, needed to explain the modern ¹⁴³Nd/¹⁴⁴Nd in OIBs and MORBs, varies as a function of the timing of its formation. According to Boyet and

Carlson (2005, 2006), the EDR would have had 6 % higher Sm/Nd ratio than the chondrites, if it had formed at 4.568 Ga. It is not only the timing of formation, but also the amount of extraction of continental crust that can affect the estimate of Sm/Nd. Different estimates for the composition of the EER are given in Carlson et al. (2015). It is interesting to note that in this scenario all mantle reservoirs (accessible mantle) are derived from the EDR, which is super-chondritic in composition (Figure 1.3).



Figure 1.3 A simplified illustrative representation for Scenario I, where Earth (BSE) starts with a chondritic composition at time t_0 (time of formation of the Solar System) and at a time t_d (time of early differentiation) it differentiates to form early formed mantle reservoirs which are chemically complimentary to each other; EDR = Early Depleted Reservoir; EER = Early Enriched Reservoir; DMM = Depleted MORB Mantle; t_{cc} = time of formation of continental crust; t_p = present day. The ¹⁴⁷Sm/¹⁴⁴Nd and ¹⁴³Nd/¹⁴⁴Nd isotopic values for the CHUR are taken from (Mcdonough and Sun, 1995) and represent present day values for CHUR and not at t_0 .

Scenario II: Non-Chondritic Earth

A second scenario for the offset in ¹⁴²Nd/¹⁴⁴Nd isotopic composition between the terrestrial rocks and the chondrites could be that the Earth did not start with a chondritic composition, but with a super-chondritic or non-chondritic Sm/Nd ratio (Boyet and Carlson, 2005, 2006;

Carlson and Boyet, 2008; Caro and Bourdon, 2010; Jackson et al. 2010; Caro, 2011; Jackson and Carlson, 2011; Jackson and Jellinek, 2013; Figure 1.4). The present day values of ¹⁴³Nd/¹⁴⁴Nd observed in rocks derived from the various mantle reservoirs and budget for other elements and their isotopic ratios can be explained by Super Chondritic Earth Model (SCHEM) or Non-Chondritic Mantle (NCM). The names SCHEM and NCM were proposed by Caro and Bourdon (2010) and Jackson and Jellinek (2013), respectively. In both the models the starting material is assumed to have non-chondritic ¹⁴³Nd/¹⁴⁴Nd of 0.513000 and ¹⁴⁷Sm/¹⁴⁴Nd of 0.2081 (Figure 1.4).



Figure 1.4 A simplified illustrative representation for scenario II where Earth (BSE) starts with a nonchondritic or super-chondritic composition at time t_0 (time of formation of solar system). DMM = Depleted MORB Mantle; SCHEM = Super Chondritic Earth Model; NCM = Non-Chondritic Mantle; t_{cc} = time of formation of continental crust; t_p = present day.

Scenario III: Nucleosynthetic ¹⁴²Nd/¹⁴⁴Nd offset between Earth and Chondrites

Isotopic offsets for various elements between Earth, meteorites (OC in particular) and other terrestrial planets can happen if there was a nucleosynthetic heterogeneity in the Solar Nebula. This would be possible if s-, r- and p- processes contribute heterogeneously in different regions of the nebula (Andreasen and Sharma 2007; Caro et al. 2015). The evidence for such a scenario comes from analyses of isotopes that are produced purely by nucleosynthetic processes. Based on such studies it has been established that the ¹⁴²Nd offset between Earth and meteorites is due to excess of s-process contribution of ¹⁴²Nd (Burkhardt et al. 2016; Andreasen and Sharma 2006; Andreasen and Sharma 2007; Saji et al. 2016). Figure 1.5 illustrates this scenario. In this scenario, an early global differentiation event is not required to explain the ¹⁴²Nd offset between Earth's accessible mantle and the OC. It simply means that the offset is not due to change in Sm/Nd ratio due to silicate differentiation. The ¹⁴²Nd/¹⁴⁴Nd ratio, which is different from that of OC, as observed for the terrestrial accessible mantle is inherited from the region of solar nebula responsible for the formation of Earth.



Figure 1.5 A simplified illustrative representation for Scenario III, where Earth (BSE) starts with a chondritic composition. Symbols and definitions are as described in Figures 1.3 and 1.4.

1.2.3 Early Differentiated Reservoirs

As is discussed in the previous section, the understanding about the early formed reservoirs due to silicate differentiation of Earth has been constantly evolving. Models are primarily dependent on the starting material assumed for the parent body for Earth, i.e., Chondritic (ordinary) or Non-chondritic. According to the most recent understanding on the topic, the geochemical reference for Earth is believed to be chondritic with an excess contribution of sprocess nuclides like ¹⁴²Nd (Burkhardt et al. 2016; Andreasen and Sharma 2006; Andreasen and Sharma 2007; Saji et al. 2016). This removes the need for an early global scale differentiation to explain the non-chondrite composition of terrestrial mantle (Burkhardt et al. 2016). The ¹⁴²Nd isotopic anomalies in terrestrial rocks with respect to ¹⁴²Nd/¹⁴⁴Nd of terrestrial mantle carry an evidence of the early differentiation of the silicate Earth. Considering the scarcity of such anomalies, the scale of early differentiation is difficult to constrain. The positive anomalies reported from Isua (Greenland) still have an implication for a mantle source that was a depleted mantle reservoir like the EDR (depleted with respect to terrestrial ¹⁴²Nd composition). A requisite for a complimentary enriched reservoir (EER) is there but with respect to the terrestrial composition and not with respect to that of the Ordinary Chondrites. In addition, question pertaining to the size of the EDR and EER also remains to be answered. In an effort to unravel some of these mysteries of the early silicate Earth I worked towards finding μ^{142} Nd anomalies in various mantle reservoirs, the details of which are given in sections 1.4 and 1.5.

1.3 Evolution of the Mantle

The evolution of the mantle since Archean is well documented from the rock records. The geochemical and isotopic studies on mantle derived rocks, especially OIBs and MORBs, have provided information on differentiation processes that have occurred and still ongoing within the mantle. Based on the studies of ^{143/144}Nd - ^{87/86}Sr - ^{206/204}Pb isotopes of young basaltic rocks, it is now known that there are at least four major geochemical end-members in the mantle; viz. DMM (Depleted MORB Mantle), HIMU (High mu mantle), EM-1 (Enriched Mantle-1) and EM-2 (Enriched Mantle-2). A fifth member that retains the undifferentiated signatures of the primordial mantle, the FOZO or C component, has also been proposed (Hart et al. 1992; Hauri et al. 1994; Stracke et al. 2005). Using trace element data along with the

isotope studies, origin and mixing relations between these components can be understood (Condie, 2012; Stracke et al. 2005), which provide valuable insight into the Phanerozoic mantle dynamics. A better understanding of the evolution of Earth's mantle since Hadean requires knowledge of the events and processes that shaped the chemical composition of the mantle during the first 500 Ma of its history.

1.4 Motivation and Objectives

The presence of the early silicate Earth differentiation signatures known to us today is limited in space to Greenland and Canada and in time to Hadean-Archean Eons. In order to get insights on the scale of these early differentiation events, nature of the early differentiated reservoirs, and temporal preservation of such signatures I took up a study of ¹⁴²Nd isotopes in mantle derived rocks from the Indian Shield. The main goals of my Ph.D. work were to determine:

 The location and nature of the earliest LILE-enriched silicate reservoir in the mantle, and
 whether there is a temporal persistence of both LILE enriched and depleted reservoirs in a highly dynamic Earth. In the process of working towards these aims, I had developed some specific objectives. These are listed below.

- Search for the evidence of the earliest LILE depleted and enriched reservoirs and understand their history of preservation in a dynamic mantle. To achieve this I investigated some of the oldest rocks (3.5 – 3.3 Ga) of India and several continental igneous rocks of varying ages (1500 – 65 Ma) for their ¹⁴²Nd isotopic compositions.
- Develop an analytical protocol for chemical separation of Nd from rock matrix and its purification for accurate determination of ¹⁴²Nd/¹⁴⁴Nd using TIMS. Nd isotopic investigations using TIMS (as Nd⁺ ions) are restricted by the isobaric interferences from Sm and Ce. In particular, for ¹⁴²Nd/¹⁴⁴Nd isotopic investigation a Ce – free Nd fraction from the rock sample is a must to avoid interference from ¹⁴²Ce.
- 3. To understand the roles of methods of data acquisition and mass fractionation correction in accurate determination of ¹⁴²Nd/¹⁴⁴Nd by TIMS. High precision isotopic ratio measurements by TIMS often requires data acquisition through a multi-dynamic mode, wherein differences in collector factors can be nullified by measuring individual ion beams in multiple Faraday cups through (magnet) peak jumping. I

studied and compared the effects of (a) number of sequences in terms of time delay between first and last sequence, and (b) correction for mass fractionation on the accuracy of data in a multi-dynamic mode.

4. Understand the effect of choice of terrestrial standard used for the calculation of $\mu^{142}Nd$ on reporting of anomalous ¹⁴²Nd compositions. I explored the possibility that different terrestrial standards used for ¹⁴²Nd study may possess different ¹⁴²Nd/¹⁴⁴Nd and thereby affect the reported $\mu^{142}Nd$ values, thus artificially creating or obliterating anomalous values.

1.5 Methodology and Approach

This study of primordial Earth is restricted by limited availability of samples of the early Earth. Since I had no access to the preserved rock records of the first five hundred million years, I had to work with the next best samples: the rocks derived from the Archean mantle and those from the supposedly non-convective domains. The reasons behind choosing such samples are discussed below.

Approach 1: Study of Archean rock record

Since the radioactive isotope of ¹⁴⁶Sm ($T_{1/2} = 103$ Ma) was extant during the first five hundred million years (Hadean Eon) of the solar system, by analysing the Hadean rocks information about the nature and timing of these early differentiation events could be directly obtained. Silicates formed during this time by differentiation would have acquired different Sm/Nd resulting in different ¹⁴²Nd/¹⁴⁴Nd isotopic compositions, which would have different ¹⁴²Nd/¹⁴⁴Nd isotopic compositions from that of the undifferentiated (starting) bulk mantle. This would have resulted in anomalous ¹⁴²Nd composition and depending on whether the mantle source was LREE enriched or depleted - the rocks could have acquired negative or positive μ^{142} Nd, respectively.

Unfortunately, Earth does not have a good preservation of the Hadean rocks. Only a couple of reports of the Hadean rocks exist in the literature. These are the (1) TTGs from Acasta, Northwest Territories, Canada – 4.03 Ga (Bowring and Williams, 1999) and (2) Faux Amphibolites from Nuvvuagittuq Greenstone Belt (NGB), Canada – 4.28 Ga (O'Neil et al. 2008). ¹⁴²Nd/¹⁴⁴Nd isotopic studies of these rocks have revealed that they carry early mantle differentiation signatures (O'Neil et al. 2008; Roth et al. 2014a). As compared to the Hadean rock records, the Archean rock records are abundant and have been reported from all the continents. Unlike the Hadean rocks, only a few Archean rocks carry signatures of the early

silicate differentiation, but indirectly in their ¹⁴²Nd/¹⁴⁴Nd isotopic compositions. Of these the Isua Supracrustal Belt (ISB), Greenland, carry the strongest evidence in the form of positive ¹⁴²Nd anomalies, which indicate a derivation from an early depleted mantle source – hence an early differentiation event before 3.8 Ga, the emplacement age of these rocks (Boyet et al. 2003; Caro et al. 2006; Caro et al. 2003; Bennett et al. 2007; Rizo et al. 2011). This information comes from metamorphic mafic igneous and sedimentary rocks and TTGs which carry LREE depleted signatures of the source. This Archean terrain also preserves an enriched signature as negative μ^{142} Nd anomaly in the Ameralik mafic (noritic) dykes (Rizo et al. 2012). Unfortunately, however, most rocks of similar age studied elsewhere do not show such anomalous μ^{142} Nd which could be explained by processes related to the early silicate differentiation (Boyet and Carlson, 2006; Caro et al. 2006; Regelous and Collerson, 1996). The exception is the 2.7 Ga thoellitic lava flows from the Abitibi Greenstone Belt (AGB), Canada which show positive μ^{142} Nd (Debaille et al. 2013). Four examples of negative μ^{142} Nd (LREE enriched) are known today (O'Neil et al. 2008; Rizo et al. 2012; Roth et al. 2014a; Roth et al. 2013; Upadhyay et al. 2009), which are vestiges of an early LILE enriched reservoir possibly representing the earliest crust (Rizo et al. 2012; Roth et al. 2014a). All of these except for one come from Hadean/Archean rocks.

More studies on the Archean rocks preserved in various continents are required to understand the scale of these early differentiation events. This is vital in the light of the proposal that the ¹⁴²Nd isotope offset between the Earth's accessible mantle and Ordinary Chondrites is of nucleosynthetic origin (Burkhardt et al. 2016). In such a model the chondritic Earth no longer requires an early global scale silicate differentiation event. In search of such early LREE depleted mantle reservoirs which can reveal more on the earliest differentiation events, I studied Archean rocks from two well dated TTG complexes of India. These are the:

- a) TTGs from the Singhbhum Craton, Odisha, Eastern India. They are one of the oldest TTGs reported from India: 3.46 Ga (U-Pb zircon; Upadhyay et al. 2014 and the references therein).
- b) Granitoids (TTG *sensu lato*) from the Aravalli Craton, Rajasthan, West India: 3.3 Ga (Gopalan et al. 1990).

Approach 2: Study of continental alkaline igneous rocks

Igneous rocks of age beyond Archean are aplenty on Earth and searching for the early differentiation signatures in these young rocks, particularly those which were derived from the non-convective mantle, is a worthy idea. There are two candidates for such mantle domains unaffected by the convective mixing: (1) the, Core-Mantle Boundary (CMB), also known as the D" layer and (2) the Sub Continental Lithospheric Mantle (SCLM). If any parts of the mantle formed in an early differentiation event and had become part of the non-convective mantle then, early differentiation signatures could be found in rocks derived from such mantle domains. In this case, the age of emplacement of the rocks would not be a factor for the preservation of such early signatures.

The best candidates for studying the D" layer are the (lower mantle) plume-derived magmas. Several attempts by earlier workers have not yielded any signature of early silicate differentiation in these magmas (Andreasen et al. 2008; Boyet and Carlson, 2006; Murphy et al. 2010). To study SCLM, alkaline igneous rocks including carbonatites are the best candidates as they are believed to represent (derived from) such mantle domains (Woolley and Bailey. 2012; Ray et al. 2013; Gwalani et al. 2016). Interestingly, the only non-Archean rocks reported to carry early silicate Earth differentiation signatures are the 1.48 Ga nepheline syenites from Khariar Alkaline Complex, India (Upadhyay et al. 2009). However, this finding has been challenged by Roth et al. (2014b) and Gautam et al. (2017).

For the present work, I studied alkaline igneous rocks and carbonatite complexes of India of varying ages (1.49 Ga to 65 Ma) for their ¹⁴²Nd isotopic composition. These complexes are listed below.

- a) 1.49 Ga Nepheline Syenites from Kishengarh, Rajasthan, Western India (Crawford, 1969).
- b) 1.48 Ga Nepheline Syenites from Khariar, Odisha, Eastern India (Upadhyay et al. 2006).
- c) 1.1 Ga Kimberlites from Eastern Dharwar Craton, Southern India (Rao et al. 2013).
- d) 65 Ma Alkali Basalts from Phenai Mata Complex, Gujarat, Western India (Basu et al. 1993).
- e) Carbonatites from:
 - i) 1.47 Ga, Newania, Rajasthan, Western India (Ray et al. 2013).
 - ii) 107 Ma, Sung Valley, Meghalaya, North-Eastern India (Ray and Pande, 2001).
 - iii) 65 Ma, Amba Dongar, Gujarat, Western India (Ray and Ramesh, 2006).
- f) 66 Ma mantle xenoliths from Deccan Basalts, Kutch, Gujarat, Western India (Pande, 1988).

1.6 Outline of the Thesis

This thesis is divided into five chapters and the contents of each chapter is briefly described below.

The *First Chapter (Introduction)*, as already discussed, provides the background information about the major planetary differentiation events that took place during the first 500 Ma of the Earth's history, resulting into a differentiated planet with a core-mantle-crust configuration. The motivation for the present study along with the detailed objectives are also discussed along with the methodology.

The *Second Chapter (Samples and Geochemical Characterization)* gives details of the geochemical characterization of the rocks analysed for their ¹⁴²Nd isotopic compositions. It also provides information about chronology and the mantle source of these rocks based on the earlier work.

The analytical methods are described in the *Third Chapter (Analytical Methods)*, where, the procedures of chemical separation developed and adopted for the present study are elaborately discussed. Details of mass spectrometric procedures used for data acquisition and reduction are presented.

The *Fourth Chapter (Results and Discussion)*, discusses in detail the results obtained for the present work. The mass spectrometry procedures and their effects on the accuracy of the results are discussed. The choice of terrestrial standard on retrieving a true anomaly in ¹⁴²Nd composition is evaluated in detail, which is one of the major findings of this work. This is followed by the information obtained from ¹⁴²Nd isotopic investigation of the Indian rocks. The implications of the results for ¹⁴²Nd evolution of Indian mantle domains are discussed at the end.

The *Fifth Chapter (Summary and Conclusions)* summarizes the results of this study and concludes the major findings. This chapter ends with a short proposal for future studies.

Table 1 List of reported $\mu^{142}\text{Nd}$ anomalies.

Sr.	Year	Nd reference	Location	Samples	μ^{142} Nd
No.					
1)	1992	CIT Ndβ	Isua SW Greenland	IE 715-28, metasediment	+33 ppm for IE 715- 28
2)	1993	La Jolla or RSES (std	Greenland (Amitsoq & Akilia) and	Felsic gneiss, mafic gneiss and ultramafic rocks	In ε , not resolvable; unable to
		of the day)	Northern Canada (Acasta)		reproduce 1992 result of Harper & Jacobsen
3)	2003	JMC Nd (MC- ICPMS)	SW Greenland, ISB	Metabasalts ; metagabbros	+30 ppm
4)	2003	Ames Nd	West Greenland, IGB	Metasediments	+15 ppm
5)	2006	Ames Nd	1. SW Greenland	 (3.65 – 3.82 Ga) Metapelites – schist (eastern sector), metabasalts (IGB, eastern sector)-different from those analysed by Boyet and Carlson 2003, orthogneisses (TTG-type), amphibolite enclaves in gneisses 	1.+8 to +15 ppm
			2. NWT, Canada	2. Gneisses (4.03 Ga; U-Pb zircon age)	2. No anomaly
			3. Kaapval craton, S. Africa	3. Barberton Komatiites (3540± 30 Ma; Sm – Nd isochron	3. No anomaly
				age)	
6)	2007	Ames Nd	 1.SW Greenland, Itsaq complex Western Australia Yilgran craton, 	 Tonalites (3.64 to 3.85 Ga) Tonalitic gneisses (3.73 Ga) 	1. +9 to +20 ppm
			Narryer gneiss complex		2. +5 ppm
7)	2008	La Jolla	NGB, Northern Quebec, Canada	1.Faux amphibolites 2. Tonalites	17 to -15 ppm 212 to -16 ppm
8)	2009	La Jolla	Khariar, Odhisha, India	Alkaline rocks- nepheline syenites	-13 ppm
9)	2011	JNdi-1	Isua, Greenland	Amphibolites	+7 to +16 ppm
10)	2012	JNdi-1	Ameralik dykes, Isua	Noritic dykes (3.4 Ga)	-10.6 ppm
11)	2013	Average of Ames Nd and La Jolla	Abitibi Greenstone Belt (AGB), Canadian craton	Thoellitic lava flow (2.7 Ga)	+7 ppm
12)	2013	JNdi-1	NSB, Que'bec, Canada (a few samples are same aliquots of O'Neil et al. 2008)	 Hornblende amphibolites cummingtonite amphibolites tonalite gneiss Trondhjemite gneisses 	1. one sample -11.1 ppm 2. one sample -8.6 ppm

					4. one sample -8.7 ppm
				 granodiorite gneisses quartzite 	Rest do not show resolvable anomaly but these results confirm results of O'Neil 2008
13)	2014	JNdi-1	Khariar, Odhisha, India	Same sample aliquots of Upadhyay et al. 2009	No anomaly
,					,
14)	2014	JNdi-1	Acasta Gneiss Complex(AGC),	granitoid gneiss and plagioclase-hornblende schist	Ten out of thirteen samples
			NorthWest territories, Canada		show values from -6.0 to -
					14.1 ppm
					Average is -9. 6 ppm
15)	2016	JNdi-1	1. Ukaliq supracrustal belt, Canada	1. amphibolites	1. 0 to -10 ppm
			2. NSB and ISB	2. BIF	2. no resolvable anomaly
16)	2016	Ames Nd	Schapenburg, South Africa	Komatiites (3.55 Ga)	-5 ppm
		(JNdi-1 at DTM)			

Data sources as per serial number (Sr. No.)

1) Harper and Jacobsen. (1992); 2) Mcculloch and Bennett. (1993); 3) Boyet et al. (2003); 4-5) Caro et al. (2003,2006); 6) Bennett et al. (2007); 7) O'Neil et al. (2008); 8) Upadhyay et al. (2009); 9-10) Rizo et al. (2011,2012); 11) Debaille et al. (2013); 12-14) Roth et al. (2013; Roth et al. 2014a, 2014b); 15) Caro et al. (2016); 16) Puchtel et al. (2016)

Chapter 2 Samples and Geochemical Characterization In this chapter I discuss the details of the rock samples collected for the present research work. The GPS locations of the samples are provided in Tables 2.1 - 2.8. The map of India in Figure 2.1 shows the general locations of the samples. Except for the carbonatites, some alkaline igneous rocks and kimberlites, all other samples were characterised geochemically using their trace element contents. The following section discusses the analytical methods used for geochemical characterization of the samples.

2.1 Geochemical Methods

Trace element concentrations including the Rare Earth Elements were determined using a Thermo X-Series 2 Q-ICPMS facility at the Geosciences Division of Physical Research Laboratory, India. The samples were dissolved using the standard protocol of HF-HNO₃ (2:1) for silicates. A complete dissolution was achieved through ~1 hour of ultra-sonication and heating at 60°C with closed cap for ~12 hours. After two rounds of 8N HNO₃ treatment and drying, stock solutions were prepared in 2 % HNO₃ with a 1000 times dilution. Further dilutions as required for the analyses were prepared from stock solutions using 2 % HNO₃.Concentrations were determined using the calibration curve obtained using different dilutions of the international rock standard BHVO-2. The same standard along with the rock standards BCR-2 and AGV-2 were used as an unknown for accuracy check. The precision of measurements for all elements were better than 3 % at 2SD. The data are presented in Table 2.9.

2.2 TTG from Singhbhum, Odisha

Tonalite, Trondhjemite and Granodiorites (TTG) are considered archetypical of the Archean Eon. The TTGs for the present study were collected from a previously well studied section of the Singhbhum Craton, Odisha. The Singhbhum Craton in Eastern India is oval in shape, bordered in the north by the North Singhbhum Mobile Belt (NSMB), to the southeast by the Eastern Ghats Belt and to the southwest by the Bastar Craton (Saha, 1994). It has extensive occurrences of greenschist to amphibolite facies TTGs and granites ranging in age from Paleoarchean (3.6 - 3.2 Ga) to Neoarchean (2.8 - 2.5 Ga)(Upadhyay et al., 2014 and references therein). As described by Saha (1994) the major Paleoarchean crustal units of the craton are the:

1. Older Metamorphic group (OMG) consisting of greenschist to amphibolite facies supracrustals

- 2. Older Metamorphic Tonalite Gneisses (OMTG) consisting primarily of the TTGs
- 3. Singhbhum Granite (SG) consisting of granitoids, tonalities; interlayered greenschist facies platformal sediments, banded iron formations (BIF), and mafic and felsic volcanic rocks of the Iron Ore Group (IOG).

Further details can be found in Upadhyay et al. (2014).Based on U-Pb ages of zircon these authors proposed a polycyclic evolution of the Archean crust in the Singhbhum Craton. They reported that tonalites and trondhjemites of OMTG were emplaced at 3.45 - 3.44 Ga together with Phase III of Singhbhum pluton.

I targeted the OMTG Group for collection of TTGs from the reported outcrops. The GPS co-ordinates of the rock samples collected by us and analysed for ¹⁴²Nd isotopic composition are given in Table 2.1.To make sure that the samples collected by us are in fact TTGs, they were geochemically characterized using the method described in section 2.1. The data are presented in Table 2.9 and are plotted Figures 2.2 - 2.4.The chondrite normalized patterns of these rocks show a strong enrichment in LREEs as compared to HREEs (Figure 2.2).On the Martin's plot (Martin and Moyen, 2002; Moyen and Martin, 2012) our samples (OD – series) fall in the Archean TTG field (Figure 2.5). Sample OD-12/2 shows a small positive Eu anomaly whereas OD-9(a) and OD-13/2 show a small negative Eu anomaly (Figure 2.2). The average composition of these three samples does not show any Eu anomaly. All three samples exhibit a positive Pb anomaly and negative anomalies in Nb and Ta (Figure 2.4), typical features of continental crustal rocks. Sample OD-12/2 exhibits a negative anomaly for Zr and Hf as well, whereas the other two samples do not show these. The lack of significant Eu, Sr anomalies and negative Nb-Ta anomalies of Singhbhum TTGs are typical of TTGs worldwide as observed by Moyen and Martin (2012).

2.3 Granitoids from Banded Gneissic Complex (BGC)-1, Rajasthan

Aravalli craton is divided into two parts, the eastern Mewar Craton and the western Marwar Craton. The eastern Mewar Craton consists of the Banded Gneissic Complex – 1, which hasthree major components - the Mewar Gneiss, Mangalwar Complex and Sandmata Complex. Of these, Mewar Gneiss consists of TTG gneiss (*sensu lato*) ranging in age from 3300 - 2900 Ma (Valdiya, 2010). The Mewar Gneiss contains multiple metamorphic components of varying ages (Wiedenbeck et al., 1996). Gopalan et al. (1990) studied biotite gneisses near the village of Jhamarkotra, SE of Udaipur (Rajasthan) and reported a six-point isochron Sm-Nd age of 3307 ± 65 (2SD) Ma, with an initial ¹⁴³Nd/¹⁴⁴Nd ratio of 0.508402 ±

52 (ϵ^{143} Nd = 1.4 ± 1). The geochemical study of Ahmad and Tamep(1994) revealed that the REE and trace element compositions of these granitoids differ from those of typical Archean TTGs. The same is also observed by me for the samples analysed in the present study (Figures 2.3 and 2.6).

For the present study, granitoid samples were collected near the village of Jhamarkotra. Although many samples of biotite gneisses and amphibolite were collected and analysed for trace element study (Figure 2.7), only two of these were analysed for their¹⁴²Nd isotopic composition. The details of GPS locations and trace element concentrations are given in Table 2.2 and Table 2.10. The trace element data reveals that these samples (JG – series) fall in the modern granitoids field of Martin (Martin, 1987; Moyen and Martin, 2012) as shown in the Figure 2.5. All except one sample, JG-01, show an enrichment in LREEs and negative Eu anomalies (Figure 2.6). The primitive mantle (PM) normalised trace element patterns show pronounced depletion in Nb and Ta and smaller depletions in Zr and Hf (Figure 2.7). They also show enrichments in Pb and Rb.

2.4 Nepheline syenites from Khariar alkaline complex, Odisha

The Khariar alkaline complex is one of the intrusives along the suture zone between Bhandhara/Eastern Dharwar cratons (EDC) and the Eastern Ghats Belt (EGB). The complex was emplaced at $1480 \pm 17 (2\sigma)$ Ma (Upadhyay et al., 2006). It has been studied in detail by Upadhyay et al.(2006, 2009). The deformation of this complex during the Pan-African tectono-thermal event has been suggested along with the rift-related setting for the magmatic activity. These authors proposed a petrogenetic model for the complex, which suggests that the basanitic parental melt was derived from a metasomatised SCLM during the initiation of rifting. Based on Sr-Nd isotope data as shown in Figure 2.8, these rocks fall in a narrow field in the enriched quadrant (Upadhyay et al., 2006).

The 1.48 Ga nepheline syenites of the complex have attracted much attention, because of a report of negative μ^{142} Nd anomalies, as low as 13 ppm (Upadhyay et al., 2009). This was an important finding since these are the only younger than Archean rocks to possess signatures of the early silicate Earth differentiation process. The report supported the hypothesis of cratonic roots being sites of preservation of early differentiated reservoirs. Considering the importance of these results, independent verification of these was required. In one such effort (described in detail in Chapter 4), we studied the alkaline silicate rocks from the same localities as in Upadhyay et al. (2009) for their ¹⁴²Nd isotopic composition. Sample details are presented in Table 2.3. In order to make sure that the samples collected by us are geochemically indistinguishable from those studied by Upadhyay et al. (2009), trace element analyses were carried out. Table 2.11 presents these data and in Figures 2.9 and 2.10 the chondrite normalized REE and primitive mantle normalized trace element patterns are plotted. The patterns observed in our samples are similar and fall well within the ranges of variations observed by Upadhyay et al. (2009).

2.5 Nepheline-syenites from Kishengarh, Rajasthan

With BGC (Banded Gneissic Complex) in the East and Delhi Supergroup to the West, the occurrence of nepheline-syenites in Kishengarh, Rajasthan, is considered unique because it is the only alkali pluton in this part of the Aravalli Craton(Roy and Dutt, 1995). There exist multiple hypotheses on the origin of these rocks. Some consider it to have formed due to alkalization of gabbro (Niyogi, 1966); others consider them of metamorphic origin (Mittal and Jain, 1955). The first study of these rocks by Heron(1924) suggested it to be of igneous origin and so did the latter studies by Srivastava(1988) and Royand Dutt(1995). The nepheline syenite pluton occurs as a conformable body within a sequence of pre-Delhi metasedimentary and metavolcanic rocks, known as Kishengarh group (Roy and Dutt, 1995). A discontinuous thin zone, consisting of fenitized rocks, forms a capping over the nepheline syenite (Roy and Dutt, 1995). The only available information on the age of emplacement of this pluton comes from a three point Rb – Sr isochron by Crawford (1970) giving an age of 1490 ± 150 (2 σ)Ma. Solanki (2011) attempted to date zircons and titanites of a nepheline syenite from this area. Zircons yielded an age (U-Pb) of ~990 Ma whereas the titanites yielded a minimum age of 1365±65 Ma. The younger age from zircons indicates their resetting during a regional thermal event. Leelanandam (2006) classified this pluton as DARC (Deformed Alkaline Rock and Carbonatite) and extended an idea of these to be a part of the Great Indian Proterozoic Fold Belt.

Three samples of nepheline syenites were collected from the outcrop of 'Nepheline Syenites Geological Monument'. The GPS locations of the samples are given in Table 2.4 and the whole rock trace element data are presented in the Table 2.12. The chondrite normalized REE and primitive mantle normalized trace element patterns are plotted in Figures2.11 and 2.12, respectively. These rocks exhibit enrichment in LREEs with an almost flat pattern for HREEs. No Ce anomaly is observed, indicating absence of plagioclase fractionation. All the three texturally different varieties of these rocks show a positive

anomaly in Pb and one of the samples (KG-02) exhibit negative anomalies for HF and Zr, suggesting a possible crustal contamination of the parental melt of these rocks, which is also supported by the enrichments in LILEs (Figure 2.12).

2.6 Kimberlites from Eastern Dharwar Craton (EDC), Karnataka

Kimberlites in India are known from the EDC (Southern India) and Bastar Craton (Central India). The kimberlites of the EDC have been well studied for their petrogenesis and precise emplacement ages by Chalapathi Rao et al. (2013) and the samples for the present study were provided by them. The study of Chalapathi Rao et al. (2013) concluded that these kimberlites were emplaced episodically at~ 1100Ma. Our kimberlite samples come from Narayanpet Kimberlite field (NKF), Raichur Kimberlite Field (RKF) and Wajrakarur Kimberlite Field (WKF). WKF is the largest among these, consists of Wajrakarur (P-5) and Chigicherla (CC-5); NKF consists of Kotakonda and Narayanpet (KK-1 and NK-1, respectively) and RKF consists of Siddanpalle (SK-1). As reported by Chalapathi Rao et al. (2013), these rocks have high abundances of alkaline earth and high field strength trace elements (> 1000 ppm) and very low Rb contents (~7 ppm). They also show considerable enrichment of REE over chondrite and LREE over HREE, and lack any Eu anomaly. Perovskites from the kimberlites, however, show a distinct trace element chemistry of the perovskite from NKF, RKF and WKF. Their Sr-Nd isotope compositions plot in a depleted quadrant, similar to the kimberlites of South Africa and Greenalnd. Chalapathi Rao et al. (2013) proposed a model of emplacement which suggested derivation of parental magmas from variably enriched metasomatised SCLM sources. Some might have had asthenospheric overprints. Sample details are given in Table 2.5.

2.7 Alkali Basalts from Phenai Mata Igneous Complex, Gujarat

The Phenai Mata Igneous Complex is a part of the Chhota Udaipuralkaline sub province of the Deccan Flood Basalt Province(Basu et al., 1993). The under-saturatedalkalic rocks of the Phenai Mata plug ($22^{\circ}7'$ N, $73^{\circ}50'$ E) intrude into the earlier formed Deccan Trap flows of tholeiitic composition. This complex was reported to have an intrusion age of 64.96 ± 0.11 (2σ) Ma, which probably marks the end phase of the Deccan volcanism on the Indian plate.Low³He/⁴He ratios (3.4 to 3.1 R_A) of these basaltshave been interpreted to represent crustal contamination of the parental magma of the complex (Figure 2.13), which is further substantiated by their low ϵ^{Nd} (t) values (-15 to -5) (Basu et al., 1993).

For the present study six samples of basalts from this plug (near village Jhajh) were collected and two of them (PMC-02and 03) were analysed for their¹⁴²Nd/¹⁴⁴Nd. The details of the sample locations are given in Table 2.6 and their trace element contents are presented in Table 2.13. The data are plotted in Figure 2.14 and 2.15 in chondrite normalized and primitive mantle normalized plots, respectively. These rocks show enrichment in LREE with almost a flat pattern for the HREEs. All samples except one (PMC-06) do not show any anomalies in Eu. The trace elements show patterns consistent with the enrichment in incompatible elements. A small positive anomaly in Pb and negative anomalies in HFSE elements are consistent with the theory of crustal contamination of the parental magma.

2.8 Carbonatites and alkaline silicate rocks from Amba Dongar, Sung Valley and Newania Complexes, India

The samples analysed in the present study from AmbaDongar and Sung Valley carbonatitealkaline complexes were originally collected by Ray (1997), who had done detailed investigations in these complexes using various geochemical and isotopic techniques and had determined their emplacement ages. The samples from Newania came from the study of Ray et al. (2013), which also have been well characterized geochemically by the authors. A total of twenty two samples of carbonatites and eleven samples of alkaline silicate rocks were analysed by me for their ¹⁴²Nd/¹⁴⁴Nd.

2.8.1 Amba Dongar Carbonatite - Alkaline Complex, Gujarat

The Amba Dongar carbonatite-alkaline complex is part of the Chhota Udaipur alkaline subprovince of the Deccan Flood Basalt Province.Most of the alkaline and carbonatite activities of this sub province have been determined to be coeval(Ray and Pande, 1999; Ray et al., 2006). The entire sub province (~1200km²) belonged to a single magmatic episode that postdated main tholeiitic pulse of Deccan flood basalts (Ray et al., 2003). The age of emplacement of this complex is 65.0 ± 0.3 (2σ) Ma which isbased on ⁴⁰Ar-³⁹Ar dating of a phlogopite from carbonatite and three whole rock alkaline rocks (Ray and Pande, 1999).Works of Ray (1998, 2009) suggest that the carbonate magma and the silicate magma of this complex share a genetic relationship and were generated by liquid immiscibility and the parent magma was crustully contaminated (up to ~ 4%).Since the carbonate rocks, the samples were analysed as separate carbonate and silicate fraction for their¹⁴²Nd/¹⁴⁴Nd
isotopic composition. The details of the samples analysed in the present study are given in Table 2.7.

2.8.2 Sung Valley Carbonatite - Alkaline Complex, Meghalaya

Sung Valley is located 49 km south of Shillong, Meghalaya. It houses the largest alkaline complex of all the Eastern Indian carbonatite – alkaline complexes (Ray, 1997). The age of emplacement of this complex is reported to be $107.2 \pm 0.8 (2\sigma)$ Ma based on 40 Ar $^{-39}$ Ar dating of three phologopite separates from carbonatite and one whole rock pyroxenite sample (Ray and Pande, 1999). Based on the Rb-Sr isochron, the age was found to be $106 \pm 11 (2\sigma)$ Ma (Ray et al., 2000). This complex consists of a variety of magmatic rocks including alkali pyroxenites and carbonatites. Unlike the Amba Dongar complex, carbonatites in this complex are a minor component. A DUPAL mantle source was suggested for these carbonatites based on the combined Pb, Sr and Nd isotopic study by Veena et al.(1998) which links the complex genetically to the Kerguelen plume. The carbonatites were studied as separate carbonate and silicate fractionsfor their¹⁴²Nd compositions. The details of the samples are given in Table 2.7.

2.8.3 Newania Carbonatite Complex, Rajasthan

This carbonatite complex is unique because it is one of the few known dolomite carbonatites of the world. It is also one of the two carbonatites-only complexes of India, with no trace of alkaline silicate rocks. It occurs around 40 km north-east of Udaipur, Rajasthan. This complex is emplaced into the 2.95 Ga Untala Gneiss of the Aravalli Craton (Choudhary et al., 1984). The age of emplacement of this complex is reported to be 1473 Ma (Sm-Nd) byRay et al. (2013). These authors also suggest that the primary melt for the complex was derived from a metasomatised subcontinental lithospheric mantle, which could have been a phlogopite bearing mantle located within garnet stability zone. The sample details are given in Table 2.8.It can be seen in Figure 2.16, that whereas the carbonatites from Amba Dongar and Sung Valley fall in the enriched mantle quadrants, the carbonatites from Newania carry signatures of metamorphism and possible derivation from SCLM.



Figure 2.1 Map of India showing general locations of the samples collected for the present study. 1-Singhbhum (3.5 Ga), 2- Banded Gneissic Complex-1 (3.3 Ga), 3-Khariar (1.5 Ga), 4-Kishengarh (1.4 Ga), 5- Newania (1.5 Ga), 6- Phenai Mata (65Ma), 7- Amba Dongar (65 Ma), 8- Eastern Dharwar Craton (1.1 Ga) and 9- Sung Valley (107 Ma).



Figure 2.2 Chondrite normalised REE patterns for TTG samples of the Singhbhum Craton. The reference values for chondrite are taken from Mcdonough and Sun (1995).



Figure 2.3 A comparison of chondrite normalised REE patterns for granitoids (shaded region) from the Singhbhum Craton and that from the Banded Gneissic Complex-1, Aravalli Craton, analysed in the present study.



Figure 2.4 Primitive Mantle (PM) normalised multi elements plot for TTG samples from Singhbhum. PM values after Sun and McDonough, (1989).



Figure 2.5 $(La/Yb)_N$ Versus $(Yb)_N$ plot of our samples in Hervé Martin diagram (Martin, 1987; Moyen and Martin, 2012). Pink field is for Archean TTGs whereas that in yellow is for the younger granitoids (Post 2.5 Ga granitoids). Primitive Mantle data used for normalization are from Sun and McDonough, (1989).



Figure 2.6 Chondrite normalised REE plot for BGC-1 rocks analysed in the present study. Sample details are in Table 2.2.



Figure 2.7 Primitive Mantle (PM) normalised multi element plot for samples from BGC-1. Sample details are given in Table 2.2.



Figure 2.8 Plot of $({}^{143}Nd/{}^{144}Nd)i$ versus $({}^{87}Sr/{}^{86}Sr)i$ for nepheline syenites from Khariar (redrawn from Upadhyay et al. 2006).DM = Depleted Mantle; EM = Enriched Mantle.



Figure 2.9 Plot of chondrite normalized REE patterns for our alkaline igneous rock samples from Khariar complex.



Figure 2.10 Plot of primitive mantle normalised multi-element plot for the alkaline igneous rock samples from Khariar complex.



Figure 2.11 Chondrite normalised REE plot for nepheline syenites from Kishengarh.



Figure 2.12 Primitive Mantle (PM) normalised trace elements plot for nepheline syenites from Kishengarh.



Figure 2.13 Plot re-drawn from Basu et al. (1993) showing He and Sr isotope composition for the pyroxene and olivine mineral separates from the rocks of Phenai Mata Igneous Complex. These rocks fall on a mixing trend between the Reunion hot spot (the plume source of these rocks) and the crust (values from Basu et al., 1993 and the references therein).



Figure 2.14 Chondrite normalised REE plot for basalts from the Phenai Mata Complex.



Figure 2.15 Primitive Mantle (PM) normalised trace elements plot for alkali basalts from the Phenai Mata Complex.



Figure 2.16 Plot of $\varepsilon_{Nd}(t)$ versus $\varepsilon_{Sr}(t)$ for samples from Amba Dongar, Sung Valley and Newania complexes, with t being the age of emplacement considered to be 65, 107 and 1473 Ma, respectively (re-drawn after Ray et al., 2013). Data as provided in (Ray et al., 2013).

Sample ID	GPS location	Rock description
OD-9(a)	N21°58′56.82″ E85°38′24.24″	Plagioclase bearing granitoid
OD-12/2	N21°58'33.78" E85°39'07.98"	Trondhjemite
OD-13/2	N21°58'49.06" E85°38'25.02"	Amphibolite

Table 2.1Details of samples collected from the Singhbhum Craton, Odisha.

Table 2.2Details of the granitoids and amphibolites collected from the Aravalli Craton, Rajasthan.

Sample ID	GPS location	Rock description
JG -01	N24°23'11″ E73°53'6″	Biotite gneiss
JG -02	N24°23'10″ E73°53'7″	Biotite gneiss
JG -03	N24°23'11″ E73°53'6″	Amphibolite
JG -04	N24°23′16″ E73°53′1″	Biotite gneiss
JG -05	N24°23′54″ E73°52′48″	Micaceous gneiss
JG -06(a)	N24°24'36″ E73°52'35″	Leucosome from migmatite
JG -06(b)	N24°24'36″ E73°52'35″	Melanosome from migmatite
JG -07	N24°26′29″ E73°52′20″	Migmatite
JG -08	N24°27′04″ E73°52′18″	Feldspar rich granite
JG -09	N24°28'17" E73°51'59"	Garnet bearing amphibolite

Table 2.3Details of samples collected from Khariar Complex, Odisha.

Sample ID	GPS location	Rock description
OD-3/3	N20°19′44.6″ E82°37′51.7″	Nepheline syenite
OD-6/1	N20°17′22.8″ E82°38′24.7″	Nepheline syenite
OD-7/1	N20°13′25.9″ E82°37′57.2″	Nepheline syenite
OD-8/1	N20°09'38.4" E82°36'55.3"	Nepheline syenite

Table 2.4Details of samples collected from Kishengarh nepheline syenite plug, Rajasthan.

Sample ID	GPS location	Rock description	
KG-01	N26°35′9″ E74°53′4″	Nepheline syenite	

Table 2.5 Details of the Kimberlite samples from the Eastern Dharwar Craton.

Sample ID	GPS location	Rock description
SK-1	N16°19′89″ E77°55′43″	Kimberlite with macrocrysts of
		olivine, mica and crustal
		xenoliths
P-7	N14°56'00" E77°22'30"	Kimberlite emplaced as dyke in
		fault in the metabasalts

NK-1	N16°46′03″ E77°29′08″	Kimberlite – north of
		Narayanpet cluster
KK-1	N16°46′05″ E77°40′08″	Kimberlite – NE of Kotakonda
CC-5	N14°31′00″ E77°38′00″	Kimberlite – crustal xenoliths
		are common

 Table 2.6Details of samples collected from the Phenai Mata Complex, Gujarat

Sample ID	GPS location	Rock description
PMC-2	N22°07'43″ E73°50'52″	Olivine bearing basalt
PMC-3	N22°07'44.63" E73°50'57.68"	Olivine basalt

Table 2.7 Details of the samples from Amba Dongar and Sung Valley carbonatite-alkaline complexes.

Sample ID	Description
Amba Dongar	
AD 1	Medium grained calcite carbonatite (collected from a small dyke)
AD 8-1	Medium grained calcite carbonatite collected from fluorite mine
AD 10-1	Very coarse grained monomineralic calcite carbonatites
AD 13-1	Fine grained calcite carbonatites
AD 14	Nephelinite from the base of the main dome
AD 16	Nephelinite (groundmass does not contain calcite)
AD 17	Nephelinite from Khadla village
AD 21	Banded (gray and red) calcite carbonatites
AD 38	Monomineralic coarse grained calcite carbonatites
AD 45	Calcite bearing tinguiate (from mine)
AD 47	Calcite bearing tinguaite
AD 48	Carbonatite(?) (from mine)
AD 54	Coarse grained calcite carbonatites
AD 65	Phonolite
AD 66	Nephelinite
AD 67	Nephelinetic tuff
AD 69	Phonolite
AD 72	Alkaline silicate
Sung Valley	
SV 1	Medium grained dolomite bearing calcite carbonatites
SV 4	Very coarse grained pyroxenite
SV 5	Phlogopite bearing calcite carbonatites
SV 6	Apatite rich calcite carbonatites
SV 10	Apatite rich calcite carbonatites
SV 13	Dolomite bearing calcite carbonatites
SV 18	Dolomite bearing calcite carbonatites
SV 19	Olivine rich, dolomite bearing calcite carbonatites

Sample ID	GPS location	Description
NW-3	N24°39.050' E 74°03.461'	Ankeritic carbonatites
NW-5	N24°38.742' E 74°03.970'	Dolomitic carbonatites
NW-7	N24°38.417' E 74°04.585'	Fine dolomitic carbonatites
NW-8	N24°38.458' E 74°04.488'	Carbonatite
NW-17	N24°38.271' E 74°04.861'	Slightly altered carbonatites
NW-25(a)	N24°38.377' E 74°04.505'	Carbonatite vein (and underlying host
		rock)
NW-29	N24°38.379' E 74°04.465'	Dolomitic carbonatite

Table 2.8 Details of the samples from the Newania, dolomite carbonatites, Rajasthan

Table 2.9 Trace element concentrations of TTGs from Singhbhum, Odisha

Element	OD-9a	OD-12/2	OD-	BHVO-2	BHVO-2	AGV-2	BCR-2
	(ppm)	(ppm)	13/2	Measured	Reported *	Measured	Measured
			(ppm)	(ppm)	(2SD)	(ppm)	(ppm)
					(ppm)		
Cs	1.39	3.90	2.02	0.11	0.1 (0.02)	1.20	1.23
Rb	78.75	177.60	64.62	9.42	9.11 (0.08)	67.55	50.10
Ba	190.00	884.10	124.70	135.40	131 (2)	1132.00	692.30
Th	10.16	1.14	23.63	1.21	1.22 (0.12)	5.77	5.69
U	2.51	0.78	2.87	0.40	0.403 (0.002)	1.70	1.57
Nb	10.86	3.16	16.80	18.37	18.1 (2)	14.82	13.81
Та	0.77	0.34	1.18	1.15	1.14 (0.12)	0.79	0.72
La	43.08	37.70	64.31	15.72	15.2 (0.2)	37.16	25.03
Ce	74.57	58.29	114.30	38.59	37.5 (0.4)	67.10	52.37
Pr	7.36	5.81	11.57	5.51	5.35 (0.34)	7.97	6.89
Pb	23.67	32.92	25.62	1.63	1.6 (0.6)	12.51	10.91
Sr	399.20	209.90	306.10	401.60	396 (2)	641.80	437.20
Nd	24.11	19.93	38.13	25.27	24.5 (0.2)	29.78	28.89
Hf	1.95	0.38	3.81	4.41	4.36 (0.28)	4.81	4.71
Zr	83.89	9.26	162.30	177.50	172 (22)	230.60	194.10
Sm	3.79	3.44	6.17	6.11	6.07 (0.02)	5.35	6.66
Eu	0.86	1.57	0.82	2.11	2.07 (0.004)	1.65	2.10
Gd	3.78	3.25	5.60	6.28	6.24 (0.06)	4.97	7.01
Tb	0.49	0.35	0.52	0.94	0.92 (0.06)	0.62	1.04
Dy	2.65	1.62	1.92	5.44	5.31 (0.04)	3.37	6.44
Y	14.78	8.73	7.05	26.85	26 (4)	21.29	43.81
Но	0.47	0.27	0.24	1.00	0.98 (0.08)	0.63	1.28
Er	1.21	0.73	0.54	2.62	2.54 (0.02)	1.76	3.66
Tm	0.14	0.10	0.05	0.34	0.33 (0.02)	0.24	0.52
Yb	0.79	0.63	0.29	2.07	2 (0.02)	1.57	3.37
Lu	0.10	0.09	0.04	0.28	0.274 (0.01)	0.23	0.48

* After Jocum et al. (2005). The associated 2SD is given in brackets.

Table 2.10 Trace element concentrations of granitoids from the Banded Gneissic Complex-1,

 Rajasthan

Element	JG-01	JG-02	JG-04	JG-6(a)	JG-6(b)	JG-7	JG-8
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Cs	0.36	0.55	0.65	1.8	4.87	1.9	0.49
Rb	18.52	27.4	39.39	54.07	187.9	65.85	71.03
Ba	157.1	535	497.2	461.5	697.4	425.6	1098
Th	17.29	4.66	3.45	5.94	5.6	6.14	5.37
U	1.19	0.53	0.47	0.65	1.57	0.29	0.67
Nb	0.4	3.85	6.95	8.93	9.66	7.27	4.5
Та	0.02	0.13	0.29	0.85	0.76	0.4	0.52
La	3.01	26.42	37.75	16.46	24.6	29.3	19.76
Ce	10.14	45.98	79.2	43.12	53.34	59	38.14
Pr	4.68	5.11	4.19	29.44	18.05	7.52	17.32
Pb	2.03	5.14	9.74	3.82	6.76	7.57	4.26
Sr	328.9	472.3	456.9	302.4	100.1	206.3	499.9
Nd	12.32	17.25	37.56	13.67	27.7	30.77	15.22
Hf	122.9	67.78	49.69	65.67	71.39	49.86	41.72
Zr	3.03	2.12	1.23	1.91	2.04	1.35	1.2
Sm	4.53	2.46	7.23	2.51	6.49	8.65	2.67
Eu	0.66	1.08	1.59	0.77	1.93	1.03	1
Gd	3.5	2.09	6.1	2.31	6.97	8.91	2.46
Tb	0.45	0.22	0.75	0.3	1.13	1.41	0.33
Dy	2.22	1.03	3.98	1.68	7.11	8.05	1.92
Y	8.5	5.4	20.79	8.84	39.63	34.27	10.84
Но	0.38	0.19	0.73	0.33	1.42	1.39	0.37
Er	0.94	0.54	2.01	0.9	3.96	3.4	1.03
Tm	0.12	0.07	0.27	0.12	0.55	0.4	0.14
Yb	0.68	0.5	1.68	0.75	3.45	2.2	0.88
Lu	0.1	0.08	0.23	0.11	0.47	0.27	0.12

Table 2.11 Trace element concentrations of alkaline rocks (nepheline syenites) from Khariar alkaline complex.

Element	OD-01	OD-02	OD-3/1	OD-3/2	OD-3/3	OD-4/1	OD-4/2	OD-05
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Cs	0.01	0.03	0.84	1.66	0.63	0.19	0.28	0.64
Rb	2.29	5.60	268.10	393.30	266.80	74.90	76.34	161.70
Ba	43.12	116.30	1271.00	1667.00	137.20	2496.00	2398.00	637.70
Th	0.20	0.51	20.96	6.20	29.79	5.99	12.62	25.83
U	0.04	0.10	5.61	1.60	3.05	0.74	0.94	2.96
Nb	4.86	6.49	274.30	47.08	212.70	7.36	14.43	62.69
Та	0.29	0.40	13.55	3.15	13.82	0.23	0.45	2.84
La	4.14	6.24	144.50	57.18	200.70	27.61	49.14	182.50
Ce	10.26	14.61	293.30	110.70	331.80	48.20	97.34	294.40
Pr	1.57	2.13	33.07	12.41	43.58	5.36	11.97	32.21
Pb	3.03	4.24	8.16	8.22	10.06	14.75	13.03	22.56
Sr	160.70	210.20	1401.00	2064.00	584.50	1116.00	672.10	699.40
Nd	7.60	9.82	117.70	44.36	141.60	19.18	47.63	124.60
Hf	0.93	0.97	13.32	3.93	6.97	1.00	0.79	4.19
Zr	25.54	21.72	375.50	131.50	235.50	31.92	27.30	149.90
Sm	2.34	2.68	20.81	6.84	20.13	3.14	10.10	16.96
Eu	0.91	0.97	1.72	1.88	4.00	1.80	2.90	3.17
Gd	3.04	3.21	18.93	6.25	18.00	2.75	9.48	15.30

Tb	0.54	0.55	2.33	0.71	1.91	0.31	1.28	1.53
Dy	3.81	3.65	11.90	3.63	8.96	1.51	7.02	6.80
Y	22.95	21.03	50.18	18.49	37.52	7.88	36.35	26.63
Но	0.82	0.77	2.01	0.65	1.46	0.27	1.26	1.09
Er	2.38	2.20	5.02	1.77	3.68	0.73	3.23	2.72
Tm	0.35	0.32	0.61	0.23	0.41	0.09	0.41	0.29
Yb	2.31	2.09	3.91	1.34	2.41	0.59	2.39	1.79
Lu	0.34	0.30	0.60	0.17	0.31	0.08	0.31	0.26

Table 2.11 (contd.) Trace element concentrations of alkaline rocks (nepheline syenites) from Khariar alkaline complex.

Element	OD-6/1	OD-6/2	OD-6/3	OD-6/4	OD-7/1	OD-7/2	OD-8/1	OD-8/4	OD-8/5
	(ppm)								
Cs	0.49	0.23	0.56	0.49	0.20	0.18	0.05	0.04	0.11
Rb	204.90	103.50	63.82	181.50	168.50	240.00	127.80	101.50	138.00
Ba	800.40	217.30	134.30	771.40	425.30	252.10	362.90	310.70	238.30
Th	8.41	10.04	3.24	3.69	0.59	0.05	1.11	0.62	0.70
U	3.40	1.16	1.12	0.49	0.09	0.02	0.08	0.04	0.08
Nb	169.50	361.20	10.98	49.05	37.01	52.48	25.22	31.90	12.44
Та	12.34	29.93	0.73	2.99	2.28	2.25	4.44	6.48	0.89
La	69.95	122.30	10.67	37.31	21.62	8.39	38.66	34.76	13.78
Ce	169.90	325.10	22.26	104.40	62.08	24.79	112.90	103.70	32.02
Pr	22.62	42.99	2.80	16.05	9.64	3.91	17.70	16.31	4.47
Pb	11.73	5.50	8.03	6.16	1.56	1.14	0.62	0.31	1.61
Sr	1267.00	501.50	318.90	1424.00	1560.00	882.70	2138.00	2388.00	1475.00
Nd	91.02	171.50	11.27	72.15	42.51	17.12	79.88	73.11	18.96
Hf	11.02	35.89	1.49	9.32	8.80	6.83	6.37	6.86	1.80
Zr	334.20	914.90	57.09	305.70	317.60	220.50	171.50	185.90	50.79
Sm	16.21	30.78	2.46	13.29	7.52	3.22	13.35	12.02	3.27
Eu	4.40	6.09	0.97	4.15	2.65	1.44	4.63	4.11	1.94
Gd	13.01	26.46	2.58	10.20	5.68	2.40	9.01	8.01	2.41
Tb	1.52	3.36	0.39	1.13	0.62	0.27	0.89	0.79	0.26
Dy	7.41	17.91	2.40	4.98	2.80	1.25	3.37	3.00	1.14
Y	31.33	80.80	13.40	18.23	9.97	4.18	9.95	8.84	4.44
Но	1.24	3.27	0.48	0.81	0.46	0.20	0.48	0.44	0.19
Er	3.30	8.94	1.35	2.11	1.27	0.52	1.27	1.18	0.51
Tm	0.44	1.22	0.19	0.30	0.19	0.07	0.17	0.17	0.07
Yb	2.86	8.34	1.26	2.38	1.72	0.61	1.45	1.55	0.61
Lu	0.43	1.32	0.18	0.44	0.35	0.13	0.29	0.31	0.12

Table 2.12 Trace element concentrations of Nepheline syenites from Kishengarh, Rajasthan.

Element	KG-X	KG-01	KG-02	KG-03	
	(ppm)	(ppm)	(ppm)	(ppm)	
Cs	1.23	2.37	1.35	0.64	
Rb	110.90	132.60	102.30	131.60	
Ва	291.60	745.30	1080.00	638.80	
Th	3.57	9.54	4.96	2.48	
U	0.82	1.75	0.99	0.29	

Nb	15 81	18 51	<i>AA</i> 11	03 78
		2 04		3.88
	2.19	2.94	2.10	J.88
La	24.99	49.42	55.59	44.44
Ce	45.62	80.23	53.92	67.61
Pr	4.98	8.21	5.45	6.66
Pb	9.45	15.60	5.12	5.53
Sr	68.34	551.70	288.70	220.90
Nd	16.91	27.59	17.39	21.07
Hf	0.37	3.19	1.04	3.12
Zr	10.10	148.70	29.35	138.80
Sm	2.77	4.73	2.83	3.39
Eu	0.61	1.53	0.98	1.08
Gd	2.75	5.04	2.87	3.36
Tb	0.38	0.66	0.39	0.44
Dy	2.20	3.97	2.34	2.63
Y	12.29	23.33	13.25	13.92
Но	0.44	0.81	0.47	0.51
Er	1.30	2.43	1.40	1.47
Tm	0.19	0.36	0.20	0.23
Yb	1.31	2.43	1.28	1.66
Lu	0.19	0.35	0.18	0.27

Table 2.13	Trace element	concentrations	of alkali	basalts fro	om Phenai	Mata Com	plex,
Gujarat.							

Element	PMC-01	PMC-02	PMC-03	PMC-04	PMC-06
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Cs	0.12	0.06	0.27	0.21	1.61
Rb	53.71	26.38	39.00	49.08	113.70
Ba	992.00	256.10	756.50	979.80	839.70
Th	12.26	2.71	5.50	11.49	18.90
U	2.33	0.64	0.87	2.39	4.01
Nb	56.81	18.31	32.23	46.78	34.48
Та	3.14	1.13	1.71	2.60	1.98
La	61.13	19.01	39.92	53.49	64.54
Ce	112.30	41.65	71.93	99.39	122.30
Pr	12.41	5.61	8.02	11.16	13.76
Pb	3.91	1.92	4.05	6.08	16.99
Sr	507.00	441.80	612.60	546.60	345.50
Nd	44.19	24.36	29.14	40.23	49.93
Hf	4.44	3.77	2.27	4.25	5.89
Zr	169.20	109.30	55.81	125.70	227.20
Sm	7.55	5.84	4.93	7.05	9.25
Eu	2.13	1.86	1.61	2.00	2.09
Gd	7.88	6.15	5.15	7.39	9.69
Tb	1.07	0.93	0.67	1.00	1.37
Dy	6.54	5.57	3.92	6.01	8.35
Ŷ	37.23	27.93	21.32	34.12	47.71
Но	1.35	1.04	0.79	1.22	1.69
Er	3.92	2.82	2.22	3.57	4.84
Tm	0.57	0.38	0.30	0.51	0.69
Yb	3.74	2.29	1.96	3.32	4.50
Lu	0.54	0.31	0.28	0.47	0.64

Chapter 3 Analytical Methods This chapter is divided into two parts: 3.1 Chemistry and 3.2 Mass Spectrometry. Section 3.1 discusses the details of the protocol developed for the chemical separation and purification of Nd. All reagents used were ultrapure in grade, including water that was de-ionized Milli – Q (resistivity 18.2M Ω . cm). HCl used for column chemistry was prepared in the laboratory by distilling commercial grade acid twice in a Savillex® PFA (Teflon) distillation unit. Section 3.2 gives details of the mass spectrometry employed to obtain high precision Nd isotopic ratios. I have compared the most commonly used data acquisition and reduction methods for their effects on the accuracy of Nd isotopic ratios. All isotopic investigations were carried out on a Triton (TIMS) at the Department of Earth Sciences, Pondicherry University, Puducherry, India. Measurements for column calibrations were carried out using a Q-ICP-MS (Quadrupole - Inductively Coupled - Mass Spectrometer) at Geosciences Division, Physical Research Laboratory, Ahmedabad, India.

3.1 Chemistry

In this section I present details of the chemical separation protocol developed to obtain a pure Nd fraction from the rock matrix. Rock samples were broken into smaller chips with the help of a jaw crusher and powdered using tungsten – carbide TEMA® mill. Kimberlite samples, for which sample amount was limited, were powdered using an agate mortar and pestle.

3.1.1 Sample Dissolution

Standard dissolution protocol for silicates/carbonates was modified depending upon the mineralogical composition of the rock. Carbonatites were analysed in two separate fractions; as carbonate and silicate. The carbonate fraction was leached from a sample using 6N HCl and the residual silicate fraction was dissolved following the dissolution protocol for silicate rocks. Since carbonate rich carbonatites generally have higher REE contents compared to carbonate poor carbonaties (Ray et al. 2013), the weight of the samples dissolved was varied between 60 mg to 200 mg depending on the carbonate content. In the case of very low concentrations of Nd (< 0.1 ppm) in samples like mantle xenoliths (peridotites), 1 - 2 g of sample powder was taken. A powdered sample was dissolved in a concentrated mixture of HF and HNO₃ (2:1). Complete dissolution was achieved through ~1 hour of ultra-sonication and heating at 60°C with closed cap for ~12 hours. After two rounds of 8N HNO₃ treatment and drying, the sample was converted to chloride form using 6N HCl (two rounds of 0.5 ml) and the final solution was prepared in 1ml of 1N HCl for

column chemistry. The sample dissolution procedures constitute the Step - 1 in the chemical protocol (Figure 3.1).

3.1.2 Column Chemistry

Various elements of interest were separated from matrix of a sample solution in the different stages of column chromatography. The flowchart (Figure 3.1) gives an overview of the stages of column chemistry routines those were followed in this work with an emphasis on the protocol followed for Ce and Sm free Nd purification process. The various steps as shown in Figure 3.1 are described below in detail.

Step – 2 (Primary Column Procedure)

- 1. The final solution of the rock sample in 1 ml of 1N HCl was loaded onto the preconditioned AG-50W-X8 resin in the primary column. The column was precalibrated for Rb, Sr and REE separation.
- 2. Elution Protocol:
 - i. 10 ml of 2N HCl Elute and discard
 - ii. 4 ml of 2N HCl Elute and collect for Rb
 - iii. 10 ml of 2N HCl Elute and discard
 - iv. 8 ml of 2N HCl Elute and collect for Sr
 - v. 18 ml of 6N HCl Elute and collect for collecting REEs
 - vi. 40 ml of 6N HCl twice for column wash
 - vii. Regeneration of the resin by Milli-Q water

Step – *3 (REE separation column procedure)*

- REE cuts in 100µl of 0.18N HCl was loaded onto the pre-conditioned Ln spec resin in column. Another 100µl of 0.18N HCl was added by washing the sample vial.
 Elution Protocol:

 18 ml of 0.18N HCl – Elute and discard
 8 ml of 0.3N HCl – Elute and collect for Nd
 - iii. 7 ml of 0.3N HCl Elute and discard
 - iv. 7 ml of 0.4N HCl Elute and collect for Sm.
 - v. Full column reservoir volume 6N HCl Wash
 - vi. Full volume Milli Q water Wash

Step – 4 (Micro column procedure with α –HIBA)

This step is critical for our experiment since here we ensure separation of pure Nd, devoid of any trace of Ce in the fraction. Every time the column chemistry was done, fresh batches of acids were prepared, and columns were loaded with fresh resin, maintaining the pH. Fresh calibration was done for every batch of acid and resin. Figure 3.3 shows a typical calibration curve obtained by us for our columns. The procedural details are described below.

α-HIBA column chemistry

Resin Preparation

- 1) Take AGW X4 resin in a Teflon container. Clean it with Milli-Q water.
- 2) Add 6N HCl to this resin and ultra-sonicate for 60 minutes.
- 3) Discard the acid and store the resin in 6N HCl overnight.
- 4) Following day repeat steps 2 and 3, twice.
- 5) Wash the resin with Milli-Q water thoroughly (three times at least).
- 6) Carefully add a few drops of liquid NH₄ onto the resin in Milli-Q untill its pH becomes 7.
- 7) Resin is now ready to be used.

Preparation of α-HIBA

- 1) This acid is prepared by dissolving alpha-HIBA crystals in Milli-Q water.
- 0.15M acid is prepared by calculating the required weight needed to be dissolved in required volume of the acid to be prepared. For example, to prepare 1L or 1000ml of 1M acid dissolve the weight equal to the molecular weight of the alpha – HIBA crystals.
- 3) The pH is adjusted to 4.8 by adding NH₄ to the acid. The acid is ready to be used.

Once the resin and acid were ready, the columns were calibrated. Teflon columns of dimension 9 cm \times 0.25 cm (internal diameter) were used. Resin filled column was used only once, after which the resin was thrown and column was filled again with the new resin before a new experiment. The Nd eluted and collected in this stage is Ce – free, however, in alpha-HIBA medium. To remove α -HIBA the collected eluent was reacted with aqua-regia (mixture of concentrated HCl-HNO₃ in 3:1 proportion) at temperatures of around 120 – 150 °C.

3.2 Mass Spectrometry

In this section I discuss the details of the mass spectrometric methods used for Nd isotope data acquisition and reduction, starting with the details of the optimization of the ion current and run conditions.

3.2.1 Run Conditions for Nd Isotope Analyses on TIMS

Neodymium was measured as Nd⁺ ions on a Triton TIMS at the Department of Earth Sciences, Pondicherry University, India. For each sample about 400 ng of Nd was loaded onto the degassed zone refined Re double filament assembly. The evaporation filament was heated to 1000-1500 mA, at a rate of 20 mA/min and the ionization filament to 4000-4300 mA, at a rate of 150 mA/min. This heating of the filaments was carried out in two steps. The first step involved heating of ionization filament to 3500 mA while evaporation filament was heated to 800 mA. Once current in the ionisation filament reached 3500 mA, the second step heating of the evaporation filament was initiated. The Nd⁺ signal for 142 mass appeared only after the evaporation filament reached 1000 mA and the corresponding ionization filament current was 4000 mA. The data acquisition was initiated when Nd⁺ (for 142 mass) reached about 2.5 - 4.0 V ($R = 10^{11} \Omega$). The Nd was maintained in a window of 80 % to 200 % of the original signal using Triton software. Details of the run conditions are given in Table 3.1. Ames Nd standard was analysed (using both 3- and 2- sequence multi-dynamic modes of data acquisition methods; Table 3.1) routinely with each batch of samples. For the 3-sequence data acquisition scheme, each run lasted for about 6-7 hours and that for the 2-sequence data acquisition scheme, around 5 hours. Isobaric interferences on Nd isotopes from Sm and Ce were monitored by measuring ¹⁴⁷Sm and ¹⁴⁰Ce, respectively.

3.2.2 Data Acquisition and Reduction Methods

High precision isotopic ratio measurements by TIMS often requires data acquisition through a multi-dynamic mode, wherein differences in collector efficiencies/factors can be nullified by measuring individual ion beams in multiple Faraday Cups through peak jumping. The Zoom Optics, a feature of *Triton* TIMS, helps in precise co-incidence and centring of peaks for various masses when magnet settings are changed during multi-dynamic data acquisition. In addition, the amplifier rotation, another feature of *Triton*, helps in minimising the errors, if any, due to unequal amplifier efficiencies. For the present study, I have carried out the Nd isotopic ratio analyses using a multidynamic mode of data acquisition. The two most commonly employed multi-dynamic methods for Nd isotopic investigations: (1) 3-sequence method (as used by Upadhyay et al., 2009) and (2) 2-sequence method (as used by Roth et al., 2014b), were used to obtain data. A comparative analysis of the two methods was done by me to understand the effect of data acquisition method on the accuracy of the ¹⁴²Nd/¹⁴⁴Nd isotopic values. The results obtained are described in Chapter 4. The details of the two methods along with their run conditions are given in Table 3.1 and 3.2.

Data reduction includes correction for isobaric interferences and mass fractionation corrections, the details of which are discussed in Chapter 4. Table 3.3 provides the details of the two commonly used fractionation correction methods employed for data reduction in the present study, viz. *exponential law* and *power (law) – normalised exponential law* (Thirwall, 1991; Upadhyay et al., 2009; Gautam et al., 2017).



Figure 3.1 Flowchart showing various stages of the protocol developed for extraction of pure Nd from samples.



Figure 3.2 Calibration curve for Nd - Sm separation using Ln spec resin, obtained by analyses of calibration cuts in a Q-ICP-MS (a) Separation of Sm from Nd during Step -2 of the element separation protocol: Ce elutes with Nd; (b) shows an enlarged view of the Nd elution.



Figure 3.3 Calibration curves for a-HIBA column chemistry. (a) shows Ce free Nd elution (b) enlarged view of the Nd elution, which shows no trace of Ce.

Table 3.1

Cup configuration and run conditions used in this study for Nd isotopic ratios measurements on a Triton

a) Three-sequence method

											Zoom	optics
Cup	L4	L3	L2	L1	С	H1	H2	Н3	H4	Integration time	Focus	Dispersion
										[sec]	[V]	[V]
Sequence 1	¹⁴⁰ Ce	¹⁴² Nd	¹⁴³ Nd	¹⁴⁴ Nd	¹⁴⁵ Nd	¹⁴⁶ Nd	147 Sm	¹⁴⁸ Nd	150 Nd	8.389	0.0	0.0
Sequence 2			¹⁴² Nd	¹⁴³ Nd	¹⁴⁴ Nd	¹⁴⁵ Nd	¹⁴⁶ Nd	¹⁴⁷ Sm	¹⁴⁹ Sm	8.389	0.0	6.0
Sequence 3		¹⁴⁰ Ce		¹⁴² Nd	¹⁴³ Nd	¹⁴⁴ Nd	¹⁴⁵ Nd	¹⁴⁶ Nd	¹⁴⁸ Nd	8.389	0.0	8.0

b) Two-sequence method

											Zoom	optics
Cup	L4	L3	L2	L1	С	H1	H2	Н3	H4	Integration time	Focus	Dispersion
										[sec]	[V]	[V]
Sequence 1	¹⁴⁰ Ce	¹⁴² Nd	¹⁴³ Nd	¹⁴⁴ Nd	¹⁴⁵ Nd	¹⁴⁶ Nd	¹⁴⁷ Sm	¹⁴⁸ Nd	¹⁵⁰ Nd	8.389	0.0	0.0
Sequence 2		¹⁴⁰ Ce		¹⁴² Nd	¹⁴³ Nd	¹⁴⁴ Nd	¹⁴⁵ Nd	¹⁴⁶ Nd	148 Nd	8.389	0.0	8.0

Note: Number of blocks = 54, No. of cycles per block = 10, Amplifier rotation to left, Baseline after every 2 blocks, Peak centring after every 8 blocks, Lens focusing after every 4 blocks, No. of integrations = 1, Idle time (sec) = 3, Cycles filtered at 2σ .

Table 3.2

Comparison of various data acquisition and reduction procedures followed by Upadhyay et al. (2009) and Roth et al. (2014b)

Parameter	Upadhyay et al. (2009)	Roth et al. (2014 b)
Number of sequences in multi-dynamic mode	Three	Two
Fractionation correction law	Power-law normalized exponential law	Exponential law
Fractionation factor	Average of all sequences : $(\beta_1 + \beta_2 + \beta_3)/3$	Calculated from sequence 1: β_1
Cup factors	Get cancelled	Do not get cancelled [*]
Multi-dynamic correction for ratios	¹⁴² Nd/ ¹⁴⁴ Nd, ¹⁴³ Nd/ ¹⁴⁴ Nd, ¹⁴⁵ Nd/ ¹⁴⁴ Nd, ¹⁴⁸ Nd/ ¹⁴⁴ Nd	¹⁴² Nd/ ¹⁴⁴ Nd
Static correction for ratios	¹⁵⁰ Nd/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd, ¹⁴⁵ Nd/ ¹⁴⁴ Nd, ¹⁴⁸ Nd/ ¹⁴⁴ Nd, ¹⁵⁰ Nd/ ¹⁴⁴ Nd

*As described in Roth *et al.* (2014 b), the cup factors do not affect the exponential law corrected $^{142}Nd/^{144}Nd$ by more than 5ppm if the difference in relative cup efficiency is less than 370ppm. The relative cup efficiency is calculated by taking the difference of static $^{142}Nd/^{144}Nd$ measured in sequence 1 and 2.

Table 3.3

Details of fractionation correction methods used in the present study

Isotope ratio	Power law normalised exponential law	Simple exponential law
¹⁴² Nd/ ¹⁴⁴ Nd	$[(^{142}Nd/^{144}Nd)_3 \times (^{146}Nd/^{144}Nd)_1/0.7219] \times (141.907731/143.910096)^{\beta} \times (1+f)^2$	$[(^{142}\text{Nd}/^{144}\text{Nd})_2] \times$ (141.907731/143.910096) ^β ₁
¹⁴³ Nd/ ¹⁴⁴ Nd	$[\{(^{143}Nd/^{144}Nd)_2 \times (^{143}Nd/^{144}Nd)_3\}/\{(^{144}Nd/^{146}Nd)_1 \times 0$.7219}]^{0.5} \times (142.909823/143.910096)^{\beta} \times (1+f)^1	$[(^{143}\text{Nd}/^{144}\text{Nd})_1] \times$ (142.909823/143.910096) ^β ₁
¹⁴⁵ Nd/ ¹⁴⁴ Nd	$[\{(^{145}\text{Nd}/^{144}\text{Nd})_2 \times (^{145}\text{Nd}/^{146}\text{Nd})_1 \times 0.7219\}]^{0.5} \times (144.912582/143.910096)^{\beta} \times (1+f)^{-1}$	$[(^{145}\text{Nd}/^{144}\text{Nd})_1] \times (144.912582/143.910096)^{\beta}_1$
¹⁴⁸ Nd/ ¹⁴⁴ Nd	$[\{(^{148}\text{Nd}/^{146}\text{Nd})_1 \times (^{144}\text{Nd}/^{146}\text{Nd})_3 \times (0.7219)^2\}] \times (147.916901/143.910096)^{\beta} \times (1+f)^{-4}$	$[(^{148}\text{Nd}/^{144}\text{Nd})_1] \times (147.916901/143.910096)^{\beta}_1$
¹⁵⁰ Nd/ ¹⁴⁴ Nd	$[(^{150}\text{Nd}/^{144}\text{Nd})_1] \times (149.9209/143.910096)^{\beta}$	$[(^{150}\text{Nd}/^{144}\text{Nd})_1] \times$ (149.9209/143.910096) ^β ₁

Here $\beta = \frac{(\beta_1 + \beta_2 + \beta_3)}{3}$ and $f = \frac{(f_1 + f_2 + f_3)}{3}$ are the average mass fractionation factors from the three sequences

- $\beta_i = ln\{(0.7219)/(\ ^{146}Nd/^{144}Nd)_i\ \}/\ ln\ (145.913126/143.910096)$
- $f_i = \{(0.7219)/(\ ^{146}Nd/^{144}Nd)_i \ \} \ ^{1/ \, (145.913126 \ \ 143.910096)}$ 1

i = 1, 2, 3 which refers to the sequence number

Chapter 4 Results and Discussion In this chapter I discuss the results of my study on the effects of mass spectrometric procedures on accurate determination of μ^{142} Nd and results obtained from our efforts in search of μ^{142} Nd anomalies in Indian rocks.

4.1 Effect of mass spectrometric procedures on accuracy of ¹⁴²Nd/¹⁴⁴Nd

The mass spectrometric procedures involve data acquisition and reduction methods. To understand the effect of these on the accuracy of ¹⁴²Nd results obtained, the 1.48 Ga alkaline rocks from Khariar were analysed as a case study. The report of negative μ^{142} Nd anomaly (-13ppm) in these rocks by Upadhyay et al. (2009) needed an independent verification since these were the only non-Archean rocks reported to have preserved signatures of early silicate Earth differentiation. Considering the highly dynamic nature of the Earth's earliest mantle and the time elapsed since its formation, it is extremely difficult to encounter μ^{142} Nd anomalies in rocks younger than Archean. All other accepted discoveries of $\mu^{142}Nd$ anomalies come from the Hadean and Archean rocks (Bennett et al. 2007; Boyet and Carlson, 2006; Boyet et al. 2003; Caro et al. 2003, 2006; O'Neil et al. 2008; Rizo et al. 2011, 2012; Roth et al. 2013, 2014a). This particular finding being from very young rocks, has the potential to change our understanding of the preservation and longevity of the evidence for the earliest crust-mantle differentiation. Since these rocks are believed to have originated from a lithospheric mantle, the authors had argued for preservation of ¹⁴²Nd anomaly in a non-convective mantle domain in cratonic roots for at least for 2.7 billion years since its formation (Upadhyay et al. 2006, 2009). However, if these anomalies turn out to be analytical artefacts then the hypothesis of continental lithospheres being sites of preservation of ¹⁴²Nd anomalies would be invalidated, restricting the anomalous signals only to the rocks of Hadean and Archean. Therefore, it is imperative that the robustness of these results is verified through independent investigations by different laboratories.

In an attempt to verify these negative ¹⁴²Nd anomalies, Roth et al. (2014b) measured ¹⁴²Nd/¹⁴⁴Nd in the same aliquots of the samples of Upadhyay et al. (2009), but could not reproduce the results. In their data acquisition protocol on TIMS, Roth et al. (2014b) had employed a 2-sequence multi-dynamic mode in contrast to a 3-sequence mode utilized by Upadhyay et al. (2009). To minimize the time delay between the measurements of ¹⁴⁴Nd/¹⁴⁶Nd and ¹⁴²Nd/¹⁴⁴Nd, Roth et al. (2014b) acquired these ratios in sequences 1 and 2, instead of sequences 1 and 3 as followed by Upadhyay et al. (2009). This was done to remove the analytical bias in the (mass) fractionation corrected ¹⁴²Nd/¹⁴⁴Nd in the 3-sequence mode,

caused by higher relative rate of fractionation ($r_f > 1$). Where r_f = average fractionation rate (r_a) /threshold fractionation rate (r_t), and r_t = external reproducibility /time gap between the sequences (1 and 2 in 2-sequence mode or 1 and 3 in 3-sequence mode). Average fractionation rate was calculated for each analysis by finding the slope of the regressed line when uncorrected ¹⁴⁶Nd/¹⁴⁴Nd from sequence-1 is plotted against the time.

Roth et al. (2014b) also proposed a correction procedure to reduce the 3-sequence data of Upadhyay et al. (2009), where r_t was lower than that in a 2-sequence mode, and showed that in all except one sample the anomalies vanished. According to the authors, this correction procedure was not advocated for general use, but rather is an approximation to reassess published data. The number of sequences was not the only analytical parameter that was different in the two studies. Another important parameter which was not given a due importance was the law of fractionation correction (e.g., exponential vs. power law). The protocol followed by Roth et al. (2014b) was grossly different from that of Upadhyay et al. (2009). The details are given in Tables 3.1 - 3.3 (Chapter 3).

It is therefore, important that we also understand the role of the fractionation correction on the accuracy of ¹⁴²Nd/¹⁴⁴Nd isotopic data and its contribution (if any) to the generation of the analytical artefacts. To study these aspects and to further investigate the accuracy of the negative μ^{142} Nd anomalies reported in the alkaline silicate rocks of the Khariar complex, India (Upadhyay et al. 2009), we analysed samples re-collected from the same geological outcrops for their Nd isotopic compositions applying different fractionation correction procedures. We followed identical experimental procedure as in the original study of Upadhyay et al. (2009) and that proposed later by Roth et al. (2014b). Experimental details are provided in Tables 3.2 and 3.3. Both the techniques were evaluated in light of over correction of ¹⁴²Nd/¹⁴⁴Nd resulting from excessive fractionation correction. We have used Ames Nd standard for normalization of ¹⁴²Nd/¹⁴⁴Nd of samples, because it was routinely analysed along with the samples in our laboratory. We have also analysed JNdi-1 standard and rock standard BHVO-2 for accuracy check.

4.1.1 Data acquisition: 2- versus 3- sequence multi dynamic mode

In this study, the effect of number of sequences used in the multi-dynamic mode of data acquisition, on the accuracy of isotopic results was studied. All standards and samples of alkaline rocks from Khariar were analysed using multi-dynamic scheme of data acquisition employing both 3- and 2-sequence modes. Fifteen and eighteen loads of Ames Nd were analysed for the 3- sequence and 2- sequence modes, respectively. In the 3-sequence mode,

isotopic ratios were corrected for mass fractionation using the *power (law)-normalised exponential law* as in Upadhyay et al. (2009) and our experiment yielded an average value of 1.1418375 for ¹⁴²Nd/¹⁴⁴Nd of Ames Nd with an external reproducibility of 7.1 ppm (Table 4.1 – a). In the 2-sequence mode, the simple *exponential fractionation law* (as in Roth et al. 2014b) was used and an average value of 1.1418390 for ¹⁴²Nd/¹⁴⁴Nd was obtained with an external reproducibility of 8.9 ppm (Table 4.1 – b). Our external precision (2 SD) is lower than that reported by most studies on such experiments (i.e., ~5 ppm), in spite of the fact that the within-run precisions are < 5ppm (2 SE). The reason for the lower external precision could be because of the aging (> 12 years old) of the Faraday Cups. Because I have used two different schemes of data acquisition for the Khariar samples and BHVO-2, the above two values of ¹⁴²Nd/¹⁴⁴Nd for Ames Nd have been used for determination of μ^{142} Nd (Figure 4.1). μ^{142} Nd values of Khariar samples obtained through a 3-sequence method appear to be slightly negative, albeit unresolvable within 2SD, compared to those obtained through a 2-sequence method.

If the external precision for ¹⁴²Nd/¹⁴⁴Nd measurements were considered to be 5 ppm, then the respective r_t values would have been 0.22 ppm/s and 0.44 ppm/s for corresponding time durations of 22.8 s and 11.4 s, respectively. Our isotopic data from the analyses of standards and Khariar samples, by both modes, show $r_a < 0.22$ ppm/s (Tables 4.1- 4.3), suggesting $r_f < 1$.This is unlike what Roth et al. (2014b) observed for the 3-sequence data of Upadhyay et al. (2009), where $r_f > 1$. Consequently, there was no need for the time correction (an empirical solution for the data of Upadhyay et al. 2009) of the data acquired in 3sequence mode to deal with any excess fractionation, as was suggested by Roth et al. (2014b).

A few analyses carried out using 3-sequence data acquisition mode prior to this experiment show r_a between 0.20 ppm/s and 0.40 ppm/s, in which case $r_f > 1$. However, if I consider the actual external precision for the present study, which is 8.9 ppm, then value of r_t for three sequence mode becomes 0.39 ppm/s instead of 0.22 ppm/s and in this case, for all the data, $r_f < 1$. In addition, there is absence of any significant correlation between the fractionation corrected ¹⁴²Nd/¹⁴⁴Nd isotopic ratios and average fraction rates (r_a), as can be seen in Figure 4.2. Therefore, it is inferred that the time-gaps between successive sequences in a multi-dynamic mode do not affect the quality of the data acquisition has no effect on the average fractionation rates (r_a).

4.1.2 Corrections for Isobaric Interferences

Isobaric interferences on Nd isotopes from Sm and Ce were monitored by measuring ¹⁴⁷Sm and ¹⁴⁰Ce, respectively. The ¹⁴⁰Ce/¹⁴²Nd for the all analysed samples is given in the tables provided at the end of this chapter. The maximum and minimum values of ¹⁴⁰Ce/¹⁴²Nd were 3.77×10^{-4} and 9.18×10^{-7} , respectively. On an average ¹⁴⁰Ce/¹⁴²Nd was in the order of 10^{-5} . ¹⁴⁷Sm/¹⁴⁴Nd values never exceeded order of 10^{-7} and hence deemed insignificant for any correction. Nonetheless, interference corrections for Ce and Sm were applied to the standard and samples. We do not see any significant correlation between ¹⁴⁰Ce/¹⁴²Nd and the corresponding fractionation corrected ¹⁴²Nd/¹⁴⁴Nd (Figure 4.3).

4.1.3 Correction for Mass Dependent Fractionation

A comparison of the pattern of mass fractionation observed in our data with the theoretical patterns expected from various empirical fractionation laws (Habfast, 1998), with the help of ¹⁴²Nd/¹⁴⁴Nd versus ¹⁵⁰Nd/¹⁴⁴Nd, reveals that the *exponential law* best explains the observed pattern in each individual sequences (Figure 4.4), which are equivalent to static mode of data acquisitions.

A fractionation line corresponding to the power-normalised exponential law for multi dynamic data acquisition cannot be drawn. We therefore compare the two commonly used empirical laws, *exponential* and *power (law)-normalised exponential laws*, for the residual correlations in the fractionation corrected data. The details of the two laws are already provided in the Table 3.3. The raw/uncorrected data for 67 Ames Nd aliquots (Table 4.3) analysed during and prior to this experiment over a period of 3 years, were corrected for mass fractionation using the (1) *power-normalised exponential law*, and (2) *exponential law*. Data acquired using 2-sequence mode were not included in this exercise, because barring ¹⁴²Nd/¹⁴⁴Nd all other Nd isotopic ratios cannot be corrected for fractionation using the first law (i.e. 1; Tables 3.1 and 3.3). The figures 4.5 and 4.6 show results of this exercise.

We observed that: (1) isotopic ratios corrected using the *power-normalised exponential law* do not show any significant inter correlation (Figures 4.5a-d and 4.6a-d), whereas the *exponential law* correction method leaves behind substantial residual correlations, especially for ¹⁵⁰Nd/¹⁴⁴Nd and ¹⁴⁸Nd/¹⁴⁴Nd (Figs. 4.5e-h and 4.6e-h); (2) *power-normalised exponential law* noticeably improves precisions (2SD) for ¹⁴³Nd/¹⁴⁴Nd (5.1 ppm), ¹⁴⁵Nd/¹⁴⁴Nd (4.6 ppm) and ¹⁴⁸Nd/¹⁴⁴Nd (11.7 ppm) ratios, compared to those obtained through *exponential correction* (Table 4.3; Figures 4.3 and 4.4), which are 17.4 ppm, 11.7 ppm and 26.5 ppm, respectively. However, the 2SD values for ¹⁵⁰Nd/¹⁴⁴Nd are similar in both

the methods because it is obtained from only one sequence (i.e., sequence-1), like that in a static mode but with different β values (Tables 3.1 and 3.2). Residual correlations as described above, in (1), are undesirable and indicate insufficiency of the method/law used for mass fractionation (Andreasen and Sharma, 2009). We, therefore, infer that application of the *power-normalised exponential law* for correction of mass dependent fractionation in a multi-dynamic method is the most appropriate data reduction approach.

Using the *power-normalised exponential law* we corrected data for Khariar samples acquired through both the 3- and 2-sequence modes (Figure 4.7), but could not reproduce the anomalies of Upadhyay et al. (2009). We, however, observed that the mean μ^{142} Nd values of some of the sample-replicates plotted outside, on the negative side, the 7.1 ppm range defined for the standard – which is also corrected using the *power-normalised exponential law*. In contrast, sample data from both 3- and 2-sequence modes corrected using the *exponential law* plotted well within the 8.9 ppm range for the standard, corrected using the *exponential law* (Figure 4.7). In addition to μ^{142} Nd, inter comparison was also done for stable Nd isotopic compositions acquired through 3-sequence mode and corrected using both the laws (Figures 4.8 and 4.9). As can be seen data corrected using the *exponential law* show larger spread compared to those corrected using the *power-normalised exponential law* (Figures 4.8 and 4.9). It is therefore evident that it is the method of fractionation correction and not the mode of acquisition that controls the quality of data.

4.1.4 Choice of Terrestrial Standard Used: Ames Nd versus JNdi-1

Because the ¹⁴²Nd/¹⁴⁴Nd isotopic ratio of the terrestrial standard is key to the definition of μ^{142} Nd it is essential that the standard has uniform and reproducible isotopic ratio and truly represents the modern accessible mantle. Several terrestrial standards have been used over the years in ¹⁴²Nd studies – such as LaJolla Nd, JNdi-1, Ames Nd and many in-house standards. Although it is expected that all the stable Nd isotopic ratios and ¹⁴²Nd/¹⁴⁴Nd of these standards are identical, observations suggest otherwise (e.g., Brandon et al. 2009; O'Neil et al. 2008; Saji et al. 2016; Wakaki and Tanaka, 2012). This may lead to appearance or disappearance of anomalies depending on choice of the standard (Gautam et al., 2017; Gautam and Ray, 2017).

I analysed two commonly used Nd terrestrial standards viz. Ames Nd and JNdi-1 during the course of this study. Eleven aliquots of JNdi-1 were analysed along with six of Ames Nd (Table 4.4(a); Figure 4.10). As can be seen in Figure 4.10 all Nd isotopic ratios of JNdi-1,

although overlap at 2SD with those of the Ames standard, show minor differences in the mean values. The average value of ¹⁴²Nd/¹⁴⁴Nd for JNdi-1 is lower by 6 ppm than the long term average of ¹⁴²Nd/¹⁴⁴Nd for Ames Nd (Figure 4.10). Since the two commonly used Nd standards do not have identical ¹⁴²Nd/¹⁴⁴Nd, the comparison in μ^{i} values can be confusing. To avoid this, ¹⁴²Nd/¹⁴⁴Nd isotopic ratios of the two standards analysed over the course of this study are directly compared in Figure 4.11. This helps in comparing the actual values instead of relative change with respect to only one standard.

When ¹⁴²Nd/¹⁴⁴Nd of Khariar samples were normalized with respect to Ames Nd and JNdi-1, the slight negative μ^{142} Nd obtained using Ames Nd became normal with respect to JNdi-1 (Figure 4.12). The mean values of μ^{142} Nd of BHVO-2 measured by us are different with respect to each standard; however, they overlap within the external reproducibility of each standard (Figure 4.12). It should be noted that Upadhyay et al. (2009) used La Jolla as reference whereas Roth et al. (2014b) used JNdi-1. La Jolla has higher ¹⁴²Nd/¹⁴⁴Nd with respect to JNdi-1 (Wakaki and Tanaka, 2012), similar to what we observe in the case of Ames Nd (Figure 4.12; Table 4.4a). We speculate that the conflicting results obtained from the same aliquots of the Khariar samples by Upadhyay et al. (2009) and Roth et al. (2014b) are a combined effect of the choice of fractionation correction law and terrestrial standard used for calculation of μ .

Because different batches of Ames are known to have different Nd isotopic compositions, JNdi-1 is a more homogenoues standard than Ames Nd. Therefore, we strongly recommend that JNdi-1 should be used as the terrestrial reference standard for ¹⁴²Nd isotopic measurements. We provide a cross-calibration for JNdi-1 and Ames Nd analysed by us (Figure 4.13). We followed the method as desribed in Tanaka et al. (2000). A total of five JNdi-1 and six Ames Nd (single batch) analyses were included in this exercise. We got a linear relationship of (¹⁴²Nd/¹⁴⁴Nd)_{JNdi-1} = $0.809695 \times (^{142}Nd/^{144}Nd)_{Ames Nd} + 0.2172901$ with a R² value of 0.89 (Figure 4.13). Using this relation, a value of 1.1418302 for JNdi-1 was obtained corresponding to our long term average of 1.1418375 for Ames Nd. We use this as the reference to compare the ¹⁴²Nd isotope composition of the samples analysed by us in various batches during the course of this study. External reproducibility obtained for for JNdi-1 was 0.0000082 (2SD; Table 4.4a).

4.2 In search of μ^{142} Nd anomalies in Indian rocks

Considering the effects of analytical parameters which affect the accuracy of 142 Nd/ 144 Nd ratio and value of μ^{142} Nd, we decided to:

- correct data for mass fractionation using the power-normalised exponential law,
- use JNdi-1 as the reference material to compare that data for any anomalous composition, and
- report the ^{142}Nd isotope composition in terms of $^{142}Nd/^{144}Nd$ values instead of μ notation.

Rock standard BHVO-2 was analysed multiple times during the course of the study. Other rock standards, BCR-2, JB-1(a) and JB-3 were also analysed. Figure 4.14 shows the ¹⁴²Nd/¹⁴⁴Nd in reference to JNdi-1 for these rock standards. Nd isotopic data is in Table 4.5. In all the plots shown hereafter, the reference value for JNdi-1 is 1.1418302 with an external precision of 0.0000082 (2SD) presented as an orange shaded area. The long term average value obtained for Ames Nd along with its external reproducibility (2SD) in the present study is also shown.

4.2.1 ¹⁴²Nd/¹⁴⁴Nd isotopic composition of continental alkaline rocks of India

Alkaline rocks from various locations and of different ages were analysed: Carbonatites from Amba Dongar, Sung Valley and Newania were analysed in two fractional aliquots for each sample as carbonates and silicates. No resolvable anomalous ¹⁴²Nd isotopic composition on the repeat analyses of these is observed with respect to JNdi-1 (Figures 4.15 – 4.17). The associated silicate rocks from Amba Dongar and Sung Valley also do not show any resolvable anomalous ¹⁴²Nd isotopic composition. Kimberlites from Eastern Dharwar Craton, alkali basalts from Phenai Mata Complex and nepheline syenites from Kishengarh lack any resolvable anomalous ¹⁴²Nd/¹⁴⁴Nd composition (Figure 4.18). The data are presented in Tables 4.6 to 4.10.

The analysed rocks are believed to have been derived from the non-convective mantle domain – SCLM, and cover a vast span of time in terms of their ages of emplacement, from 1.5 Ga to 65 Ma. The absence of anomalous ¹⁴²Nd isotope composition in these suggests that the SCLM region involved in the generation of these magmas, did not inherit any signature of the early silicate differentiation events. Also, if at all any such signatures were acquired, they have been lost to dilution because of contamination in the source or within the crust.
Mantle xenoliths from Kutch could not be analysed as the Nd+ signal for 142 mass was not sufficient to run the sample. This is due to the low concentration of Nd (less than 0.01ppm) in these peridotites.

4.2.2 ¹⁴²Nd/¹⁴⁴Nd of Archean rocks

TTGs (3.5 Ga) from Singhbhum Craton and biotite gneisses (3.3 Ga) from BGC-1, Aravalli Craton, were analysed for their ¹⁴²Nd isotopic composition. With respect to Ames Nd, TTGs from Singhbhum do not show any resolvable anomalous ¹⁴²Nd composition (Figure 4.19), however, with respect to JNdi-1, these rocks show resolvable higher ¹⁴²Nd/¹⁴⁴Nd ratios. In terms of μ^{142} Nd calculated with respect to JNdi-1, TTGs of Singhbhum show a +13 ppm anomaly. The biotite gneisses from BGC-1 do not show any resolvable anomalous ¹⁴²Nd composition with respect to both, Ames Nd and JNdi-1. The values are given in Table 4.11. Whereas, it is clear that the Archean rocks of BGC-1 do not carry any evidence of early silicate differentiation, a possibility of the preservation of such evidence is hinted at in the Singhbhum TTGs. Therefore, it is essential to replicate the results for Singhbhum rocks.

Studying the 3.45 Ga Archean rocks of India we find a hint of preservation of an EDR signature in the mantle source of the TTGs of Singhbhum. If true, this would be the first evidence from Indian Shield for an early silicate differentiation process. On a global perspective, this is interesting as the 3.8 Ga Archean TTGs from Greenland (+15 ppm) and 3.73 Ga Yilgran (+5 ppm) carry positive anomalies (Bennett et al. 2007; Caro et al. 2006), whereas those from 4.28 Ga Canada rocks show negative (-16 ppm) anomalies (O'Neil et al. 2008). Our finding suggests that high positive anomalies persisted at least 350 million years beyond the formation of the TTGs of Greenland.

4.2.3 ¹⁴²Nd evolution of Indian mantle domains

Our attempts to extract information about earliest silicate differentiation from the mantle domains that formed Indian Shield have yielded some interesting information. We found that Archean mantle responsible for the generation of the Singhbhum TTGs appears to possess signature of the EDR, whereas the mantle sources of the 200 million years younger BGC-1 granitoids have no trace of such evidence (Figure 4.20). The latter could be explained by the loss of μ^{142} Nd excess to mixing with magmas derived from EER type of mantle domains (Figure 4.20). Alternately, their generation involved neither EDR nor EER but, was a mantle domain that had remained unaffected by the earliest silicate differentiation. The non-

convective mantle studied by us, as represented in carbonatites, kimberlites and alkaline rocks, shows no evidence of any of the early formed reservoirs.

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Figure 4.1 μ^{142} Nd values of 1.48 Ga alkaline rocks from Khariar analysed in this study: (a) data acquired using a 3-sequence multi dynamic mode and corrected for mass fractionation using the power-normalised exponential law; (b) data acquired using a 2- sequence multi dynamic mode and corrected for mass fractionation using the exponential law. The average values of Ames Nd used for calculating μ^{142} Nd in (a) and (b) are 1.1418375 ±7.1

ppm (2RSD, n = 15) and 1.1418390 ±8.9 ppm (2RSD, n = 18), respectively. The grey bands encompass ± 2RSD, external reproducibility, for Ames Nd standard.



Figure 4.2 Plot shows fractionation corrected ${}^{142}Nd/{}^{144}Nd$ versus average fractionation rate (r_a) for Khariar and other sample analysed during the course of this study.



Figure 4.3 Interference monitor ¹⁴⁰Ce/¹⁴²Nd versus corrected ¹⁴²Nd/¹⁴⁴Nd for Khariar and other samples analysed during the course of this study. Data are corrected using power-normalised exponential law. This lack of correlation suggests that the interference corrections applied for Ce did not bias the final ¹⁴²Nd/¹⁴⁴Nd data and therefore, were robust.



Figure 4.4 (a) Plot of uncorrected ¹⁵⁰Nd/ ¹⁴⁴Nd versus ¹⁴²Nd/¹⁴⁴Nd isotopic ratios for Ames Nd standard acquired using a 3-sequence multi-dynamic mode. ¹⁴²Nd/ ¹⁴⁴Nd values are from all the three sequences and ¹⁵⁰Nd/⁴⁴⁴Nd from the first sequence only. Each point is an average of 10 cycles (one block) and the plot contains data from 752 blocks for 14 analyses. Lines corresponding to different fractionation laws are also shown; (b) and (c) represent enlarged versions of the marked segments of the plot.



Figure 4.5 Plots of Nd isotopic ratios (except for ${}^{143}Nd/{}^{144}Nd$) for Ames Nd standard (n = 67) obtained during 3-sequence data acquisition method (data are in Table 4.3). Each datum (raw, corrected only for interference corrections) is corrected offline using the power-normalised exponential law (a-d) as well as the exponential law (e-h).



Figure 4.6 ¹⁴³Nd/¹⁴⁴Nd isotopic ratio of Ames Nd is compared with the other Nd isotopic ratios (n=67). The data was acquired during 3-sequence method (Table 4.3) and corrected offline for mass fractionation using both the laws, i.e. power-normalised exponential law (a-h) and exponential law (e-h).



Figure 4.7 μ^{142} Nd of Khariar rocks and BHVO-2 analysed in this study, with respect to the Ames Nd. The data acquired in both 3- and 2-sequences are corrected offline for mass fractionation using both the power-normalised exponential law and the exponential law. The average values of four replicates for each sample are also plotted with errors; 2SE for individual analyses and 2SD for the average values (Table 4.2). The external reproducibility (2RSD) for the Ames Nd standard is 7.1 ppm for power-normalised exponential law (inner light grey band) and 8.9 ppm for exponential law (outer dark grey band).



Figure 4.8 Plot showing average $\mu^i Nd$ (i= 142, 145, 148 and 150) calculated from two replicates of the four samples and BHVO-2. The raw data are taken from 3-sequence mode and corrected using (a) the power-normalised exponential law and (b) the exponential law. The data acquired during 2-sequence mode, corrected using the exponential law is shown in (c). 2RSD for respective $\mu^i Nd$ is represented by the light brown bar (power -normalised exponential law) and dark brown bar (exponential law). The external reproducibilities for ¹⁵⁰Nd in figures (b) and (c) extend beyond the scale in the figure.



Figure 4.9 Plot of $\mu^i Nd$ (i = 142, 145 and 148) for the data acquired during the 3-sequence mode. The plot is similar to Figure 4.8 except that the individual measurements are also shown along with the average value for each sample. Left panel (a - d) shows the data corrected using the power- normalised exponential law and right panel (e - h) shows the data corrected using the exponential law. The coloured bars refer to the external reproducibilities (2RSD).



Figure 4.10 Comparison of various Nd isotopic compositions of JNdi-1 (n=11) and Ames Nd (n=6) in μ notation. $\mu^{i} = (({}^{i}Nd/{}^{144}Nd)_{JNdi-1}/({}^{i}Nd/{}^{144}Nd)_{Ames})-1)\times 10^{6}$, where i = 142, 145, 148 and 150. Data are given in Table 4.4. Pink squares represent individual measurements of the JNdi-1and green square (cross - haired) represents average value for JNdi-1. The green shaded area shows external reproducibility (2RSD) for JNdi-1 whereas grey shaded area represents the same for Ames Nd.



Figure 4.11 ¹⁴²Nd/¹⁴⁴Nd isotopic ratio of individual measurements of Ames Nd analysed between April 2014 – November 2016 (n = 73) and JNdi-1 analysed during October-November 2016 (n = 11). The long term averages for both the standards with external reproducibility (2σ) are also shown. For Ames Nd, it is 1.1418372±111 and for JNdi-1 it is 1.1418306±82.



Figure 4.12 This plot shows¹⁴²Nd/¹⁴⁴Nd of the Khariar alkaline rocks and terrestrial standard BHVO-2

analysed by us. The reference value for Ames Nd is 1.1418375, whereas for JNdi-1 it is 1.1418306. Pink shaded area shows external reproducibility for Ames Nd (2RSD) and yellow shaded area shows external reproducibility (2RSD) of JNdi-1. Errors of individual points are 2SE and that for average values is 2SD.



Figure 4.13 Cross calibration of 142 Nd/ 144 Nd value of JNdi-1 against that of Ames Nd. Data for each aliquot of JNdi-1 is plotted against averaged Ames Nd data measured before and after the JNdi-1. The data are given in Table 4.4(b).



Figure 4.14 ¹⁴²Nd/¹⁴⁴Nd of BHVO-2 and other rock standards analysed in this study. The average ¹⁴²Nd/¹⁴⁴Nd of JNdi-1 is shown in yellow line with its 2SD as a shaded envelope. Errors on individual data points are 2SE whereas the long term average value of Ames Nd (shown in blue data point) shows 2SD.



Figure 4.15 Plot of ¹⁴²Nd/¹⁴⁴Nd of carbonatites and associated silicate rocks from Amba Dongar. C and S represent carbonate and silicate fractions, respectively, of carbonatite samples. Errors as shown in Figure 4.14.



Figure 4.16 Plot of ¹⁴²Nd/¹⁴⁴Nd of carbonatites and associated silicate alkaline rocks from Sung Valley. C and S represent carbonate and silicate fractions, respectively, of carbonatite samples. Errors as shown in Figure 4.14.



Figure 4.17 Plot of ${}^{142}Nd/{}^{144}Nd$ of carbonatites from Newania. . C and S represent carbonate and silicate fractions, respectively, of carbonatite samples. Errors as shown in Figure 4.14.



Figure 4.18 Plot of ¹⁴²Nd/¹⁴⁴Nd of alkali basalts from Phenai Mata Complex, Kimberlites from Eastern Dharwar Craton and nepheline synite from Kishengarh. Errors as shown in Figure 4.14.



Figure 4.19 Plot of ¹⁴²Nd/¹⁴⁴Nd of TTGs from Singhbhum Craton and granitoids of BGC-1 from Aravalli Craton. Errors as in Figure 4.14.



Figure 4.20 Schematic illustration of the results obtained for ¹⁴²Nd study of Indian rocks. Grey shaded area shows the external reproducibility (7.2 ppm) for JNdi-1 analysed by us, representing the modern accessible mantle devoid of any early differentiation signatures. Orange arrows show mixing of EDR and EER. Evolution of EDR and EER are from Rizo et al. (2012).

Tables

Table 4.1

Nd isotopic ratios of AMES standard analysed during the course of our experiment.

(a) Data for three sequence method – corrected for fractionation using power law normalised exponential law

Sr. No	¹⁴² Nd/ ¹⁴⁴ Nd	u ¹⁴² Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	¹⁴⁵ Nd/ ¹⁴⁴ Nd	u ¹⁴⁵ Nd	¹⁴⁸ Nd/ ¹⁴⁴ Nd	u ¹⁴⁸ Nd	150 NJ /144 NJ	"120 Md	Av.Fr.Rate
51. 140.	inu/ inu	μινα	inu/ inu	INU/ INU	μινα	inu/ inu	μινα	inu/ inu	μινα	(ppm/s)
1	1.1418373 (56)	-0.2	0.5119596 (18)	0.3484052 (12)	4.3	0.2415821 (16)	9.9	0.2364556 (18)	12.7	0.05
2	1.1418373 (90)	-0.1	0.5119586 (30)	0.3484037 (20)	0.0	0.2415791 (26)	-2.5	0.2364587 (30)	25.8	0.10
3	1.1418332 (56)	-3.8	0.5119581 (18)	0.3484045 (12)	2.3	0.2415805 (16)	3.3	0.2364532 (18)	2.5	0.06
4	1.1418288 (58)	-7.6	0.5119594 (20)	0.3484034 (12)	-0.9	0.2415802 (16)	2.1	0.2364631 (18)	44.4	0.10
5	1.1418426 (48)	4.5	0.5119590 (16)	0.3484032 (10)	-1.4	0.2415765 (14)	-13.2	0.2364502 (16)	-10.2	0.08
6	1.1418393 (64)	1.6	0.5119611 (20)	0.3484046 (14)	2.6	0.2415794 (18)	-1.2	0.2364504 (20)	- 9.3	0.04
7	1.1418417 (56)	3.7	0.5119596 (18)	0.3484035 (12)	-0.6	0.2415795 (16)	-0.8	0.2364488 (18)	-16.1	0.04
8	1.1418311 (48)	-5.6	0.5119591 (16)	0.3484044 (10)	2.0	0.2415799 (14)	0.8	0.2364493 (16)	-14.0	0.03
9	1.1418370 (64)	-0.4	0.5119588 (22)	0.3484020 (14)	-4.9	0.2415808 (20)	4.6	0.2364560 (20)	14.4	0.09
10	1.1418376 (44)	0.1	0.5119582 (14)	0.3484044 (10)	2.0	0.2415801 (14)	1.7	0.2364518 (14)	- 3.4	0.06
11	1.1418405 (46)	2.6	0.5119574 (16)	0.3484033 (10)	-1.1	0.2415788 (16)	-3.7	0.2364509 (16)	- 7.2	0.05
12	1.1418363 (44)	-1.1	0.5119587 (14)	0.3484044 (10)	2.0	0.2415796 (14)	-0.4	0.2364525 (14)	- 0.4	0.05
13	1.1418365 (48)	-0.9	0.5119588 (16)	0.3484034 (10)	-0.9	0.2415800 (12)	1.2	0.2364479 (16)	-19.9	0.10
14	1.1418413 (62)	3.3	0.5119572 (18)	0.3484025 (14)	-3.4	0.2415799 (18)	0.8	0.2364491 (20)	-14.8	0.05
15	1.1418421 (58)	4.0	0.5119568 (18)	0.3484023 (12)	-4.0	0.2415793 (16)	-1.7	0.2364517 (18)	- 3.8	0.04
Average	1.1418375		0.5119587	0.3484037		0.2415797		0.2364526		
2RSD (ppm)	0.0000071		0.0000042	0.0000053		0.0000099		0.0000352		

Sr. No	142NJJ/144NJJ	u ¹⁴² Nd	143NJd/144NJd	145Nd/144Nd	¹⁴⁵ Nd	148NJ/144NJ	¹⁴⁸ Nd	150 NJA /144 NJA	¹⁵⁰ Nd	Av.Fr.Rate
51.110.		μινα	inu/ inu	nu/ nu	μιια	inu/ inu	μιια	inu/ inu	μινα	(ppm/s)
1	1.1418353 (60)	-3.2	0.5119636 (28)	0.3484037 (16)	0.9	0.2415894 (20)	20.3	0.2364629 (27)	44.0	0.01
2	1.1418414 (76)	2.1	0.5119614 (36)	0.3484022 (22)	-3.4	0.2415820 (26)	-10.3	0.2364479 (34)	-19.5	0.02
3	1.1418355 (61)	-3.1	0.5119622 (28)	0.3484031 (19)	-0.9	0.2415821 (21)	-9.9	0.2364494 (27)	-13.1	0.04
4	1.1418374 (54)	-1.4	0.5119639 (26)	0.3484017 (16)	-4.9	0.2415905 (19)	24.8	0.2364600 (25)	31.7	0.004
5	1.1418371 (54)	-1.7	0.5119645 (25)	0.3484051 (16)	4.9	0.2415840 (19)	-2.1	0.2364506 (26)	-8.0	0.03
6	1.1418355 (57)	-3.1	0.5119636 (27)	0.3484038 (17)	1.1	0.2415841 (20)	- 1.7	0.2364507 (26)	-7.6	0.02
7	1.1418330 (69)	-5.3	0.5119669 (32)	0.3484023 (20)	-3.2	0.2415852 (23)	2.9	0.2364515 (32)	-4.2	0.05
8	1.1418388 (57)	-0.2	0.5119662 (28)	0.3484060 (17)	7.5	0.2415833 (19)	- 5.0	0.2364489 (28)	-15.2	0.06
9	1.1418436 (136)	4.0	0.5119671 (64)	0.3484030 (41)	-1.1	0.2415812 (48)	-13.7	0.2364492 (66)	-14.0	0.10
10	1.1418393 (50)	0.3	0.5119649 (24)	0.3484023 (15)	-3.2	0.2415840 (18)	- 2.1	0.2364531 (23)	2.5	0.03
11	1.1418376 (53)	-1.2	0.5119647 (27)	0.3484024 (16)	-2.9	0.2415819 (18)	-10.8	0.2364493 (24)	-13.5	0.06
12	1.1418426 (56)	3.2	0.5119643 (26)	0.3484042 (16)	2.3	0.2415815 (19)	-12.4	0.2364494 (24)	-13.1	0.09
13	1.1418364 (50)	-2.3	0.5119634 (26)	0.3484050 (14)	4.6	0.2415889 (18)	18.2	0.2364620 (23)	40.2	0.05
14	1.1418334 (52)	-4.9	0.5119649 (23)	0.3484025 (15)	-2.6	0.2415882 (17)	15.3	0.2364598 (24)	30.9	0.06
15	1.1418460 (54)	6.1	0.5119666 (26)	0.3484036 (16)	0.6	0.2415842 (19)	-1.2	0.2364492 (25)	-14.0	0.10
16	1.1418486 (58)	8.4	0.5119664 (27)	0.3484064 (17)	8.6	0.2415833(20)	-5.0	0.2364496 (27)	-12.3	0.03
17	1.1418320 (46)	-6.1	0.5119624 (20)	0.3484011 (13)	-6.6	0.2415842 (15)	-1.2	0.2364496 (20)	-12.3	0.10
18	1.1418482 (52)	8.1	0.5119675 (25)	0.3484026 (16)	-2.3	0.2415833 (18)	-5.0	0.2364520 (23)	-2.1	0.10
Average	1.1418390		0.5119647	0.3484034		0.2415845		0.2364525		
2RSD (ppm)	0.0000089		0.0000070	0.0000085		0.0000235		0.0000420		

(b) Data for two sequence method – corrected for fractionation using simple exponential law

Table 4.2

Nd isotopic ratio data for Khariar samples analysed in this work.

Sample ID	Method	¹⁴² Nd/ ¹⁴⁴ Nd	u ¹⁴² Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	¹⁴⁵ Nd/ ¹⁴⁴ Nd	¹⁴⁸ Nd/ ¹⁴⁴ Nd	¹⁵⁰ Nd/ ¹⁴⁴ Nd	¹⁴⁰ Co/ ¹⁴² Nd	Av. Fr. Rate
Sample ID	Witthou	itu/ itu	μιια	nu/ nu	110/ 110	114/ 114	itu/ itu		(ppm/s)
OD-8/1									
(1)	3- sequence	1.1418219 (38)	-13.7	0.5116305 (12)	0.3484050 (09)	0.2415817 (11)	0.2364475 (13)	1.08E-04	0.02
(2)	3- sequence	1.1418311 (41)	- 5.6	0.5116324 (146)	0.3484047 (08)	0.2415802 (11)	0.2364510 (13)	8.31E-05	0.08
Average		1.1418265 (130)	- 9.6	0.5116315 (27)	0.3484049 (04)	0.2415810 (21)	0.2364493 (49)		
(3)	2- sequence	1.1418298 (42)	- 8.1	0.5116386 (19)	0.3484049 (12)	0.2415835 (14)	0.2364485 (19)	9.25E-05	0.05
(4)	2- sequence	1.1418312 (45)	- 6.8	0.5116380 (21)	0.3484037 (13)	0.2415847 (15)	0.2364516 (20)	2.07E-05	0.06
Average		1.1418305 (20)	- 7.4	0.5116383 (8)	0.3484043 (17)	0.2415841 (17)	0.2364501 (44)		
OD-7 /1									
(1)	3- sequence	1.1418272 (41)	- 9.0	0.5116740 (12)	0.3484036 (09)	0.2415803 (12)	0.2364503 (13)	5.47E-05	0.08
(2)	3- sequence	1.1418389 (49)	1.2	0.5116776 (15)	0.3484044 (10)	0.2415799 (15)	0.2364546 (17)	1.25E-05	0.06
Average		1.1418331 (165)	- 3.9	0.5116758 (51)	0.3484040 (11)	0.2415801 (06)	0.2364525 (61)		
(3)	2- sequence	1.1418304 (41)	- 7.5	0.5116803 (19)	0.3484049 (11)	0.2415828 (14)	0.2364504 (19)	3.56E-05	0.10
(4)	2- sequence	1.1418322 (47)	- 6.0	0.5116812 (21)	0.3484066 (14)	0.2415869 (16)	0.2364559 (23)	3.29E-05	0.07
Average		1.1418313 (25)	- 6.7	0.5116808 (13)	0.3484058 (24)	0.2415849 (58)	0.2364532 (78)		
OD-6/1									
(1)	3- sequence	1.1418226 (57)	-13.0	0.5116595 (18)	0.3484044 (12)	0.2415815 (16)	0.2364463 (19)	8.28E-05	0.01
(2)	3- sequence	1.1418309 (45)	- 5.8	0.5116573 (14)	0.3484044 (10)	0.2415809 (12)	0.2364554 (14)	6.76E-05	0.02
Average		1.1418268 (117)	- 9.4	0.5116584 (31)	0.3484044 (0)	0.2415812 (08)	0.2364509 (129)		
(3)	2- sequence	1.1418290 (40)	- 8.8	0.5116601 (20)	0.3484056 (11)	0.2415811 (13)	0.2364488 (18)	5.98E-05	0.10
(4)	2- sequence	1.1418382 (41)	- 0.7	0.5116611 (17)	0.3484064 (11)	0.2415876 (14)	0.2364583 (18)	7.68E-05	0.02

Average		1.1418336 (130)	- 4.7	0.5116606 (14)	0.3484060 (11)	0.2415844 (92)	0.2364536 (134)		
OD-3/3									
(1)	3- sequence	1.1418269 (40)	- 9.3	0.5115282 (11)	0.3484051 (08)	0.2415813 (11)	0.2364546 (13)	6.48E-05	0.02
(4)	3- sequence	1.1418239 (37)	-11.9	0.5115335 (11)	0.3484048 (07)	0.2415809 (11)	0.2364506 (12)	1.20E-05	0.02
Average		1.1418254 (42)	-10.6	0.5115309 (75)	0.3484050 (04)	0.2415811 (06)	0.2364526 (57)		
(2)	2- sequence	1.1418311 (43)	- 6.9	0.5115413 (19)	0.3484050 (12)	0.2415877 (15)	0.2364580 (20)	8.09E-05	0.01
(3)	2- sequence	1.1418332 (39)	- 5.1	0.5115408 (19)	0.3484023 (12)	0.2415853 (15)	0.2364546 (18)	2.13E-05	0.08
Average		1.1418322 (30)	- 6.0	0.5115411 (07)	0.3484037 (38)	0.2415865 (34)	0.2364563 (48)		
BHVO-2									
(A)	3-sequence	1.1418246 (52)	-11.3	0.5129695 (16)	0.3484046 (12)	0.2415814 (15)	0.2364523 (17)	7.60E-05	0.08
(C)	3-sequence	1.1418444 (57)	6.0	0.5129723(19)	0.3484034(13)	0.2415797(17)	0.2364513(18)	1.79E-05	0.04
Average		1.1418345(279)	- 2.6	0.5129709(39)	0.3484040(18)	0.2415805(24)	0.2364518(14)		
(B)	2- sequence	1.1418365(49)	- 2.2	0.5129762(21)	0.3484053(13)	0.2415834(16)	0.2364470(22)	1.49E-04	0.07
(B)-2	2- sequence	1.1418339(42)	- 4.5	0.5129732(19)	0.3484057(13)	0.2415858(14)	0.2364533(19)	2.70E-05	0.08
(C)-2	2- sequence	1.1418403(45)	1.1	0.5129763(20)	0.3484036(12)	0.2415841(15)	0.2364526(20)	6.80E-05	0.20
Average		1.1418369(64)	- 1.8	0.5129753(35)	0.3484049(22)	0.2415844(24)	0.2364510(69)		

Note: 3-sequence and 2-sequence μ^{142} Nd values were determined using AMES Nd standard ¹⁴²Nd/¹⁴⁴Nd of 1.1418375 and 1.4148390, respectively. It should be noted that the 3-sequence data have been corrected for mass fractionation using a power- normalized exponential law, whereas that of 2-sequence using exponential law. The internal precision (2SE) is given in parentheses. For average values, 2 standard-deviations (2SD) are given in the parentheses. Av. Fr. Rate = Average Fractionate Rate = slope of the linear regression in a plot of ¹⁴⁶Nd/¹⁴⁴Nd from the first sequence versus time.

Sr No	¹⁴² Nd/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	¹⁴⁵ Nd/ ¹⁴⁴ Nd	¹⁴⁸ Nd/ ¹⁴⁴ Nd	¹⁵⁰ Nd/ ¹⁴⁴ Nd	Avg fr. Rate
51.100	itu/ itu	(ppm/sec)				
1.	1.1418364 (57)	0.5119585 (19)	0.3484036 (14)	0.2415805 (17)	0.2364642 (21)	0.04
2.	1.1418353 (57)	0.5119602 (18)	0.3484050 (14)	0.2415812 (18)	0.2364567 (20)	0.06
3.	1.1418436 (54)	0.5119586 (19)	0.3484047 (13)	0.2415826 (17)	0.2364610 (20)	0.01
4.	1.1418401 (57)	0.5119617 (20)	0.3484034 (13)	0.2415802 (18)	0.2364599 (20)	0.01
5.	1.1418439 (64)	0.5119609 (24)	0.3484030 (15)	0.2415792 (20)	0.2364560 (21)	0.01
6.	1.1418309 (62)	0.5119582 (21)	0.3484041 (14)	0.2415819 (17)	0.2364640 (22)	0.02
7.	1.1418408 (55)	0.5119606 (20)	0.3484054 (13)	0.2415821 (18)	0.2364562 (20)	0.02
8.	1.1418401 (56)	0.5119597 (20)	0.3484029 (14)	0.2415789 (18)	0.2364560 (23)	0.07
9.	1.1418438 (64)	0.5119606 (22)	0.3484041 (14)	0.2415807 (18)	0.2364633 (21)	0.01
10.	1.1418332 (58)	0.5119592 (25)	0.3484046 (13)	0.2415807 (17)	0.2364607 (20)	0.04
11.	1.1418353 (72)	0.5119583 (25)	0.3484045 (15)	0.2415805 (21)	0.2364609 (25)	0.01
12.	1.1418322 (58)	0.5119576 (20)	0.3484039 (14)	0.2415817 (17)	0.2364600 (23)	0.02
13.	1.1418335 (61)	0.5119602 (18)	0.3484047 (13)	0.2415794 (17)	0.2364547 (21)	0.09
14.	1.1418368 (51)	0.5119605 (16)	0.3484055 (11)	0.2415793 (15)	0.2364594 (17)	0.04
15.	1.1418256 (59)	0.5119568 (18)	0.3484050 (13)	0.2415812 (19)	0.2364633 (19)	0.07
16.	1.1418340 (59)	0.5119576 (21)	0.3484039 (13)	0.2415778 (17)	0.2364596 (20)	0.04
17.	1.1418283 (57)	0.5119586 (20)	0.3484026 (13)	0.2415793 (19)	0.2364554 (21)	0.10
18.	1.1418426 (58)	0.5119589 (20)	0.3484039 (13)	0.2415779 (17)	0.2364552 (19)	0.04
19.	1.1418383 (60)	0.5119591 (19)	0.3484033 (14)	0.2415802 (17)	0.2364546 (21)	0.04
20.	1.1418245 (52)	0.5119559 (18)	0.3484042 (14)	0.2415826 (17)	0.2364624 (19)	0.03
21.	1.1418357 (57)	0.5119575 (16)	0.3484053 (12)	0.2415808 (16)	0.2364574 (18)	0.03
22.	1.1418323 (54)	0.5119574 (18)	0.3484043 (11)	0.2415812 (17)	0.2364623 (19)	0.05

Table 4.3 Nd isotope ratios of Ames Nd analysed using 3-sequence method.

(a)

23.	1.1418278 (58)	0.5119566 (17)	0.3484042 (12)	0.2415815 (17)	0.2364597 (19)	0.03
24.	1.1418455 (60)	0.5119597 (21)	0.3484032 (13)	0.2415802 (19)	0.2364581 (22)	0.02
25.	1.1418474 (73)	0.5119601 (25)	0.3484029 (16)	0.2415798 (21)	0.2364537 (24)	0.05
26.	1.1418415 (62)	0.5119604 (20)	0.3484043 (13)	0.2415799 (19)	0.2364571 (22)	0.04
27.	1.1418369 (62)	0.5119605 (20)	0.3484032 (14)	0.2415779 (18)	0.2364579 (21)	0.07
28.	1.1418353 (62)	0.5119586 (21)	0.3484031 (14)	0.2415807 (19)	0.2364602 (21)	0.05
29.	1.1418386 (62)	0.5119579 (19)	0.3484040 (14)	0.2415798 (18)	0.2364594 (21)	0.02
30.	1.1418289 (60)	0.5119587 (21)	0.3484036 (14)	0.2415816 (18)	0.2364623 (24)	0.02
31.	1.1418444 (49)	0.5119603 (17)	0.3484034 (10)	0.2415789 (14)	0.2364565 (16)	0.05
32.	1.1418401 (58)	0.5119570 (19)	0.3484030 (13)	0.2415783 (17)	0.2364571 (20)	0.03
33.	1.1418432 (67)	0.5119576 (21)	0.3484024 (13)	0.2415796 (19)	0.2364572 (22)	0.01
34.	1.1418290 (67)	0.5119578 (17)	0.3484042 (10)	0.2415750 (17)	0.2364511 (22)	0.20
35.	1.1418385 (46)	0.5119582 (14)	0.3484030 (10)	0.2415805 (13)	0.2364560 (14)	0.05
36.	1.1418501 (47)	0.5119611 (15)	0.3484035 (09)	0.2415777 (13)	0.2364526 (15)	0.08
37.	1.1418362 (49)	0.5119605 (17)	0.3484043 (11)	0.2415805 (15)	0.2364631 (18)	0.02
38.	1.1418339 (45)	0.5119591 (15)	0.3484036 (10)	0.2415783 (13)	0.2364537 (14)	0.07
39.	1.1418407 (38)	0.5119601 (12)	0.3484035 (08)	0.2415791 (12)	0.2364573 (13)	0.05
40.	1.1418361 (41)	0.5119578 (13)	0.3484037 (09)	0.2415797 (12)	0.2364532 (14)	0.07
41.	1.1418415 (52)	0.5119588 (16)	0.3484025 (11)	0.2415787 (15)	0.2364511 (18)	0.10
42.	1.1418310 (48)	0.5119576 (14)	0.3484032 (10)	0.2415803 (13)	0.2364535 (15)	0.06
43.	1.1418271 (34)	0.5119586 (13)	0.3484048 (08)	0.2415772 (11)	0.2364580 (13)	0.20
44.	1.1418384 (40)	0.5119590 (13)	0.3484036 (09)	0.2415795 (12)	0.2364562 (13)	0.07
45.	1.1418333 (45)	0.5119581 (14)	0.3484039 (10)	0.2415776 (14)	0.2364523 (16)	0.10
46.	1.1418384 (46)	0.5119590 (14)	0.3484047 (09)	0.2415799 (13)	0.2364582 (15)	0.03
47.	1.1418463 (51)	0.5119598 (15)	0.3484044 (09)	0.2415783 (14)	0.2364529 (16)	0.08
48.	1.1418388 (56)	0.5119612 (16)	0.3484034 (11)	0.2415783 (14)	0.2364530 (16)	0.05

49.	1.1418398 (46)	0.5119599 (15)	0.3484045 (11)	0.2415785 (13)	0.2364510 (15)	0.09
50.	1.1418332 (43)	0.5119586 (14)	0.3484050 (10)	0.2415801 (14)	0.2364581 (15)	0.06
51.	1.1418409 (39)	0.5119608 (12)	0.3484037 (08)	0.2415803 (12)	0.2364557 (13)	0.04
52.	1.1418428 (45)	0.5119611 (14)	0.3484034 (09)	0.2415794 (13)	0.2364622 (15)	0.02
53.	1.1418374 (90)	0.5119586 (30)	0.3484037 (20)	0.2415791 (26)	0.2364587 (30)	0.10
54.	1.1418288 (57)	0.5119594 (19)	0.3484034 (12)	0.2415802 (16)	0.2364631 (18)	0.10
55.	1.1418426 (47)	0.5119590 (15)	0.3484032 (11)	0.2415765 (14)	0.2364502 (15)	0.08
56.	1.1418393 (64)	0.5119611 (19)	0.3484046 (14)	0.2415794 (18)	0.2364504 (20)	0.04
57.	1.1418373 (57)	0.5119596 (18)	0.3484052 (13)	0.2415821 (17)	0.2364556 (18)	0.05
58.	1.1418332 (55)	0.5119581 (17)	0.3484045 (12)	0.2415805 (16)	0.2364532 (17)	0.06
59.	1.1418370 (65)	0.5119588 (22)	0.3484020 (14)	0.2415808 (19)	0.2364560 (21)	0.09
60.	1.1418376 (45)	0.5119582 (13)	0.3484044 (09)	0.2415801 (13)	0.2364518 (15)	0.06
61.	1.1418363 (44)	0.5119587 (15)	0.3484044 (10)	0.2415796 (14)	0.2364525 (14)	0.05
62.	1.1418413 (62)	0.5119572 (18)	0.3484025 (14)	0.2415799 (17)	0.2364491 (20)	0.05
63.	1.1418405 (47)	0.5119574 (16)	0.3484033 (11)	0.2415788 (15)	0.2364509 (16)	0.05
64.	1.1418421 (58)	0.5119568 (18)	0.3484023 (12)	0.2415793 (16)	0.2364517 (19)	0.04
65.	1.1418365 (48)	0.5119588 (15)	0.3484034 (10)	0.2415800 (12)	0.2364479 (15)	0.10
66.	1.1418311 (48)	0.5119591 (15)	0.3484044 (11)	0.2415799 (15)	0.2364493 (17)	0.03
67.	1.1418417 (55)	0.5119596 (17)	0.3484035 (11)	0.2415795 (15)	0.2364488 (18)	0.04
Average	1.1418372	0.5119590	0.3484038	0.2415797	0.2364564	
2SD	0.0000109	0.0000026	0.0000016	0.0000028	0.0000085	
2RSD (ppm)	0.0000096	0.0000051	0.0000046	0.0000117	0.0000360	

Data is corrected for mass fractionation using (a) a power-normalised exponential law. 2SE associated with each measurement is given in the parentheses. Average fractionation rate (calculated as explained in the main text) is given.

Sr. No.	¹⁴² Nd/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	¹⁴⁵ Nd/ ¹⁴⁴ Nd	¹⁴⁸ Nd/ ¹⁴⁴ Nd	¹⁵⁰ Nd/ ¹⁴⁴ Nd
1.	1.1418370 (57)	0.5119509 (28)	0.3484040 (18)	0.2415853 (20)	0.2364613 (27)
2.	1.1418356 (57)	0.5119518 (29)	0.3484024 (19)	0.2415839 (21)	0.2364569 (29)
3.	1.1418467 (54)	0.5119553 (26)	0.3484024 (17)	0.2415839 (20)	0.2364577 (27)
4.	1.1418410 (58)	0.5119504 (28)	0.3484027 (19)	0.2415822 (21)	0.2364546 (27)
5.	1.1418463 (64)	0.5119573 (29)	0.3484023 (20)	0.2415795 (24)	0.2364554 (28)
6.	1.1418317 (62)	0.5119536 (27)	0.3484038 (17)	0.2415866 (20)	0.2364614 (25)
7.	1.1418425 (56)	0.5119571 (27)	0.3484028 (17)	0.2415822 (20)	0.2364542 (26)
8.	1.1418412 (56)	0.5119524 (26)	0.3484032 (20)	0.2415808 (21)	0.2364547 (26)
9.	1.1418438 (63)	0.5119581 (28)	0.3484031 (18)	0.2415839 (21)	0.2364593 (28)
10.	1.1418347 (58)	0.5119542 (24)	0.3484043 (16)	0.2415854 (19)	0.2364589 (26)
11.	1.1418368 (72)	0.5119576 (36)	0.3484054 (21)	0.2415817 (24)	0.2364576 (32)
12.	1.1418349 (58)	0.5119545 (28)	0.3484036 (17)	0.2415863 (19)	0.2364595 (28)
13.	1.1418337 (62)	0.5119571 (26)	0.3484032 (18)	0.2415843 (20)	0.2364567 (29)
14.	1.1418391 (51)	0.5119585 (24)	0.3484064 (15)	0.2415827 (18)	0.2364565 (24)
15.	1.1418276 (59)	0.5119560 (28)	0.3484062 (18)	0.2415873 (21)	0.2364632 (27)
16.	1.1418351 (60)	0.5119592 (27)	0.3484063 (17)	0.2415826 (20)	0.2364581 (27)
17.	1.1418278 (57)	0.5119577 (27)	0.3484047 (19)	0.2415816 (20)	0.2364534 (26)
18.	1.1418442 (58)	0.5119598 (26)	0.3484049 (18)	0.2415802 (19)	0.2364537 (25)
19.	1.1418396 (60)	0.5119571 (28)	0.3484047 (18)	0.2415828 (19)	0.2364526 (27)
20.	1.1418273 (52)	0.5119568 (25)	0.3484062 (17)	0.2415874 (18)	0.2364632 (24)
21.	1.1418393 (57)	0.5119561 (26)	0.3484064 (16)	0.2415849 (20)	0.2364577 (25)

22.	1.1418338 (55)	0.5119574 (22)	0.3484087 (15)	0.2415897 (17)	0.2364641 (24)
23.	1.1418304 (58)	0.5119571 (26)	0.3484086 (16)	0.2415882 (20)	0.2364595 (27)
24.	1.1418458 (60)	0.5119614 (26)	0.3484057 (19)	0.2415819 (21)	0.2364540 (28)
25.	1.1418471 (74)	0.5119581 (36)	0.3484048 (20)	0.2415807 (26)	0.2364532 (34)
26.	1.1418425 (62)	0.5119591 (29)	0.3484045 (19)	0.2415831 (22)	0.2364564 (31)
27.	1.1418358 (62)	0.5119625 (29)	0.3484071 (18)	0.2415825 (21)	0.2364568 (28)
28.	1.1418350 (62)	0.5119604 (27)	0.3484088 (19)	0.2415880 (23)	0.2364600 (28)
29.	1.1418392 (63)	0.5119659 (28)	0.3484077 (17)	0.2415872 (21)	0.2364606 (29)
30.	1.1418282 (60)	0.5119626 (28)	0.3484097 (17)	0.2415881 (21)	0.2364612 (27)
31.	1.1418432 (49)	0.5119598 (23)	0.3484077 (14)	0.2415844 (16)	0.2364563 (21)
32.	1.1418395 (58)	0.5119633 (27)	0.3484065 (18)	0.2415842 (20)	0.2364557 (28)
33.	1.1418421 (67)	0.5119609 (31)	0.3484033 (19)	0.2415801 (21)	0.2364537 (28)
34.	1.1418249 (68)	0.5119637 (20)	0.3484072 (12)	0.2415854 (14)	0.2364572 (20)
35.	1.1418369 (46)	0.5119632 (19)	0.3484063 (13)	0.2415833 (15)	0.2364542 (19)
36.	1.1418490 (47)	0.5119631 (21)	0.3484049 (12)	0.2415793 (16)	0.2364508 (20)
37.	1.1418364 (50)	0.5119615 (23)	0.3484082 (15)	0.2415893 (17)	0.2364648 (22)
38.	1.1418406 (38)	0.5119649 (18)	0.3484069 (11)	0.2415865 (13)	0.2364582 (18)
39.	1.1418360 (41)	0.5119654 (20)	0.3484059 (12)	0.2415823 (14)	0.2364520 (20)
40.	1.1418397 (52)	0.5119655 (24)	0.3484077 (14)	0.2415811 (16)	0.2364498 (22)
41.	1.1418314 (49)	0.5119644 (22)	0.3484062 (13)	0.2415862 (16)	0.2364551 (21)
42.	1.1418256 (34)	0.5119612 (16)	0.3484098 (09)	0.2415884 (11)	0.2364615 (15)
43.	1.1418378 (40)	0.5119633 (19)	0.3484071 (12)	0.2415878 (13)	0.2364593 (18)
44.	1.1418305 (45)	0.5119632 (22)	0.3484067 (14)	0.2415857 (17)	0.2364555 (22)
45.	1.1418372 (46)	0.5119634 (22)	0.3484057 (13)	0.2415872 (14)	0.2364597 (20)

46.	1.1418437 (51)	0.5119652 (21)	0.3484066 (13)	0.2415829 (16)	0.2364522 (21)
47.	1.1418361 (56)	0.5119654 (23)	0.3484059 (14)	0.2415842 (16)	0.2364546 (21)
48.	1.1418384 (46)	0.5119683 (22)	0.3484062 (13)	0.2415840 (16)	0.2364516 (21)
49.	1.1418329 (43)	0.5119622 (21)	0.3484076 (14)	0.2415904 (17)	0.2364629 (22)
50.	1.1418421 (39)	0.5119638 (18)	0.3484053 (12)	0.2415858 (14)	0.2364573 (19)
51.	1.1418411 (45)	0.5119628 (21)	0.3484077 (12)	0.2415915 (14)	0.2364675 (20)
52.	1.1418346 (90)	0.5119618 (40)	0.3484070 (28)	0.2415914 (30)	0.2364627 (40)
53.	1.1418289 (57)	0.5119598 (26)	0.3484083 (17)	0.2415914 (18)	0.2364651 (26)
54.	1.1418430 (47)	0.5119633 (21)	0.3484042 (14)	0.2415787 (16)	0.2364502 (22)
55.	1.1418393 (64)	0.5119661 (28)	0.3484042 (19)	0.2415867 (21)	0.2364548 (28)
56.	1.1418378 (57)	0.5119680 (25)	0.3484080 (17)	0.2415898 (19)	0.2364621 (26)
57.	1.1418339 (55)	0.5119639 (25)	0.3484049 (17)	0.2415842 (18)	0.2364543 (25)
58.	1.1418361 (65)	0.5119673 (31)	0.3484012 (19)	0.2415891 (23)	0.2364597 (29)
59.	1.1418383 (45)	0.5119645 (20)	0.3484043 (13)	0.2415850 (14)	0.2364535 (20)
60.	1.1418380 (44)	0.5119674 (22)	0.3484040 (13)	0.2415839 (16)	0.2364528 (20)
61.	1.1418421 (63)	0.5119669 (29)	0.3484038 (18)	0.2415795 (20)	0.2364458 (26)
62.	1.1418403 (47)	0.5119666 (24)	0.3484044 (15)	0.2415824 (18)	0.2364508 (23)
63.	1.1418402 (58)	0.5119648 (27)	0.3484044 (17)	0.2415837 (19)	0.2364522 (26)
64.	1.1418370 (49)	0.5119645 (21)	0.3484031 (14)	0.2415816 (16)	0.2364476 (22)
65.	1.1418324 (48)	0.5119639 (22)	0.3484020 (15)	0.2415856 (17)	0.2364543 (23)
66.	1.1418437 (55)	0.5119667 (25)	0.3484021 (16)	0.2415808 (18)	0.2364491 (25)
Average	1.1418374	0.5119610	0.3484055	0.2415847	0.2364566
2SD	0.0000109	0.0000089	0.0000041	0.0000064	0.0000089
2RSD (ppm)	0.0000095	0.0000174	0.0000117	0.0000265	0.0000377
1					

Data is corrected for mass fractionation using (b) an exponential law. 2SE associated with each measurement is given in the parentheses.

Table 4.4

Neodymium isotopic ratios of JNdi-1 and Ames analysed with JNdi-1.

(a)

Sample ID	¹⁴² Nd/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	¹⁴⁵ Nd/ ¹⁴⁴ Nd	¹⁴⁸ Nd/ ¹⁴⁴ Nd	¹⁵⁰ Nd/ ¹⁴⁴ Nd
JNdi-1					
091116	1.1418241 (49)	0.5120979 (17)	0.3484048 (11)	0.2415805 (16)	0.2364540 (19)
111116	1.1418328 (52)	0.5120989 (15)	0.3484037 (12)	0.2415789 (16)	0.2364452 (17)
131116	1.1418327 (54)	0.5121015 (16)	0.3484033 (12)	0.2415806 (16)	0.2364483 (17)
181116	1.1418313 (57)	0.5120997 (18)	0.3484048 (12)	0.2415809 (16)	0.2364513 (17)
191116	1.1418259 (53)	0.5120983 (17)	0.3484047 (11)	0.2415805 (15)	0.2364465 (18)
211116	1.1418377 (54)	0.5121003 (17)	0.3484050 (12)	0.2415792 (16)	0.2364503 (19)
181116	1.1418274 (48)	0.5120976 (15)	0.3484058 (12)	0.2415817 (14)	0.2364501 (17)
211116	1.1418328 (58)	0.5121000 (19)	0.3484044 (12)	0.2415818 (16)	0.2364546 (19)
101116	1.1418272 (52)	0.5120997 (17)	0.3484051 (10)	0.2415796 (15)	0.2364496 (16)
091116	1.1418300 (67)	0.5121006 (23)	0.3484047 (15)	0.2415799 (20)	0.2364483 (22)
221116	1.1418349 (69)	0.5121019 (21)	0.3484047 (14)	0.2415814 (19)	0.2364554 (23)
Average	1.1418306	0.5120997	0.3484046	0.2415805	0.2364503
2SD	0.0000082	0.0000028	0.0000013	0.0000020	0.0000066
Ames Nd					
081116	1.1418269 (54)	0.5119586 (17)	0.3484044 (14)	0.2415819 (17)	0.2364496 (17)
081116	1.1418324 (58)	0.5119571 (18)	0.3484036 (12)	0.2415801 (16)	0.2364490 (18)
101116	1.1418378 (45)	0.5119625 (14)	0.3484052 (11)	0.2415800 (14)	0.2364475 (16)

111116	1.1418339 (51)	0.5119573 (15)	0.3484045 (10)	0.2415816 (14)	0.2364491 (16)
141116	1.1418348 (51)	0.5119585 (17)	0.3484034 (11)	0.2415775 (16)	0.2364435 (17)
141116	1.1418460 (51)	0.5119606 (17)	0.3484039 (11)	0.2415784 (17)	0.2364524 (18)
Average	1.1418353	0.5119591	0.3484042	0.2415799	0.2364485
2SD	0.0000127	0.0000042	0.0000013	0.0000035	0.0000059

The data is acquired using three sequence multi dynamic mode and corrected for the fractionation using power-normalised exponential law (normalised to $^{146}Nd/^{144}Nd = 0.7219$). Internal precision is given in brackets (2SE). For average values, 2standard deviation (2SD) is given.

(b) Data used for cross-calibration of 142 Nd/ 144 Nd of JNdi-1 and Ames Nd.

Sr. No.	(¹⁴² Nd/ ¹⁴⁴ Nd) JNdi-1	(¹⁴² Nd/ ¹⁴⁴ Nd) AMES
1.	1.1418241	1.1418297
2.	1.1418300	1.1418351
3.	1.1418272	1.1418359
4.	1.1418328	1.1418400
5.	1.1418327	1.1418404

The values of Ames Nd are the average value calculated before and after the measurements of JNdi-1, from single batch.

Semale ID	142n. J /144n. J	143nt J /144nt J	145nt J /144nt J	148nta/144nta	150 N.J. /144 N.J.	¹⁴⁰ Ce/ ¹⁴² Nd	Av. Fr. Rate
Sample ID	INU/ INU	inu/ inu	inu/ inu	INU/ INU	INU/ INU		ppm/s
BHVO-2	1.1418274 (54)	0.5126199 (17)	0.3484062 (12)	0.2415784 (15)	0.2364511 (19)	6.48E-05	0.20
BHVO-2(a)	1.1418178 (53)	0.5129692 (17)	0.3484059 (10)	0.2415775 (14)	0.2364520 (17)	1.01E-04	0.10
BHVO-2(b)	1.1418342 (90)	0.5129701 (26)	0.3484031 (17)	0.2415778 (25)	0.2364501 (31)	7.08E-05	0.20
BHVO-2(A)	1.1418246 (52)	0.5129695 (16)	0.3484046 (12)	0.2415814 (15)	0.2364523 (17)	7.60E-05	0.08
BHVO-2(B)	1.1418328 (42)	0.5129732 (19)	0.3484057 (13)	0.2415858 (14)	0.2364533 (19)	1.49E-04	0.02
BHVO-2(C)	1.1418413 (45)	0.5129763 (20)	0.3484036 (12)	0.2415841 (15)	0.2364526 (20)	6.80E-05	0.20
BHVO-2(B) (2SQ)	1.1418389 (49)	0.5129762 (21)	0.3484053 (13)	0.2415834 (16)	0.2364470 (22)	2.70E-05	0.07
BHVO-2(C)	1.1418444 (57)	0.5129723 (19)	0.3484034 (13)	0.2415797 (17)	0.2364513 (18)	1.79E-05	0.04
BHVO-2(E)	1.1418278 (48)	0.5129699 (15)	0.3484050 (10)	0.2415796 (14)	0.2364488 (15)	1.76E-04	0.07
Average	1.1418321	0.5129330	0.3484048	0.2415809	0.2364509		
2SD	0.0000172	0.0002349	0.0000023	0.0000060	0.0000040		
BCR-2	1.1418224 (99)	0.5129715 (30)	0.3484038 (19)	0.2415887 (30)	0.2364593 (33)	1.36E-04	0.30
JB-1(a)	1.1418319 (56)	0.5127699 (18)	0.3484047 (12)	0.2415807 (17)	0.2364595 (20)	1.32E-04	0.09
JB-3	1.1418400 (57)	0.5130424 (19)	0.3484014 (13)	0.2415774 (17)	0.2364537 (20)	1.27E-04	0.10

Table 4.5 Nd isotopic ratios rock standards analysed during the course of this study.

Sample ID	¹⁴² Nd/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	¹⁴⁵ Nd/ ¹⁴⁴ Nd	¹⁴⁸ Nd/ ¹⁴⁴ Nd	¹⁵⁰ Nd/ ¹⁴⁴ Nd	¹⁴⁰ Ce/ ¹⁴² Nd	Av. Fr. Rate
Sample ID	1147 114	nu, nu	114/ 114	itu, itu	itu/ itu		ppm/s
AD-1-(C)	1.1418325 (48)	0.5123949 (15)	0.3484057 (11)	0.2415817 (14)	0.2364542 (16)	6.22E-05	0.02
AD-8-1(C)	1.1418287 (49)	0.5124947 (15)	0.3484060 (12)	0.2415818 (16)	0.2364524 (18)	3.48E-05	0.03
AD-10/1(C)	1.1418261 (46)	0.5125085 (15)	0.3484067 (10)	0.2415812 (14)	0.2364567 (16)	3.35E-05	0.07
AD-13/1 (C)	1.1418353 (52)	0.5124610 (16)	0.3484056 (11)	0.2415787 (15)	0.2364473 (16)	3.77E-04	0.04
AD-13/1(T)(C)	1.1418282 (47)	0.5124573 (16)	0.3484033 (11)	0.2415805 (14)	0.2364614 (17)	9.18E-07	0.03
Average	1.1418318	0.5124592	0.3484045	0.2415796	0.2364544		
2SD	0.0000100	0.0000052	0.0000033	0.0000025	0.0000199		
AD-13/1(S)	1.1418287 (47)	0.5124590 (14)	0.3484059 (10)	0.2415771 (13)	0.2364458 (15)	5.78E-05	0.30
AD-13/1(T)(S)	1.1418349 (54)	0.5124593 (17)	0.3484036 (10)	0.2415801 (14)	0.2364589 (17)	5.89E-05	0.03
Average	1.1418318	0.5124592	0.3484048	0.2415786	0.2364524		
2SD	0.0000088	0.0000004	0.0000033	0.0000042	0.0000185		
AD-14	1.1418347 (106)	0.5124342 (34)	0.3484015 (21)	0.2415754 (33)	0.2364575 (35)	5.04E-05	0.30
AD-14(3)	1.1418259 (45)	0.5124363 (21)	0.3484030 (13)	0.2415860 (16)	0.2364554 (20)	7.00E-05	0.05
AD-14(4)	1.1418300 (35)	0.5124341 (11)	0.3484042 (07)	0.2415795 (10)	0.2364512 (11)	2.26E-05	0.08
Average	1.1418302	0.5124349	0.3484029	0.2415803	0.2364547		
2SD	0.0000088	0.0000025	0.0000027	0.0000107	0.0000064		

Table 4.6 Nd isotopic ratios of rocks (carbonatites and associated alkaline silicate rocks) analysed from Amba Dongar, Gujarat.

	Р	age	94

AD-16	1.1418332 (57)	0.5124132 (19)	0.3484057 (12)	0.2415791 (17)	0.2364538 (18)	1.58E-04	0.07
AD-17	1.1418226 (56)	0.5123637 (19)	0.3484060 (11)	0.2415813 (17)	0.2364604 (18)	5.74E-05	0.06
AD-17	1.1418266 (51)	0.5124361 (14)	0.3484042 (10)	0.2415796 (14)	0.2364526 (16)	2.81E-05	0.04
Average	1.1418246	0.5123999	0.3484051	0.2415805	0.2364565		
2SD	0.0000057	0.0001024	0.0000025	0.0000024	0.0000110		
AD- 21(T)(C)	1.1418346 (45)	0.5124957 (14)	0.3484041 (10)	0.2415800 (12)	0.2364604 (14)	-5.03E-07	-0.007
AD-21(C)	1.1418416 (33)	0.5124965 (10)	0.3484046 (07)	0.2415810 (10)	0.2364587 (11)	7.56E-06	0.005
Average	1.1418381	0.5124961	0.3484044	0.2415805	0.2364596		
2SD	0.0000099	0.0000011	0.0000007	0.0000014	0.0000024		
AD-21(T)(S)	1.1418403 (53)	0.5124971 (15)	0.3484044 (10)	0.2415800 (15)	0.2364593 (16)	2.67E-05	-0.006
AD-38(C)	1.1418250 (55)	0.5125573 (19)	0.3484051 (13)	0.2415736 (16)	0.2364413 (20)	5.75E-06	0.30
AD-38(S)	1.1418324 (101)	0.5125473 (27)	0.3484060 (18)	0.2415742 (25)	0.2364458 (30)	1.74E-04	0.40
AD-45(C)	1.1418254 (34)	0.5124029 (10)	0.3484052 (07)	0.2415785 (10)	0.2364501 (10)	2.00E-04	0.10
AD-47	1.1418207 (63)	0.5114563 (20)	0.3484045 (12)	0.2415786 (18)	0.2364644 (19)	6.30E-05	0.20
AD-47	1.1418299 (51)	0.5114579 (17)	0.3484049 (12)	0.2415790 (16)	0.2364553 (18)	8.02E-05	0.08
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AD-47(3)	1.1418349 (46)	0.5114614 (21)	0.3484054 (12)	0.2415869 (15)	0.2364559 (20)	4.59E-05	0.20
AD-47(4)	1.1418345 (46)	0.5114537 (14)	0.3484035 (09)	0.2415784 (13)	0.2364536 (15)	8.17E-05	0.10
Average	1.1418300	0.5114573	0.3484046	0.2415807	0.2364573		
2SD	0.0000132	0.0000064	0.0000016	0.0000082	0.0000097		
AD-48	1.1418338 (51)	0.5122114 (15)	0.3484044 (10)	0.2415793 (15)	0.2364600 (16)	5.26E-05	0.06
AD-48(T)-(C)	1.1418196 (47)	0.5122088 (16)	0.3484051 (11)	0.2415790 (13)	0.2364615 (18)	4.52E-05	0.03
AD-48-C(3)	1.1418265 (41)	0.5122872 (21)	0.3484034 (12)	0.2415840 (14)	0.2364526 (20)	4.92E-05	0.07
AD-48-C(4)	1.1418412 (60)	0.5122854 (18)	0.3484023 (12)	0.2415778 (18)	0.2364475 (19)	9.22E-07	0.20
Average	1.1418291	0.5122605	0.3484036	0.2415803	0.2364539		
2SD	0.0000221	0.0000895	0.0000028	0.0000066	0.0000142		
AD-48(T)-(S)	1.1418252 (53)	0.5122049 (17)	0.3484045 (11)	0.2415796 (17)	0.2364644 (17)	1.25E-04	0.06
AD-48(4)	1.1418323 (50)	0.5122960 (23)	0.3484040 (14)	0.2415812 (18)	0.2364458 (23)	3.45E-05	0.20
AD-48(4)	1.1418361 (54)	0.5122927 (19)	0.3484028 (12)	0.2415779 (16)	0.2364472 (18)	4.57E-06	0.05
Average	1.1418312	0.5122645	0.3484038	0.2415796	0.2364525		
2SD	0.0000111	0.0001033	0.0000017	0.0000033	0.0000207		
AD-54	1.1418193 (41)	0.5124838 (14)	0.3484054 (09)	0.2415810 (13)	0.2364534 (15)	2.45E-05	0.03
AD-54-N	1.1418312 (29)	0.5124856 (09)	0.3484050 (06)	0.2415806 (08)	0.2364532 (09)	7.89E-06	0.03
AD-54(N)-(4)	1.1418379 (46)	0.5124952 (22)	0.3484046 (14)	0.2415865 (16)	0.2364570 (20)	2.91E-05	-0.002
AD-54(N)-(4)	1.1418318 (56)	0.5124869 (16)	0.3484024 (11)	0.2415773 (15)	0.2364456 (17)	2.73E-06	0.04
Average	1.1418301	0.5124879	0.3484044	0.2415814	0.2364523		
1							

2SD	0.0000156	0.0000101	0.0000027	0.0000076	0.0000096		
54-S	1.1418451 (48)	0.5124889 (14)	0.3484044 (09)	0.2415802 (14)	0.2364547 (16)	4.25E-06	0.003
AD-54(a)(N)(C)	1.1418295 (43)	0.5124885 (14)	0.3484078 (09)	0.2415757 (13)	0.2364389 (14)	7.65E-05	0.10
AD-54(N)(T)(C)	1.1418270 (43)	0.5124860 (13)	0.3484047 (09)	0.2415796 (12)	0.2364650 (14)	7.94E-07	0.08
AD-54(N)-C(3)	1.1418257 (44)	0.5124912 (21)	0.3484057 (12)	0.2415839 (15)	0.2364486 (19)	1.68E-04	0.02
AD-54(N)-C(4)	1.1418244 (51)	0.5124820 (17)	0.3484057 (11)	0.2415793 (15)	0.2364462 (17)	4.00E-05	0.03
Average	1.1418303	0.5124873	0.3484057	0.2415797	0.2364507		
2SD	0.0000169	0.0000070	0.0000027	0.0000058	0.0000196		
54-R	1.1418337 (60)	0.5124887 (21)	0.3484034 (18)	0.2415847 (22)	0.2364563 (23)	2.58E-04	0.02
AD-54(a)(S)	1.1418138 (106)	0.5124850 (31)	0.3484059 (21)	0.2416062 (29)	0.2364613 (35)	1.92E-04	0.40
AD-54(a) (N) (S)	1.1418132 (55)	0.5124833 (16)	0.3484053 (11)	0.2415794 (16)	0.2364425 (17)	3.93E-05	0.30
AD-54(N)(T)(S)	1.1418262 (39)	0.5124866 (11)	0.3484049 (09)	0.2415810 (12)	0.2364521 (14)	1.59E-05	0.06
Average	1.1418217	0.5124859	0.3484049	0.2415878	0.2364531		
2SD	0.0000200	0.0000046	0.0000021	0.0000249	0.0000160		
AD-65	1.1418244 (56)	0.5124756 (17)	0.3484043 (12)	0.2415786 (16)	0.2364570 (18)	2.73E-05	0.10
AD-66	1.1418368 (57)	0.5124252 (18)	0.3484033 (12)	0.2415790 (15)	0.2364562 (17)	3.71E-05	0.04
AD-67	1.1418281 (55)	0.5123712 (18)	0.3484044 (13)	0.2415778 (17)	0.2364494 (19)	5.09E-05	0.06
AD-69	1.1418249 (54)	0.5126833 (16)	0.3484048 (11)	0.2415811 (17)	0.2364553 (18)	1.14E-04	0.01

AD-72 1.1418263 (54) 0.5123275 (18) 0.3484042 (13) 0.2415791 (16) 0.2364638 (20) 1.67E-04	
	0.10

Table 4.7 Nd isotopic ratios of rocks (carbonatites) analysed from Newania, Rajasthan.

Sampla ID	142 _{Nd} /144 _{Nd}	143 _{Nd} /144 _{Nd}	145 _{Nd} /144 _{Nd}	148NJJ/144NJJ	150NJ/144NJ	$140 C_0 / 142 N_d$	Av. Fr. Rate
Sample ID	INU/ INU	inu/ inu	inu/ inu		inu/ inu	Cer Nu	ppm/s
NW-3(C)	1.1418305 (39)	0.5115192 (12)	0.3484071 (08)	0.2415765 (11)	0.2364512 (13)	1.49E-05	0.10
NW-3(S)	1.1418241 (35)	0.5110260 (12)	0.3484049 (08)	0.2415801 (11)	0.2364500 (12)	3.29E-05	0.03
NW-5(T) (C)	1.1418218 (36)	0.5115806 (10)	0.3484055 (08)	0.2415795 (11)	0.2364622 (12)	6.28E-05	0.01
NW-5C-(2)	1.1418349 (51)	0.5115843 (24)	0.3484005 (14)	0.2415855 (18)	0.2364512 (25)	9.16E-05	0.00
NW-5C-(2)	1.1418259 (53)	0.5115794 (17)	0.3484050 (11)	0.2415807 (15)	0.2364525 (16)	4.39E-05	0.01
Average	1.1418275	0.5115814	0.3484037	0.2415819	0.2364553		
2SD	0.0000134	0.0000051	0.0000055	0.0000063	0.0000120		
NW-5(T)(S)	1.1418218 (36)	0.5113425 (12)	0.3484057 (07)	0.2415803 (11)	0.2364528 (12)	3.02E-05	0.05
NW-5(2)	1.1418261 (61)	0.5112577 (28)	0.3484036 (19)	0.2415815 (23)	0.2364480 (29)	1.02E-04	0.06
NW-5(2)	1.1418425 (49)	0.5112562 (15)	0.3484034 (11)	0.2415803 (14)	0.2364527 (17)	2.09E-05	0.06
Avg	1.1418301	0.5112855	0.3484042	0.2415807	0.2364512		
2SD	0.0000218	0.0000988	0.0000025	0.0000014	0.0000055		

NW-7(C)	1.1418230 (48)	0.5114537 (16)	0.3484048 (11)	0.2415826 (14)	0.2364520 (16)	3.46E-05	0.02
NW-8(C)	1.1418186 (46)	0.5114059 (14)	0.3484056 (09)	0.2415776 (13)	0.2364534 (14)	2.57E-05	0.10
NW-8C-(2)	1.1418271 (48)	0.5114112 (21)	0.3484033 (12)	0.2415857 (15)	0.2364542 (21)	8.95E-05	0.10
NW-8C-(2)	1.1418299 (52)	0.5115785 (16)	0.3484047 (11)	0.2415788 (15)	0.2364512 (17)	2.58E-05	0.01
Avg	1.1418252	0.5114652	0.3484045	0.2415807	0.2364529		
2SD	0.0000118	0.0001963	0.0000023	0.0000087	0.0000031		
NW-17(C)	1.1418269 (44)	0.5116009 (14)	0.3484051 (09)	0.2415793 (13)	0.2364504 (15)	3.20E-05	0.04
NW-25(a)(C)	1.1418284 (38)	0.5115738 (13)	0.3484055 (08)	0.2415798 (11)	0.2364484 (12)	9.00E-05	0.01
NW-29(C)	1.1418351 (46)	0.5115306 (14)	0.3484045 (10)	0.2415821 (13)	0.2364580 (15)	4.20E-05	0.03

Table 4.8 Nd isotopic ratios of rocks (carbonatites and associated alkaline silicate rocks) analysed from Sung-Valley, Meghalaya.

Sample ID	¹⁴² Nd/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	¹⁴⁵ Nd/ ¹⁴⁴ Nd	¹⁴⁸ Nd/ ¹⁴⁴ Nd	¹⁵⁰ Nd/ ¹⁴⁴ Nd	¹⁴⁰ Ce/ ¹⁴² Nd	Av. Fr. Rate ppm/s
SV-1(C)	1.1418309 (46)	0.5126411 (15)	0.3484048 (10)	0.2415789 (13)	0.2364553 (14)	1.66E-05	0.08
SV-4	1.1418216 (56)	0.5126304 (18)	0.3484034 (12)	0.2415791 (17)	0.2364535 (19)	6.89E-05	0.20
SV-4(3)	1.1418246 (35)	0.5126348 (16)	0.3484064 (10)	0.2415873 (12)	0.2364563 (16)	7.01E-05	0.10
SV-4(5)	1.1418315 (50)	0.5126323 (16)	0.3484040 (10)	0.2415796 (14)	0.2364494 (15)	1.30E-04	0.08
SV-4(6)	1.1418311 (41)	0.5126309 (12)	0.3484041 (08)	0.2415783 (11)	0.2364472 (14)	1.32E-04	0.09
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Average	1.1418257	0.5126316	0.3484044	0.2415806	0.2364517		
2SD	0.0000108	0.0000042	0.0000023	0.0000076	0.0000071		
SV-5(C)	1.1418235 (56)	0.5126322 (18)	0.3484046 (11)	0.2415802 (16)	0.2364536 (18)	1.89E-05	0.04
SV-6(C)	1.1418311 (54)	0.5126358 (17)	0.3484038 (12)	0.2415801 (17)	0.2364567 (19)	2.09E-07	0.007
SV-10(C)	1.1418259 (46)	0.5126388 (14)	0.3484073 (10)	0.2415821 (13)	0.2364550 (15)	4.49E-05	0.01
SV-10(C)	1.1418214 (52)	0.5126394 (17)	0.3484067 (11)	0.2415801 (15)	0.2364555 (16)	7.75E-05	0.01
SV-10(3)	1.1418300 (43)	0.5126435 (20)	0.3484034 (11)	0.2415878 (14)	0.2364587 (22)	1.41E-04	0.02
SV-10(4)	1.1418214 (47)	0.5126367 (14)	0.3484036 (10)	0.2415824 (12)	0.2364514 (15)	4.98E-05	0.04
Average	1.1418247	0.5126396	0.3484053	0.2415831	0.2364552		
2SD	0.0000083	0.0000057	0.0000041	0.0000066	0.0000060		
SV-13(C)	1.1418323 (51)	0.5126387 (16)	0.3484046 (11)	0.2415810 (17)	0.2364561 (17)	1.08E-04	0.003
SV-18(C)	1.1418268 (39)	0.5126393 (12)	0.3484056 (08)	0.2415809 (11)	0.2364521 (13)	4.54E-05	0.04
SV-19(C)	1.1418308 (50)	0.5126396 (19)	0.3484051 (12)	0.2415800 (15)	0.2364618 (19)	3.69E-05	0.06
SV-19(S)	1.1418256 (55)	0.5126586 (21)	0.3484047 (13)	0.2415837 (16)	0.2364522 (22)	1.13E-04	0.08

Table 4.9 Nd isotopic ratios of alkaline rocks analysed from Phenai Mata Complex (alkali basalts), Gujarat and Kishengarh (nepheline syenites),Rajasthan.

Sample ID	142NJ/144NJ	143 N.J./144 N.J	145NJJ/144NJJ	148NJJ/144NJJ	150NJ /144NJ	¹⁴⁰ Ce/ ¹⁴² Nd	Av. Fr. Rate
Sample ID	INU/ INU	INU/ INU	INU/ INU	INU/ INU	inu/ inu		ppm/s
PMC-2(1)	1.1418297 (38)	0.5127007 (18)	0.3484037 (11)	0.2415825 (12)	0.2364498 (17)	1.48E-04	0.07
PMC-2(2)	1.1418340 (40)	0.5126953 (12)	0.3484040 (08)	0.2415784 (12)	0.2364517 (13)	9.66E-05	0.07
Average	1.1418319	0.5126980	0.3484039	0.2415805	0.2364508		
2SD	0.0000061	0.0000076	0.0000004	0.0000058	0.0000027		
PMC-3(1)	1.1418281 (48)	0.5120854 (20)	0.3484026 (13)	0.2415816 (16)	0.2364441 (21)	7.78E-05	0.08
PMC-3(2)	1.1418511 (58)	0.5120809 (17)	0.3484030 (12)	0.2415760 (16)	0.2364498 (19)	2.39E-05	0.03
Average	1.1418396	0.5120832	0.3484028	0.2415788	0.2364470		
2SD	0.0000325	0.0000064	0.0000006	0.0000079	0.0000081		
KG-1(1)	1.1418295 (47)	0.5117437 (23)	0.3484031 (13)	0.2415844 (15)	0.2364510 (22)	1.18E-04	0.10
KG-1(2)	1.1418277 (45)	0.5117244 (15)	0.3484047 (01)	0.2415787 (13)	0.2364451 (15)	7.15E-05	0.08
Average	1.1418286	0.5117341	0.3484039	0.2415816	0.2364481		
2SD	0.0000025	0.0000273	0.0000023	0.0000081	0.0000083		

Sampla ID	¹⁴² Nd/ ¹⁴⁴ Nd	143Nd/144Nd	145 _{NId} /144 _{NId}	148NJ/144NJ	150 N.d./144 N.d	¹⁴⁰ Ce/ ¹⁴² Nd	Av. Fr. Rate
Sample ID	INU/ INU	INU/ INU	INU/ INU	inu/ inu	INU/ INU		ppm/s
CC-5	1.1418303 (44)	0.5119822 (20)	0.3484022 (13)	0.2415878 (16)	0.2364582 (20)	4.08E-05	0.06
CC-5(3SEQ)	1.1418308 (43)	0.5119785 (15)	0.3484039 (10)	0.2415805 (13)	0.2364562 (15)	2.05E-05	0.03
Average	1.1418306	0.5119804	0.3484031	0.2415842	0.2364572		
2SD	0.0000007	0.0000052	0.0000024	0.0000103	0.0000028		
KK-1	1.1418312 (42)	0.5119987 (20)	0.3484038 (12)	0.2415849 (14)	0.2364524 (20)	4.93E-05	0.08
KK-1(3SEQ)	1.1418325 (54)	0.5119909 (16)	0.3484042 (11)	0.2415813 (15)	0.2364520 (17)	2.96E-05	0.02
Average	1.1418319	0.5119948	0.3484040	0.2415831	0.2364522		
2SD	0.0000018	0.0000110	0.0000006	0.0000051	0.0000006		
NK-1	1.1418313 (42)	0.5119638 (20)	0.3483996 (13)	0.2415839 (15)	0.2364496 (20)	5.90E-05	0.09
NK-1(3SEQ)	1.1418319 (47)	0.5119582 (16)	0.3484046 (10)	0.2415791 (14)	0.2364499 (16)	7.38E-05	0.03
Average	1.1418316	0.5119610	0.3484021	0.2415815	0.2364498		
2SD	0.0000008	0.0000079	0.0000071	0.0000068	0.0000004		
P-7	1.1418390 (51)	0.5116737 (24)	0.3484024 (15)	0.2415832 (18)	0.2364497 (23)	5.03E-05	0.05
P-7(3SEQ)	1.1418316 (51)	0.5116671 (16)	0.3484044 (11)	0.2415805 (14)	0.2364510 (17)	1.89E-05	0.05
Average	1.1418353	0.5116704	0.3484034	0.2415819	0.2364504		
2SD	0.0000105	0.0000093	0.0000028	0.0000038	0.0000018		
SK-1	1.1418240 (38)	0.5119946 (18)	0.3484066 (10)	0.2415899 (13)	0.2364629 (17)	1.40E-04	0.02

Table 4.10 Nd isotopic ratios of kimberlites analysed from Eastern Dharwar Craton, Karnataka.

SK-1(3SEQ)	1.1418242 (43)	0.5119889 (15)	0.3484036 (10)	0.2415810 (13)	0.2364595 (15)	6.31E-05	0.007
Average	1.1418241	0.5119918	0.3484051	0.2415855	0.2364612		
2SD	0.0000003	0.0000081	0.0000042	0.0000126	0.0000048		

Table 4.11 Nd isotopic ratios of Archean rocks analysed from BGC-1 (granitoids) from Rajasthan and TTGs from Singhbhum craton, Odisha.

Sample ID	¹⁴² Nd/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	¹⁴⁵ Nd/ ¹⁴⁴ Nd	¹⁴⁸ Nd/ ¹⁴⁴ Nd	¹⁵⁰ Nd/ ¹⁴⁴ Nd	¹⁴⁰ Ce/ ¹⁴² Nd	Av. Fr. Rate
Sample ID	nu/ nu	itu/ itu	inu/ inu	inu/ inu	inu/ inu		ppm/s
JG-1(1)	1.1418271 (43)	0.5124740 (13)	0.3484041 (09)	0.2415784 (12)	0.2364517 (14)	8.31E-05	0.10
JG-1(2)	1.1418330 (39)	0.5124831 (19)	0.3484014 (11)	0.2415867 (13)	0.2364547 (18)	1.77E-04	0.10
Average	1.1418301	0.5124786	0.3484028	0.2415826	0.2364532		
2SD	0.0000083	0.0000129	0.0000038	0.0000117	0.0000042		
JG-2(1)	1.1418362 (59)	0.5106304 (19)	0.3484031 (11)	0.2415773 (17)	0.2364521 (20)	6.44E-05	0.09
JG-2(2)	1.1418425 (45)	0.5106311 (21)	0.3484038 (12)	0.2415841 (15)	0.2364504 (20)	5.24E-05	0.10
Average	1.1418394	0.5106308	0.3484035	0.2415807	0.2364513		
2SD	0.0000089	0.0000010	0.0000010	0.0000096	0.0000024		
OD-9(a)	1.1418378 (56)	0.5106004 (26)	0.3484031 (15)	0.2415848 (19)	0.2364527 (24)	1.11E-04	0.30
OD-12/2	1.1418455 (53)	0.5106809 (25)	0.3484045 (14)	0.2415823 (17)	0.2364489 (22)	5.65E-05	0.05
OD-13/2	1.1418462 (50)	0.5105013 (24)	0.3484035 (15)	0.2415845 (17)	0.2364486 (23)	1.39E-04	0.10

Chapter 5 Summary and Conclusion

5.1 Summary of Analytical Methods

I summarise the analytical methods developed for this research work, in terms of chemistry and mass spectrometry. A chemical separation protocol was developed using α – HIBA chemistry to obtain a pure Nd fraction from rock matrices. Using this protocol, I was able to attain a successful separation of Nd from Ce, where Ce was removed to the background level. This ensured no isobaric interference in the measurement of ¹⁴²Nd/¹⁴⁴Nd by TIMS. The effects of data acquisition and data reduction methods on the accuracy of ¹⁴²Nd results were studied in detail. In particular, the effect of the number of sequences employed in a multidynamic data acquisition scheme on the accuracy of results was investigated in light of higher average fractionation rates. No such effect was observed. However, we observed that the accuracy of ¹⁴²Nd/¹⁴⁴Nd data heavily depended on the method of mass fractionation correction used. The power-normalised exponential law was found to be the most appropriate method for the mass fractionation correction for data acquired by TIMS. The homogeneity of terrestrial 142 Nd/ 144 Nd is crucial for inter-comparison of μ^{142} Nd data which uses ratio measured in terrestrial standards. To validate this point we analysed two commonly used terrestrial standards; Ames Nd and JNdi-1, for their ¹⁴²Nd isotopic compositions. To our surprise, a 6 ppm difference in their ¹⁴²Nd isotopic compositions was observed, which is significant in context of the magnitude of the anomalies reported and therefore, is important for the inferences on the early silicate Earth differentiation since this can lead to appearance or disappearance of the anomalies in the μ notation. We observed this effect in our data for the 1.48 Ga alkaline igneous rocks of Khariar. Our study finds that JNdi-1 is a homogeneous standard and we strongly encourage use of JNdi-1 as terrestrial reference. We also provide a cross-calibration for the ${}^{142}Nd/{}^{144}Nd$ of JNdi-1 and Ames Nd: $({}^{142}Nd/{}^{144}Nd)_{JNdi-1} =$ $0.809695 \times (^{142}\text{Nd}/^{144}\text{Nd})_{\text{Ames Nd}} + 0.2172901$. Using this relationship we obtained a value of 1.1418302 for JNdi-1 corresponding to our long term average of 1.1418375 for Ames Nd. This value was used for the calculation of μ^{142} Nd for various rocks analysed in the present study.

5.2 Summary of ¹⁴²Nd Isotope Composition of the Analysed Rocks

Using the analytical protocols and measuring techniques developed by us, I carefully analysed and reduced the data obtained for different magmatic rocks of India. The analyses of Archean rocks from Singhbhum (3.45 Ga) and Aravalli (3.3 Ga) Cratons reveal that the granitoids from Aravalli Craton do not possess any signature of early silicate Earth

differentiation, whereas the TTGs from Singhbhum appears to carry a positive μ^{142} Nd anomaly with respect to JNdi-1 standard. This hints at involvement of the EDR in generation of the Singhbhum TTGs, which in turn suggests that positive ¹⁴²Nd anomalies persisted for at least 350 million years beyond the formation of the TTGs of Greenland. Analyses of SCLM derived alkaline silicate rocks, kimberlites and carbonatites of varying ages (1.5 Ga to 65 Ma) from various parts of India did not yield any anomalous ¹⁴²Nd isotopic composition.

5.3 Important Findings

The major findings of my thesis work are the following:

- The number of sequences used to acquire data during multi-dynamic mode of data acquisition in Nd isotopic analysis by TIMS has no effect on the average (and relative) fractionation rate and hence, does not affect the accuracy of the data acquired.
- 2. The accuracy of the Nd isotopic data depends on the method of mass fractionation correction used. For data acquired using multi-dynamic mode, a power-normalised exponential law is the most appropriate method for fractionation correction.
- 3. A comparative study of the two commonly used Nd standards, Ames Nd (used for routine measurements in our laboratory) and JNdi-1, was done and we find that ¹⁴²Nd/¹⁴⁴Nd isotopic composition of JNdi-1 is lower by 6ppm (in μ^{142} Nd notation) with respect to that of Ames Nd.
- 4. We obtained a cross-calibration relation: $(^{142}Nd/^{144}Nd)_{JNdi-1} = 0.809695 \times (^{142}Nd/^{144}Nd)_{Ames}$ _{Nd} + 0.2172901 (R² = 0.89), for inter-comparison of $^{142}Nd/^{144}Nd$ data with respect to JNdi-1 and Ames Nd.
- 5. The value of μ^{142} Nd varies with the choice of the terrestrial standard used for calculation of μ . This has important implications for the discovery of anomalous compositions.
- 6. Alkaline rocks from Khariar show no resolvable anomaly in μ^{142} Nd notation, with respect to Ames Nd. However, the values obtained were nominally negative. These negative values became zero (in μ^{142} Nd notation) when normalised with respect to JNdi-1.
- 7. A combined effect of the choice of fractionation correction method and of the terrestrial standard used for normalization, led to the two contradicting results from the same sample aliquots of Khariar alkaline rocks, as were reported by Upadhyay et al. (2009) and Roth et al. (2014).

- 8. The 3.45 Ga Archean rocks of India (TTGs from Singhbhum Craton) hint at preservation of EDR signature in their mantle source. This suggests preservation of the positive anomalies for at least 350 million years beyond the formation of TTGs of Greenland.
- 9. The alkaline rocks and carbonatites derived from SCLM do not carry and/or preserve the early silicate Earth differentiation signatures beyond 1.5 Ga in the Indian mantle domains.

5.4 Concluding Remarks

In conclusion, I would like to stress on the importance of understanding the role of analytical methods in the possible generation of the analytical artefacts in the measurements of ¹⁴²Nd for study of early silicate Earth differentiation. A significant dependency is observed between the method of fractionation correction employed for data reduction and accuracy of the results obtained. However, the mode of data acquisition is found to of have little effect on the accuracy of the final results. In addition, the difference in the ¹⁴²Nd/¹⁴⁴Nd isotopic compositions of the two most commonly used terrestrial standards - Ames Nd and JNdi-1, may lead to appearance or disappearance of anomalous μ^{142} Nd, depending upon the choice of standard used for calculation of μ . It is therefore, strongly recommended for the future studies to use a homogenous standard like JNdi-1 for easy comparison and reproduction of ¹⁴²Nd results. Non-convecting mantle domains may not be the sites for preservation of the signatures of the EER. The oldest Archean craton of India may have preserved evidence of the EDR.

5.5 Future Studies

¹⁴⁶Sm-¹⁴²Nd is the best known tracer to understand the early silicate earth differentiation. Since analytical methods and choice of terrestrial (lab/international) standard have profound effect on the accuracy of measurements and calculation of μ^{142} Nd, I would like to propose the following investigations to make the methodology robust and free of errors.

- Cross-calibration of the various commonly used Nd terrestrial standards, in particular La Jolla, JNdi-1 and Ames Nd. This will facilitate comparison of data from different labs.
- 2) International campaign to provide an accurate and precise ¹⁴²Nd/¹⁴⁴Nd ratio for the highly homogeneous standard JNdi-1.
- 3) Further studies on Archean rocks, in particular TTGs, from different Indian cratons in my continued effort in search of the illusive EER.

References

- Ahmad, T., and Tamep, J., 1994. Geochemistry and petrogenesis of late Archaean Aravalli volcanics, basement enclaves and granitoids, Rajasthan. Precambrian Res. 65, 1–23.
- Amelin, Y., Krot, A.N., Hutcheon, I.D., Ulyanov, A.A., 2002. Lead Isotopic Ages of Chondrules and Calcium-Aluminum Rich Inclusions. Science. 297, 1678–1683.
- Anders, E., and Grevesse, N., 1989. Abundances of the elements: Meteoritic and Solar. Geochim. Cosmochim. Acta 53, 197–214.
- Andreasen, R., and Sharma, M., 2009. Fractionation and mixing in a thermal ionization mass spectrometer source: Implications and limitations for high-precision Nd isotope analyses. Int. J. Mass Spectrom. 285, 49–57. doi:10.1016/j.ijms.2009.04.004
- Andreasen, R., and Sharma, M., 2007. Mixing and Homogenization in the Early Solar System: Clues from Sr, Ba, Nd, and Sm Isotopes in Meteorites. Astrophys. J. 665, 874– 883. doi:10.1086/518819
- Andreasen, R., and Sharma, M., 2006. Solar Nebula Heterogeneity in p-Process Samarium and Neodymium Isotopes. Science. 314, 806–809. doi:10.1126/science.1131708
- Andreasen, R., Sharma, M., Subbarao, K. V., Viladkar, S.G., 2008. Where on Earth is the enriched Hadean reservoir? Earth Planet. Sci. Lett. 266, 14–28. doi:10.1016/j.epsl.2007.10.009
- Arndt, N.T., 2013. The Formation and Evolution of the Continental Crust. Geochemical Perspect. 2, 405. doi:10.7185/geochempersp.2.3
- Basu, A.R., Renne, P.R., Dasgupta, D.K., Teichmann, F., Poreda, R.J., 1993. Early and Late Alkali Igneous Pulses and a High-³He Plume Origin for the Deccan Flood Basalts. Science 261, 902–906. doi:10.1126/science.261.5123.902
- Bennett, V.C., Brandon, A.D., Nutman, A.P., 2007. Coupled ¹⁴²Nd-¹⁴³Nd isotopic evidence for Hadean mantle dynamics. Science. 318, 1907–1910. doi:10.1126/science.1145928
- Blichert-Toft, J., Albarède, F., 2008. Hafnium isotopes in Jack Hills zircons and the formation of the Hadean crust. Earth Planet. Sci. Lett. 265, 686–702. doi:10.1016/j.epsl.2007.10.054
- Bouvier, A., Wadhwa, M., 2010. The age of the Solar System redefined by the oldest Pb Pb age of a meteoritic inclusion. Nat. Geosci. 3, 637–641. doi:10.1038/ngeo941
- Bowring, S.A., and Williams, I.S., 1999. Priscoan (4.00 4.03 Ga) orthogneisses from northwestern Canada. Contrib. to Mineral. Petrol. 134, 3 16.

- Boyet, M., Blichert-Toft, J., Rosing, M., Storey, M., Télouk, P., Albarède, F., 2003. ¹⁴²Nd evidence for early Earth differentiation. Earth Planet. Sci. Lett. 214, 427–442. doi:10.1016/S0012-821X(03)00423-0
- Boyet, M., and Carlson, R.W., 2006. A new geochemical model for the Earth's mantle inferred from ¹⁴⁶Sm-¹⁴²Nd systematics. Earth Planet. Sci. Lett. 250, 254–268. doi:10.1016/j.epsl.2006.07.046
- Boyet, M., and Carlson, R.W., 2005. ¹⁴²Nd evidence for early (>4.53 Ga) global differentiation of the silicate earth. Science. 309, 576.
- Boyet, M., Carlson, R.W., Horan, M., 2010. Old Sm-Nd ages for cumulate eucrites and redetermination of the solar system initial ¹⁴⁶Sm/¹⁴⁴Sm ratio. Earth Planet. Sci. Lett. 291. doi:10.1016/j.epsl.2010.01.010
- Brandon, A.D., Lapen, T.J., Debaille, V., Beard, B.L., Rankenburg, K., Neal, C., 2009. Reevaluating ¹⁴²Nd/¹⁴⁴Nd in lunar mare basalts with implications for the early evolution and bulk Sm/Nd of the Moon. Geochim. Cosmochim. Acta 73, 6421–6445. doi:10.1016/j.gca.2009.07.015
- Burkhardt, C., Borg, L.E., Brennecka, G.A., Shollenberger, Q.R., Dauphas, N., Kleine, T., 2016. A nucleosynthetic origin for the Earth's anomalous ¹⁴²Nd composition. Nature 537, 394–398.
- Carlson, R.W., and Boyet, M., 2008. Composition of the Earth's interior: the importance of early events. Philos. Trans. A. Math. Phys. Eng. Sci. 366, 4077–4103. doi:10.1098/rsta.2008.0166
- Carlson, R.W., Boyet, M., O'Neil, J., Rizo, H., and Walker, R.J., 2015. The Early Earth: Accretion and Differentiation, First. ed. John Wiley & Sons.
- Caro, G., 2011. Early Silicate Earth Differentiation. Annu. Rev. Earth Planet. Sci. 39, 31–58. doi:10.1146/annurev-earth-040610-133400
- Caro, G., Bourdon, B., 2010. Non-chondritic Sm/Nd ratio in the terrestrial planets: Consequences for the geochemical evolution of the mantle-crust system. Geochim. Cosmochim. Acta 74, 3333–3349. doi:10.1016/j.gca.2010.02.025
- Caro, G., Bourdon, B., Birck, J., 2003. ¹⁴⁶Sm ¹⁴²Nd evidence from Isua metamorphosed sediments for early differentiation of the Earth's mantle. Nature 423, 428–432. doi:10.1038/nature01639.1.
- Caro, G., Bourdon, B., Birck, J.L., Moorbath, S., 2006. High-precision ¹⁴²Nd/¹⁴⁴Nd measurements in terrestrial rocks: Constraints on the early differentiation of the Earth's mantle. Geochim. Cosmochim. Acta 70, 164–191. doi:10.1016/j.gca.2005.08.015
- Caro, G., Morino, P., Mojzsis, S.J., Cates, N.L., Bleeker, W., 2016. Sluggish Hadean geodynamics: Evidence from coupled ^{146,147}Sm-^{142,143}Nd systematics in Eoarchean supracrustal rocks of the Inukjuak domain (Québec). Earth Planet. Sci. Lett. 457, 23–37. doi:10.1016/j.epsl.2016.09.051

- Cavosie, A.J., Valley, J.W., Wilde, S.A., 2005. Magmatic δ^{18} O in 4400-3900 Ma detrital zircons: A record of the alteration and recycling of crust in the Early Archean. Earth Planet. Sci. Lett. 235, 663–681. doi:10.1016/j.epsl.2005.04.028
- Choudhary, A.K., Gopalan, K., Anjaneya, C., 1984. Present status of the geochronology of the Precambrian rocks of Rajasthan. Tectonophysics 105, 131–140.
- Condie, K.C., 2012. Earth as an evolving planetary system, Second. ed. Elsevier.
- Crawford, A.R., 1970. The Precambrian geochronology of Rajasthan and Bundelkhand, northern India. Can. J. Earth Sci. 7, 91–110. doi:10.1139/e70-007
- Crawford, A.R., 1969. Reconnaissance Rb-Sr dating of the Precambrian rocks of northern Peninsular India. J. Geol. Soc. India 10, 117–166.
- Debaille, V., O'Neill, C., Brandon, A.D., Haenecour, P., Yin, Q.Z., Mattielli, N., Treiman, A.H., 2013. Stagnant-lid tectonics in early Earth revealed by ¹⁴²Nd variations in late Archean rocks. Earth Planet. Sci. Lett. 373, 83–92. doi:10.1016/j.epsl.2013.04.016
- Dickin, A.P., 2005. Radiogenic Iostope Geology, Second. ed. Cambridge University Press.
- Gautam, I., Ray, J.S., Bhutani, R., Balakrishnan, S., Dash, J.K., 2017. Role of fractionation correction in accurate determination of ¹⁴²Nd /¹⁴⁴Nd by TIMS : A case study of 1.48 Ga alkaline rocks from Khariar , India. Chem. Geol. 466, 479–490. doi:10.1016/j.chemgeo.2017.06.036
- Gopalan, K., Macdougall, J.D., Roy, A.B., Murali, A.V., 1990. Sm-Nd evidence for 3.3 Ga old rocks in Rajasthan, northwestern India. Precambrian Res. 48, 287–297. doi:10.1016/0301-9268(90)90013-G
- Gwalani, L.G., Jaques, A.L., Downes, P.J., Rao, N.V.C., 2016. Kimberlites , lamproites , carbonatites and associated alkaline rocks: a tribute to the work of Rex T . Prider. Mineral. Petrol. 110, 149–153. doi:10.1007/s00710-016-0429-3
- Habfast, K., 1998. Fractionation correction and multiple collectors in thermal ionization isotope ratio mass spectrometry. Int. J. Mass Spectrom. 176, 133–148. doi:10.1016/S1387-3806(98)14030-7
- Harper, C. L. Jr & Jacobsen, S.B., 1992. Evidence from coupled ¹⁴⁷Sm-¹⁴³Nd and ¹⁴⁶Sm-¹⁴²Nd systematics for very early (4.5-Gyr) differentiation of the Earth's mantle. Nature 360, 728–732.
- Harrison, T.M., Schmitt, A.K., McCulloch, M.T., Lovera, O.M., 2008. Early (≥ 4.5 Ga) formation of terrestrial crust: Lu-Hf, δ18O, and Ti thermometry results for Hadean zircons. Earth Planet. Sci. Lett. 268, 476–486. doi:10.1016/j.epsl.2008.02.011
- Hart, S.R., Hauri, E.H., Oschmann, L.A., Whitehead, J.A., 1992. Mantle plumes and entrainment: Isotopic evidence. Science. 256, 517–520.

- Hauri, E.H., Whitehead, J.A., Hart, S.R., 1994. Fluid dynamic and geochemical aspects of entrainment in mantle plumes. J. Geophys. Res. 24, 275–300.
- Heron, A.M., 1924. The soda bearing rocks of Kishangarh. Rajputana. Rec. Geol. Surv. India 56, 179–197.
- Jackson, M.G., Carlson, R.W., 2011. An ancient recipe for flood-basalt genesis. Nature 476, 316–319. doi:10.1038/nature10326
- Jackson, M.G., Carlson, R.W., Kurz, M.D., Kempton, P.D., Francis, D., Blusztajn, J., 2010. Evidence for the survival of the oldest terrestrial mantle reservoir. Nature 466, 853–856. doi:10.1038/nature09287
- Jackson, M.G., Jellinek, A.M., 2013. Major and trace element composition of the high ³He/ ⁴He mantle: Implications for the composition of a nonchonditic Earth. Geochemistry, Geophys. Geosystems. 14, 2954–2976. doi:10.1002/ggge.20188
- Jacobsen, S.B., 2005. The Hf-W isotopic system and the origin of the Earth and Moon. Annu. Rev. Earth Planet. Sci. 33, 531–70. doi:10.1146/annurev.earth.33.092203.122614
- Jacobsen, S.B., Ranen, M.C., Petaev, M.I., Remo, J.L., O'Connell, R. J., Sasselov, D.D., 2008. Isotopes as clues to the origin and earliest differentiation history of the Earth. Phil. Trans. R. Soc. London 366A, 4129–4162. doi:10.1098/rsta.2008.0174
- Jacobson, S.A., Morbidelli, A., Raymond, S.N., O'Brien, D.P., Walsh, K.J., Rubie, D.C., 2014. Highly siderophile elements in Earth's mantle as a clock for the Moon-forming impact. Nature 508, 84–7. doi:10.1038/nature13172
- Jacobson, S.A., and Walsh, K.J., 2015. The Early Earth: Accretion and Differentiation, First Edit. ed. John Wiley & Sons.
- Jochum, K.P., Nohl, U., Herwig, K., Lammel, E., Stoll, B., Hofmann, A.W., 2005. GeoReM: A New Geochemical Database for Reference Materials and Isotopic Standards. Geostand. Geoanalytical Res. 29, 333–338. doi:10.1111/j.1751-908X.2005.tb00904.x
- Kargel, J.S., and Lewis, J.S., 1993. The Composition and Early Evolution of Earth. Icarus 105, 1–25.
- Kinoshita N., Paul M., Collon P., Deibel M., DiGiovine B., Greene J.P., Henderson D.J., Jiang C.L., Marley S.T., Nakanishi T., Pardo R.C., Rehm K.E., Robertson D., Scott R., Schmitt C., Tang X.D., Vondrasek R.Y.A., 2012. A Shorter ¹⁴⁶Sm half-life measured and implications for ¹⁴⁶Sm-¹⁴²Nd chronology in the solar system. Science. 335, 1614– 1617.
- Kleine, T., Touboul, M., Bourdon, B., Nimmo, F., Mezger, K., Palme, H., Jacobsen, S.B., Yin, Q., Halliday, A.N., 2009. Hf – W chronology of the accretion and early evolution of asteroids and terrestrial planets. Geochim. Cosmochim. Acta 73, 5150–5188. doi:10.1016/j.gca.2008.11.047

- Leelanandam, C., Burke, K., Ashwal, L.D., Webb, S.J., 2006. Proterozoic mountain building in Peninsular India: an analysis based primarily on alkaline rock distribution. Geol. Mag. 143, 195–212. doi:10.1017/S0016756805001664
- Lodders, K., 2010. Solar system abundances of the elements. Astrophys. Sp. Sci. Proc. 379–417.
- Lodders, K., 2003. Solar system abundances and condensation temperatures of the elements. Astrophys. J. 591, 1220–1247.
- Lodders, K., Palme, H., Gail, H.-P., 2009. Abundances of the elements in the Solar System. Landolt-Börnstein, New Ser. Astron. Astrophys. doi:10.1007/978-3-540-88055-4_34
- Marks, N.E., Borg, L.E., Hutcheon, I.D., Jacobsen, B., Clayton, R.N., 2014. Samariumneodymium chronology and rubidium-strontium systematics of an Allende calciumaluminum-rich inclusion with implications for ¹⁴⁶Sm half-life. Earth Planet. Sci. Lett. 405, 15–24. doi:10.1016/j.epsl.2014.08.017
- Martin, H., 1987. Petrogenesis of Archaean Trondhjemites, Tonalites, and Granodiorites from Eastern Finland : Major and Trace Element Geochemistry. J. Petrol. 28, 921–953.
- Martin, H., Moyen, J.F., 2002. Secular changes in tonalite-trondhjemite-granodiorite composition as markers of the progressive cooling of Earth. Geology 30, 319–322. doi:10.1130/0091-7613(2002)030<0319:SCITTG>2.0.CO
- Mcculloch, M.T., Bennett, V.C., 1993. Evolution of the early Earth Constraints from ¹⁴³Nd-¹⁴²Nd isotopic systematics. Lithos 30, 237–255. doi:10.1016/0024-4937(93)90038-E
- Mcdonough, W.F., Sun, S., 1995. The composition of the Earth. Chem. Geol. 120, 223–253.
- Mittal, R.S. and Jain, R.S., 1955. On the origin of nepheline syenite of Kishangarh, Rajasthan. J. Sci. Res. Banaras Hindu Univ. 37 46.
- Moyen, J.F., Martin, H., 2012. Forty years of TTG research. Lithos 148, 312–336. doi:10.1016/j.lithos.2012.06.010
- Murphy, D.T., Brandon, A.D., Debaille, V., Burgess, R., Ballentine, C., 2010. In search of a hidden long-term isolated sub-chondritic ¹⁴²Nd/¹⁴⁴Nd reservoir in the deep mantle: Implications for the Nd isotope systematics of the Earth. Geochim. Cosmochim. Acta 74, 738–750. doi:10.1016/j.gca.2009.10.005
- Nimmo, F., and Kleine, T., 2015. The Early Earth: Accretion and Differentiation. John Wiley & Sons.
- Niyogi, D., 1966. Petrology of the alkalic rocks of Kishangarh, Rajasthan, India. Geol. Soc. Am. Bull. 77, 65–82.
- O'Neil, J., Carlson, R.W., Francis, D., Stevenson, R.K., 2008. Neodymium-142 Evidence for Hadean Mafic Crust. Science. 321, 1828–1832. doi:10.1126/science.1161925

- O'Neill, H.S., and Palme, H., 2008. Collisional erosion and the non-chondritic composition of the terrestrial planets. Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. 366, 4205 LP 4238.
- Palme, H., Lodders, K., Jones, A., 2013. Solar System Abundances of the Elements. Treatise Geochemistry Second Ed. 2, 15–36. doi:10.1016/B978-0-08-095975-7.00118-2
- Palme, H.A., O'Neill, Hugh. St C., 2014. Cosmochemical Estimates of Mantle Composition, 2nd ed. Elsevier Ltd. doi:10.1016/B978-0-08-095975-7.00201-1
- Pande, K., 1988. Isotopic and chemical studies of ultramafic nodules in alkali basalts from Kutch, Western India.
- Puchtel, I.S., Blichert-Toft, J., Touboul, M., Horan, M.F., and Walker, R.J., 2016. The coupled ¹⁸²W-¹⁴²Nd record of early terrestrial mantle differentiation. Geochemistry Geophys. Geosystems 17, 2168–2193. doi:10.1002/2016GC006324
- Rao, N.V.C., Wu, F., Mitchell, R.H., Li, Q., Lehmann, B., 2013. Mesoproterozoic U Pb ages, trace element and Sr Nd isotopic composition of perovskite from kimberlites of the Eastern Dharwar craton, southern India : Distinct mantle sources and a widespread 1.1 Ga tectonomagmatic event. Chem. Geol. 353, 48–64. doi:10.1016/j.chemgeo.2012.04.023
- Ray, J.S., 2009. Radiogenic Isotopic Ratio Variations in Carbonatites and Associated Alkaline Silicate Rocks: Role of Crustal Assimilation. J. Petrol. 50, 1955–1971. doi:10.1093/petrology/egp063
- Ray, J.S., 1997. Stable and radioisotopic constraints on carbonatite-alkaline complexes of India.
- Ray, J.S., Pande, K., 2001. ⁴⁰Ar-³⁹Ar age of carbonatite-alkaline magmatism in Sung Valley, Meghalaya, India. Proc. Indian Acad. Sci. Earth Planet. Sci. 110, 185–190. doi:10.1007/BF02702233
- Ray, J.S., Pande, K., Bhutani, R., Shukla, A.D., Rai, V.K., Kumar, A., Awasthi, N., Smitha, R.S., Panda, D.K., 2013. Age and geochemistry of the Newania dolomite carbonatites, India: Implications for the source of primary carbonatite magma. Contrib. to Mineral. Petrol. 166, 1613–1632. doi:10.1007/s00410-013-0945-7
- Ray, J.S., Ramesh, R., 2006. Stable Carbon and Oxygen Isotopic Compositions of Indian Carbonatites. Int. Geol. Rev. 48, 17–45. doi:10.2747/0020-6814.48.1.17
- Ray, J.S., Trivedi, J.R., Dayal, A.M., 2000. Strontium isotope systematics of Amba Dongar and Sung Valley carbonatite-alkaline complexes , India: evidence for liquid immiscibility, crustal contamination and long-lived Rb / Sr enriched mantle sources. J. Asian Earth Sci. 18, 585 – 594.
- Ray, J.S., and Pande, K., 1999. Carbonatite alkaline magmatism associated with continental flood basalts at stratigraphic boundaries: Cause for mass extinctions. Geophys. Res. Lett. 26, 1917–1920.

- Ray, J.S., 1998. Trace element and isotope evolution during concurrent assimilation, fractional crystallization, and liquid immiscibility of a carbonated silicate magma. Geochim. Cosmochim. Acta 62, 3301–3306.
- Ray, J.S., Pande, K., and Pattanayak, S.K., 2003. Evolution of the Amba Dongar carbonatite complex: Condtraints from ⁴⁰Ar-³⁹Ar chronologies of the inner basalt and an alkaline plug. Int. Geol. Rev. 45, 857–862.
- Regelous, M., Collerson, K.D., 1996. ¹⁴⁷Sm-¹⁴³Nd, ¹⁴⁶Sm-¹⁴²Nd systematics of early Archaean rocks and implications for crust-mantle evolution. Geochim. Cosmochim. Acta 60, 3513–3520. doi:10.1016/0016-7037(96)00203-7
- Rizo, H., Boyet, M., Blichert-Toft, J., Neil, J.O., Rosing, M.T., Paquette, J., 2012. The elusive Hadean enriched reservoir revealed by ¹⁴²Nd deficits in Isua Archaean rocks. Nature 490, 96–100. doi:10.1038/nature11565
- Rizo, H., Boyet, M., Blichert-Toft, J., Rosing, M., 2011. Combined Nd and Hf isotope evidence for deep-seated source of Isua lavas. Earth Planet. Sci. Lett. 312, 267–279. doi:10.1016/j.epsl.2011.10.014
- Roth, A.S.G., Bourdon, B., Mojzsis, S.J., Rudge, J.F., Guitreau, M., Blichert-Toft, J., 2014a. Combined ^{147,146}Sm - ^{143,142}Nd constraints on the longevity and residence time of early terrestrial crust. Geochemistry Geophys. Geosystems 15, 2329–2345. doi:10.1002/2014GC005313.Received
- Roth, A.S.G., Bourdon, B., Mojzsis, S.J., Touboul, M., Sprung, P., Guitreau, M., Blichert-Toft, J., 2013. Inherited ¹⁴²Nd anomalies in Eoarchean protoliths. Earth Planet. Sci. Lett. 361, 50–57. doi:10.1016/j.epsl.2012.11.023
- Roth, A.S.G., Scherer, E.E., Maden, C., Mezger, K. and Bourdon, B., 2014b. Revisiting the ¹⁴²Nd deficits in the 1.48Ga Khariar alkaline rocks, India. Chem. Geol. 386, 238–248. doi:10.1016/j.chemgeo.2014.06.022
- Roy, A.B., and Dutt, K., 1995. Tectonic evolution of the nepheline syenite and associated rocks of Kishengarh, District Ajmer, Rajasthan.
- Rubie, D.C., Nimmo, F.A., Melosh, H.J., 2015. Formation of the Earth's Core, Treatise on Geophysics. Elsevier B.V. doi:10.1016/B978-0-444-53802-4.00154-8
- Saha, A.K., 1994. Crustal evolution of Singhbhum-North Orissa, Eastern India. Memoir G.S. of India,;27.
- Saji, N.S., Wielandt, D., Paton, C., Bizzarro, M., 2016. Ultra-high-precision Nd-isotope measurements of geological materials by MC-ICPMS. J. Anal. At. Spectrom. 31, 1490– 1504. doi:10.1039/C6JA00064A
- Solanki, A.M., 2011. A petrographic, geochemical and geochronological investigation of deformed granitoids from SW Rajasthan: Neoproterozoic age of formation and evidence of Pan-African imprint. University of the Witwatersrand.

- Srivastava, R.K., 1988. Magmatism in the Aravalli Mountain range and its environs. Mem. Geol. Soc. India 7, 78 93.
- Stracke, A., Hofmann, A.W., Hart, S.R., 2005. FOZO, HIMU, and the rest of the mantle zoo. Geochemistry, Geophys. Geosystems 6. doi:10.1029/2004GC000824
- Sun, S., McDonough, W.F., 1989. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. Geol. Soc. London, Spec. Publ. 42, 313–345. doi:10.1144/GSL.SP.1989.042.01.19
- Tanaka, T., Togashi, S., Kamioka, H., Amakawa, H., Kagami, H., Hamamoto, T., Yuhara, M., Orihashi, Y., Yoneda, S., Shimizu, H., Kunimaru, T., Takahashi, K., Yanagi, T., Nakano, T., Fujimaki, H., Shinjo, R., Asahara, Y., Tanimizu, M., Dragusanu, C., 2000. JNdi-1: A neodymium isotopic reference in consistency with LaJolla neodymium. Chem. Geol. 168, 279–281. doi:10.1016/S0009-2541(00)00198-4
- Thirlwall, M.F., 1991. Long-term reproducibility of multicollector Sr and Nd isotope ratio analysis. Chem. Geol. 94, 85–104. doi:10.1016/0168-9622(91)90002-E
- Upadhyay, D., Chattopadhyay, S., Kooijman, E., Mezger, K., Berndt, J., 2014. Magmatic and metamorphic history of Paleoarchean tonalite–trondhjemite–granodiorite (TTG) suite from the Singhbhum craton, eastern India. Precambrian Res. 252, 180–190. doi:10.1016/j.precamres.2014.07.011
- Upadhyay, D., Raith, M.M., Mezger, K., Bhattacharya, A., Kinny, P.D., 2006. Mesoproterozoic rifting and Pan-African continental collision in SE India: Evidence from the Khariar alkaline complex. Contrib. to Mineral. Petrol. 151, 434–456. doi:10.1007/s00410-006-0069-4
- Upadhyay, D., Scherer, E.E., Mezger, K., 2009. (¹⁴²)Nd evidence for an enriched Hadean reservoir in cratonic roots. Nature 459, 1118–1121. doi:10.1038/nature08089
- Valdiya, K.S., 2010. The Making of India: Geodynamic Evolution. Springer.
- Valley, J.W., Cavosie, A.J., Ushikubo, T., Reinhard, D.A., Lawrence, D.F., Larson, D.J., Clifton, P.H., Kelly, T.F., Wilde, S.A., Moser, D.E., Spicuzza, M.J., 2014. Hadean age for a post-magma-ocean zircon confirmed by atom-probe tomography. Nat. Geosci. 7, 219–223. doi:10.1038/ngeo2075
- Valley, J.W., Lackey, J.S., Cavosie, A.J., Clechenko, C.C., Spicuzza, M.J., Basei, M.A.S., Bindeman, I.N., Ferreira, V.P., Sial, A.N., King, E.M., Peck, W.H., Sinha, A.K., Wei, C.S., 2005. 4.4 billion years of crustal maturation: oxygen isotope ratios of magmatic zircon. Contrib. to Mineral. Petrol. 150, 561–580. doi:10.1007/s00410-005-0025-8
- Veena, K., Pandey, B.K., Krishnamurthy, P., Gupta, J.N., 1998. Pb , Sr and Nd Isotopic Systematics of the Carbonatites of Sung Valley , Meghalaya , Northeast India : Implications for Contemporary Plume-Related Mantle Source Characteristics. J. Petrol. 39, 1875–1884.

- Wakaki, S., Tanaka, T., 2012. Stable isotope analysis of Nd by double spike thermal ionization mass spectrometry. Int. J. Mass Spectrom. 323-324, 45–54. doi:10.1016/j.ijms.2012.06.019
- Wiedenbeck, M., Goswami, J.N., Roy, A.B., 1996. Stabilization of the Aravalli craton of northwestern India at 2 . 5 Ga : An ion microprobe zircon study. Chem. Geol. 129, 325–340.
- Wilde, S.A., Valley, J.W., Peck, W.H., Graham, C.M., 2001. Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. Nature 409, 175–178. doi:10.1038/35051550
- Woolley, A.R., A., Bailey, D.K., 2012. The crucial role of lithospheric structure in the generation and release of carbonatites: geological evidence. Mineral. Mag. 76, 259–270. doi:https://doi.org/10.1180/minmag.2012.076.2.02

List of publications

- Gautam, I., Ray, J.S., Bhutani, R., Balakrishnan, S., Dash, J.K., 2017. Role of fractionation correction in accurate determination of ¹⁴²Nd /¹⁴⁴Nd by TIMS : A case study of 1.48 Ga alkaline rocks from Khariar, India. Chem. Geol. 466, 479–490. doi:10.1016/j.chemgeo.2017.06.036
- **Gautam, I**., 2017. Hunt for the early silicate Earth differentiation Signatures. Proceedings of the Indian National Science Academy (Under review)

Abstracts in International Conferences

- Gautam I & Ray JS (2017) Dependence of μ¹⁴²Nd Anomalies on the Choice of Terrestrial Standard, submitted to *Goldschmidt Abstracts* (gold2017:abs:2017005451)
- **Gautam I**, (2017) Hunt for the early silicate Earth differentiation Signatures. International Conference: Geology: Emerging Methods and Applications (GEM-2017) abstract volume 1, Page 22, Kerala, India.
- Gautam I & Ray JS (2016) A Comparative study of two- versus threesequence multi-dynamic modes for ¹⁴²Nd analyses by TIMS, *Goldschmidt Abstracts*, 909

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

Role of fractionation correction in accurate determination of ¹⁴²Nd/¹⁴⁴Nd by TIMS: A case study of 1.48 Ga alkaline rocks from Khariar, India

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ARTICLE INFO

Keywords: 142Nd/144Nd analyses TIMS 1.48 Ga Khariar rocks

ABSTRACT

The short-lived isotopic systematics of ¹⁴⁶Sm-¹⁴²Nd is a tracer of early silicate Earth differentiation events. Evidence for these events comes from anomalous $^{142}Nd/^{144}Nd$, defined in terms of $\mu^{142}Nd$ ($\mu^{142}Nd$ = $[{(^{142}Nd/^{144}Nd)_{sample} / (^{142}Nd/^{144}Nd)_{standard}} - 1] \times 10^6)$ with respect to a terrestrial standard representing the modern accessible mantle. This requires measurement of accurate and highly precise ¹⁴²Nd/¹⁴⁴Nd, which is carried out by Thermal Ionisation Mass Spectrometry (TIMS). Since multiple factors affect the accuracy of the final results, we carried out a detailed investigation on the effect of various data acquisition, fractionation correction and normalization methods on the accuracy of ¹⁴²Nd/¹⁴⁴Nd determinations. Based on the analyses of Ames Nd standard using various combinations of the most commonly employed methods we observed that for a multi-dynamic mode of data acquisition, the power-normalised exponential law is the most appropriate method for mass fractionation correction. The time delays between successive sequences in a multi-dynamic mode had little effect on the final value of ¹⁴²Nd/¹⁴⁴Nd. The different standards have different ¹⁴²Nd/¹⁴⁴Nd ratios and therefore, their uses yield different μ^{142} Nd values for the same sample. We extended this information to understand the two contradicting results from 1.48 Ga alkaline rocks from Khariar, India, carried out on the same sample aliquots (Upadhyay et al. 2009; Roth et al. 2014b). A confirmation of ¹⁴²Nd anomalies in such younger rocks is important because it could establish the longevity of early silicate differentiation signatures beyond Archean. Our experiment on freshly collected samples from the same outcrops, using identical analytical procedures, could not reproduce the results of Upadhyay et al. (2009). We did, however, observe slightly negative μ^{142} Nd values with respect to Ames Nd, which became normal with respect to JNdi-1.

1. Introduction

The near absence of rock record from the first 500 million years of the Earth's history makes it difficult to understand the earliest differentiation processes that caused the separation of its various reservoirs. Short lived radionuclides and their decay products have been useful in such studies as they provide critical information about these processes from meteorites and ancient magmatic systems. ¹⁴⁶Sm-¹⁴²Nd (t_{1/} $_{2} = 103$ Ma; (Marks et al., 2014) or 68 Ma; Kinoshita et al., 2012) is one such systematics which has been widely utilized to decode the early silicate Earth differentiation. Anomalous abundances of ¹⁴²Nd with respect to terrestrial standards, expressed as $\mu^{142}Nd$ ($\mu^{142}Nd = [\{(^{142}Nd/^{144}Nd)_{sample} / (^{142}Nd/^{144}Nd)_{standard}\} - 1] \times 10^6)$, provide provide clues to fractionation of Sm/Nd during the differentiation events that took place during the first 500 million years of the Earth's formation, when ¹⁴⁶Sm was extant. Considering the highly dynamic nature of the Earth's earliest mantle and the time elapsed since its formation, it is extremely difficult to encounter $\mu^{142}Nd$ anomalies in rocks younger than Archean. Also, because of the small magnitude of these anomalies and isobaric interferences of Sm and Ce on various Nd isotopes including ¹⁴²Ce (11.4% abundance) on ¹⁴²Nd (27.2%), their detection through mass spectrometry is analytically challenging. All of the accepted discoveries of $\mu^{142}\text{Nd}$ anomalies come from the Hadean and Archean rocks. The positive anomalies possibly represent the earliest Large Ion Lithophile Element (LILE) depleted source (Bennett et al., 2007; Boyet and Carlson, 2006; Boyet et al., 2003; Caro et al., 2006, 2003; Rizo et al., 2011). Only four examples of negative $\mu^{142}Nd$ anomalies are known today (O'Neil et al., 2008; Rizo et al., 2012; Roth et al., 2014a; Roth et al., 2013; Upadhyay et al., 2009), which are believed to be vestiges of a Hadean LILE enriched reservoir, possibly representing the earliest crust (Rizo et al., 2012; Roth et al., 2014a) and/ or non-convecting lithospheric mantle (Upadhyay et al., 2009).

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http://dx.doi.org/10.1016/j.chemgeo.2017.06.036

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Received 11 April 2017; Received in revised form 18 June 2017; Accepted 26 June 2017 Available online 01 July 2017

Table 1

Comparison of various data acquisition and reduction procedures followed by Upadhyay et al. (2009) and Roth et al. (2014b).

Parameter	Upadhyay et al. (2009)	Roth et al. (2014b)
Number of sequences in multi-dynamic mode	Three	Two
Fractionation correction law	Power-law normalized exponential law	Exponential law
Fractionation factor	Average of all sequences : $(\beta_1 + \beta_2 + \beta_3)/3$	Calculated from sequence 1: β_1
Cup factors	Get cancelled	Do not get cancelled ^a
Multi-dynamic correction for ratios	¹⁴² Nd/ ¹⁴⁴ Nd, ¹⁴³ Nd/ ¹⁴⁴ Nd, ¹⁴⁵ Nd/ ¹⁴⁴ Nd, ¹⁴⁸ Nd/ ¹⁴⁴ Nd	¹⁴² Nd/ ¹⁴⁴ Nd
Static correction for ratios	¹⁵⁰ Nd/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd, ¹⁴⁵ Nd/ ¹⁴⁴ Nd, ¹⁴⁸ Nd/ ¹⁴⁴ Nd, ¹⁵⁰ Nd/ ¹⁴⁴ Nd

^a As described in Roth et al. (2014b), the cup factors do not affect the exponential law corrected ¹⁴²Nd/¹⁴⁴Nd by > 5 ppm if the difference in relative cup efficiency is < 370 ppm. The relative cup efficiency is calculated by taking the difference of static ¹⁴²Nd/¹⁴⁴Nd measured in sequence 1 and 2.

Significantly, one of these negative anomalies was reported from 1.48 Ga alkaline rocks by Upadhyay et al. (2009), a finding that has the potential to change our understanding of the preservation and longevity of the evidence for the earliest crust-mantle differentiation. Since these rocks are believed to have originated from the lithospheric mantle, the authors argued for preservation of 142 Nd anomaly in a non-convective mantle domain in cratonic roots for at least for 2.7 billion years since its formation (Upadhyay et al., 2009, 2006). However, if these anomalies turn out to be analytical artefact then the hypothesis of continental lithospheres being sites of preservation of 142 Nd anomalies would be invalidated, restricting the anomalous signals only to the rocks of Hadean and Archean. Therefore, it is imperative that the robustness of these results is verified through independent investigations by different laboratories.

In an attempt to verify the negative ¹⁴²Nd anomalies in the 1.48 Ga Khariar samples, Roth et al. (2014b) measured ¹⁴²Nd/¹⁴⁴Nd in the same aliquots of the samples of Upadhyay et al. (2009), but could not reproduce the results. In their data acquisition protocol on TIMS, Roth et al. (2014b) had employed a 2-sequence multi-dynamic mode in contrast to a 3-sequence mode utilized by Upadhyay et al. (2009). To

minimize the time delay between the measurements of ¹⁴⁴Nd/¹⁴⁶Nd and ¹⁴²Nd/¹⁴⁴Nd, Roth et al. (2014b) acquired these ratios in sequences 1 and 2, instead of sequences 1 and 3 as followed by Upadhyay et al. (2009). This was done to remove the analytical bias in the (mass) fractionation corrected ¹⁴²Nd/¹⁴⁴Nd in the 3-sequence mode, caused by higher relative rate of fractionation ($r_f > 1$). Where r_f = average fractionation rate (r_a) / threshold fractionation rate (r_t), and r_t . = external reproducibility / time gap between the sequences (1 and 2 in 2-sequence mode or 1 and 3 in 3-sequence mode). Average fractionation rate is calculated for each analysis by finding the slope of the regressed line when uncorrected ¹⁴⁶Nd/¹⁴⁴Nd from sequence-1 is plotted against the time.

Roth et al. (2014b) also proposed a correction procedure to reduce the 3-sequence data of Upadhyay et al. (2009), where r_t was lower than that in a 2-sequence mode, and showed that in all except one sample the anomalies vanished. According to the authors, this correction procedure was not advocated for general use, but rather is an approximation to re-assess published data. The number of sequences was not the only analytical parameter that was different in the two studies. Another important parameter which was not given a due importance was the

Table 2

Details of fractionation correction methods used in the present study. When exponential law is used to correct data acquired using 3-sequence multi-dynamic mode, sequence 2 in the given formulae are replaced by sequence 3.

Isotopic ratio	Power - normalised exponential law	Exponential law
¹⁴² Nd/ ¹⁴⁴ Nd	$[({}^{142}\text{Nd}/{}^{144}\text{Nd})_3 \times ({}^{146}\text{Nd}/{}^{144}\text{Nd})_1/0.7219] \times (141.907731/143.910096)^{\text{B}} \times (1+f)^2$	$[(^{142}\text{Nd}/^{144}\text{Nd})_2] \times (141.907731/143.910096)^{\text{B}_1}$
¹⁴³ Nd/ ¹⁴⁴ Nd	$\begin{array}{l} [\{(^{143}\text{Nd}/^{144}\text{Nd})_2\times(^{143}\text{Nd}/^{144}\text{Nd})_3\}/\\ \{(^{144}\text{Nd}/^{146}\text{Nd})_1\times0.7219\}]^{0.5}\times(142.909823/143.910096)^{\text{B}}\times(1+f)^1\end{array}$	$[(^{143}\text{Nd}/^{144}\text{Nd})_1] \times (142.909823/143.910096)^{B_1}$
¹⁴⁵ Nd/ ¹⁴⁴ Nd	$[\{(^{145}\text{Nd}/^{144}\text{Nd})_2\times(^{145}\text{Nd}/^{146}\text{Nd})_1\times0.7219\}]^{0.5}\times(144.912582/143.910096)^8\times(1+f)^{-1}$	$[({}^{145}Nd/{}^{144}Nd)_1] \times (144.912582/\\ 143.910096)^{B_1}$
¹⁴⁸ Nd/ ¹⁴⁴ Nd	$[\{(^{148}\text{Nd}/^{146}\text{Nd})_1\times(^{144}\text{Nd}/^{146}\text{Nd})_3\times(0.7219)^2\}]\times(147.916901/143.910096)^8\times(1+f)^{-4}$	$[(^{148}\text{Nd}/^{144}\text{Nd})_1] \times (147.916901/143.910096)^{\text{B}_1}$
¹⁵⁰ Nd/ ¹⁴⁴ Nd	$[(^{150}\text{Nd}/^{144}\text{Nd})_1] \times (149.9209/143.910096)^{\text{B}}$	$[(^{150}\text{Nd}/^{144}\text{Nd})_1] \times (149.9209/143.910096)^{B_1}$

Here $\beta = \frac{(\beta_1 + \beta_2 + \beta_3)}{2}$ and $f = \frac{(f_1 + f_2 + f_3)}{2}$ are the average mass fractionation factors from the three sequences.

 $\beta_i = \ln\{(0.7219) / ({^{146}\text{Nd}}/{^{144}\text{Nd}})_i\} / \ln(145.913126/143.910096).$

 $f_i = \{(0.7219) / ({}^{146}\text{Nd} / {}^{144}\text{Nd})_i\} {}^{1/(145.913126 - 143.910096)} - 1.$

i = 1, 2, 3 which refers to the sequence number.

a) Three-sequence method												
										Zoom optics		
Cup	L4	L3	12	L1	U	H	H2	H3	H4	Integration time [sec]	Focus [V]	Dispersion[V]
Sequence 1	¹⁴⁰ Ce	¹⁴² Nd	¹⁴³ Nd	¹⁴⁴ Nd	¹⁴⁵ Nd	¹⁴⁶ Nd	¹⁴⁷ Sm	¹⁴⁸ Nd	¹⁵⁰ Nd	8.389	0.0	0.0
Sequence 2 Sequence 3		¹⁴⁰ Ce	PN	¹⁴² Nd	143Nd	Nd 144Nd	¹⁴⁵ Nd	¹⁴⁶ Nd	¹⁴⁸ Nd	8.389 8.389	0.0	6.0 8.0
b) Two-sequence method												
										Zoom optics		
Cup	L4	L3	12	11	C	Н	H2	H3	H4	Integration time [sec]	Focus [V]	Dispersion [V]
Sequence 1 Sequence 2	¹⁴⁰ Ce	¹⁴² Nd ¹⁴⁰ Ce	¹⁴³ Nd	¹⁴⁴ Nd ¹⁴² Nd	^{1 45} Nd ^{1 43} Nd	¹⁴⁶ Nd ¹⁴⁴ Nd	¹⁴⁷ Sm ¹⁴⁵ Nd	¹⁴⁸ Nd ¹⁴⁶ Nd	¹⁵⁰ Nd ¹⁴⁸ Nd	8.389 8.389	0.0	0.0 8.0
Note: Number of blocks = 54 , No. of c. 2σ .	ycles per block	= 10, Amplifiei	r rotation to left	t, Baseline after	every 2 blocks,	Peak centring	after every 8 bl	ocks, Lens focu	sing after every	4 blocks, No. of integrations $= 1$, Idle time (sec) =	3, Cycles filtered at

law of fractionation correction (e.g., exponential vs. power law). The protocol followed by Roth et al. (2014b) was grossly different from that of Upadhyay et al. (2009). The details are given in Tables 1 and 2.

It is therefore, important that we understand the role of the fractionation correction in the accuracy of $^{142}\text{Nd}/^{144}\text{Nd}$ isotopic data and its contribution (if any) to the generation of the analytical artefacts. To study these aspects and to further investigate the accuracy of the negative $\mu^{142}\text{Nd}$ anomalies reported in the alkaline silicate rocks of the Khariar complex, India (Upadhyay et al., 2009), we analysed samples re-collected from the same geological outcrops for their Nd isotopic compositions applying different fractionation correction procedures. We followed identical experimental procedure as in the original study of Upadhyay et al. (2009) and that proposed later by Roth et al. (2014b). Experimental details are provided in Table 3. Both the techniques were evaluated in light of over correction of $^{142}\text{Nd}/^{144}\text{Nd}$ resulting from excessive fractionation correction.

2. Samples and methods

The GPS locations of the four samples collected by us are given in Table S-1 of the Supplementary Information. The samples collected by us are geochemically similar to that presented in the original study, the details of which are provided in the Supplementary Information (Fig. S-1(a), (b) and S-2; Table S-2). The samples were powdered using a tungsten carbide mill and processed for chemical separation of Nd followed by isotopic ratio measurements using TIMS. Four samples with four replicates each were processed. Each replicate is a separate dissolution, passed through column and loaded on filament as an independent sample. Out of four replicates, two replicates were analysed for ¹⁴²Nd/¹⁴⁴Nd using 3-sequence multi-dynamic data acquisition scheme of Upadhyay et al. (2009) and the other two replicates using 2sequence multi-dynamic scheme of Roth et al. (2014b); (Table 3). About $\sim 100 \text{ mg}$ of sample powder was dissolved in a concentrated mixture of HF and HNO₃ (2:1). Complete dissolution was achieved through ~ 1 h of ultra-sonication and heating at 60 °C with closed cap for ~ 12 h. After two rounds of 8 N HNO₃ treatment and drying, the sample was converted to chloride form using 6 N HCl and the final solution was prepared in 1 ml of 1 N HCl for column chemistry. Rare Earth Elements (REEs) were separated from the rock matrix using A-G®50W-X8 cation exchange resin (200-400 mesh) with 6 N HCl as an elutant. Nd was separated from Sm using Ln-spec resin (50-100 µm) from Eichrom[®] with 0.3N HCl as elutant. This step was repeated twice to effectively remove all Sm from Nd cut. Effective removal of Ce from Nd was achieved by using AG®50W-X4 resin (200-400 mesh) with 0.15 M alpha-Hydroxyisobutyric Acid (α -HIBA) at a pH of 4.8 as elutant. To remove α -HIBA from the collected Nd, the eluate was heated with concentrated HNO₃ followed by aqua-regia treatment at 150 °C. Total procedural Nd blank was < 120 pg.

Neodymium was measured as Nd⁺ ions on a Triton TIMS at the Department of Earth Sciences, Pondicherry University, India. Nearly 400 ng of Nd was loaded on to the degassed zone refined Re double filament assembly. The evaporation filament was heated to 1000-1500 mA, at a rate of 20 mA/min and the ionization filament to 4000-4300 mA, at a rate of 150 mA/min. This heating of the filaments was carried out in two steps. The first step involved heating of ionization filament to 3500 mA while evaporation filament was heated to 800 mA. Once the ionization filament reaches 3500 mA, in the second step heating of the evaporation filament was resumed. The Nd⁺ signal for 142 mass appeared only after the evaporation filament reached 1000 mA and the corresponding ionization filament current was 4000 mA. The data acquisition was started when Nd⁺ (for 142 mass) reached about 2.5–4.0 V ($R = 10^{11} \Omega$). The Nd was maintained in a window of 80% to 200% of the original signal using Triton software. Details of the run conditions and the fractionation laws used are given in Tables 3 and 2, respectively. Ames Nd standard was analysed (using both 3- and 2- sequence modes; Table 4) as the terrestrial reference for

Table 3

Cup configuration and run conditions used in this study for Nd isotopic ratios measurements on a Triton.

	equence method - correcte	d for fractionation	ı usıng power law norma	lised exponential law						
Sr. No.	142Nd/144Nd	μ ¹⁴² Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	¹⁴⁵ Nd/ ¹⁴⁴ Nd	μ ¹⁴⁵ Nd	¹⁴⁸ Nd/ ¹⁴⁴ Nd	μ ¹⁴⁸ Nd	¹⁵⁰ Nd/ ¹⁴⁴ Nd	μ ¹⁵⁰ Nd	Av. Fr. Rate (ppm/s)
1	1.1418373 (56)	- 0.2	0.5119596 (18)	0.3484052 (12)	4.3	0.2415821 (16)	6.6	0.2364556 (18)	12.7	0.05
2	1.1418373 (90)	-0.1	0.5119586 (30)	0.3484037 (20)	0.0	0.2415791 (26)	- 2.5	0.2364587 (30)	25.8	0.10
3	1.1418332 (56)	- 3.8	0.5119581 (18)	0.3484045 (12)	2.3	0.2415805 (16)	3.3	0.2364532 (18)	2.5	0.06
4	1.1418288 (58)	- 7.6	0.5119594 (20)	0.3484034 (12)	- 0.9	0.2415802 (16)	2.1	0.2364631 (18)	44.4	0.10
5	1.1418426 (48)	4.5	0.5119590 (16)	0.3484032 (10)	-1.4	0.2415765 (14)	-13.2	0.2364502 (16)	-10.2	0.08
50	1.1418393 (64)	1.6	0.5119611 (20)	0.3484046 (14)	2.6	0.2415794 (18)	- 1.2	0.2364504 (20)	- 9.3	0.04
2	1.1418417 (56)	3.7	0.5119596 (18)	0.3484035 (12)	- 0.6	0.2415795 (16)	- 0.8	0.2364488 (18)	-16.1	0.04
8	1.1418311 (48)	- 5.6	0.5119591 (16)	0.3484044 (10)	2.0	0.2415799 (14)	0.8	0.2364493 (16)	-14.0	0.03
•	1.1418370 (64)	-0.4	0.5119588 (22)	0.3484020 (14)	- 4.9	0.2415808 (20)	4.6	0.2364560 (20)	14.4	0.09
10	1.1418376 (44)	0.1	0.5119582 (14)	0.3484044 (10)	2.0	0.2415801 (14)	1.7	0.2364518 (14)	- 3.4	0.06
11	1.1418405(46)	2.6	0.5119574 (16)	0.3484033 (10)	- 1.1	0.2415788 (16)	- 3.7	0.2364509 (16)	- 7.2	0.05
[2	1.1418363 (44)	- 1.1	0.5119587 (14)	0.3484044 (10)	2.0	0.2415796 (14)	- 0.4	0.2364525 (14)	-0.4	0.05
13	1.1418365 (48)	- 0.9	0.5119588 (16)	0.3484034 (10)	- 0.9	0.2415800 (12)	1.2	0.2364479 (16)	- 19.9	0.10
[4	1.1418413 (62)	3.3	0.5119572 (18)	0.3484025 (14)	- 3.4	0.2415799 (18)	0.8	0.2364491 (20)	- 14.8	0.05
15	1.1418421 (58)	4.0	0.5119568 (18)	0.3484023 (12)	- 4.0	0.2415793 (16)	-1.7	0.2364517 (18)	- 3.8	0.04
Average	1.1418375		0.5119587	0.3484037		0.2415797		0.2364526		
2RSD (ppm)	0.0000071		0.0000042	0.0000053		0.000099		0.0000352		
b) Data for two) sequence method – correc	ted for fractionati	on using simple exponen	tial law						
r. No.	¹⁴² Nd/ ¹⁴⁴ Nd	μ ¹⁴² Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	¹⁴⁵ Nd/ ¹⁴⁴ Nd	u ¹⁴⁵ Nd	¹⁴⁸ Nd/ ¹⁴⁴ Nd	и ¹⁴⁸ Nd	¹⁵⁰ Nd / ¹⁴⁴ Nd	1 ¹⁵⁰ Nd	Av. Fr. Bate (nnm/

(b) Data for two	sequence method – correc	cted for fractiona	tion using simple exponen	tial law						
Sr. No.	142Nd/144Nd	μ ¹⁴² Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	¹⁴⁵ Nd/ ¹⁴⁴ Nd	μ ¹⁴⁵ Nd	¹⁴⁸ Nd/ ¹⁴⁴ Nd	μ ¹⁴⁸ Nd	150Nd/ ¹⁴⁴ Nd	μ ¹⁵⁰ Nd	Av. Fr. Rate (ppm.
1	1.1418353 (60)	- 3.2	0.5119636 (28)	0.3484037 (16)	0.9	0.2415894 (20)	20.3	0.2364629 (27)	44.0	0.01
2	1.1418414 (76)	2.1	0.5119614 (36)	0.3484022 (22)	- 3.4	0.2415820 (26)	- 10.3	0.2364479 (34)	- 19.5	0.02
ŝ	1.1418355 (61)	- 3.1	0.5119622 (28)	0.3484031 (19)	- 0.9	0.2415821 (21)	- 9.9	0.2364494 (27)	-13.1	0.04
4	1.1418374 (54)	-1.4	0.5119639 (26)	0.3484017 (16)	- 4.9	0.2415905 (19)	24.8	0.2364600 (25)	31.7	0.004
J.	1.1418371 (54)	-1.7	0.5119645 (25)	0.3484051 (16)	4.9	0.2415840 (19)	-2.1	0.2364506 (26)	- 8.0	0.03
9	1.1418355 (57)	- 3.1	0.5119636 (27)	0.3484038 (17)	1.1	0.2415841 (20)	- 1.7	0.2364507 (26)	- 7.6	0.02
7	1.1418330 (69)	- 5.3	0.5119669 (32)	0.3484023 (20)	- 3.2	0.2415852 (23)	2.9	0.2364515 (32)	- 4.2	0.05
8	1.1418388 (57)	-0.2	0.5119662 (28)	0.3484060 (17)	7.5	0.2415833 (19)	- 5.0	0.2364489 (28)	-15.2	0.06
6	1.1418436	4.0	0.5119671 (64)	0.3484030 (41)	- 1.1	0.2415812 (48)	- 13.7	0.2364492 (66)	-14.0	0.10
	(136)									
10	1.1418393 (50)	0.3	0.5119649 (24)	0.3484023 (15)	- 3.2	0.2415840 (18)	-2.1	0.2364531(23)	2.5	0.03
11	1.1418376 (53)	- 1.2	0.5119647 (27)	0.3484024 (16)	- 2.9	0.2415819 (18)	- 10.8	0.2364493 (24)	- 13.5	0.06
12	1.1418426 (56)	3.2	0.5119643 (26)	0.3484042 (16)	2.3	0.2415815 (19)	- 12.4	0.2364494 (24)	- 13.1	0.09
13	1.1418364 (50)	- 2.3	0.5119634 (26)	0.3484050 (14)	4.6	0.2415889 (18)	18.2	0.2364620 (23)	40.2	0.05
14	1.1418334 (52)	- 4.9	0.5119649 (23)	0.3484025 (15)	- 2.6	0.2415882 (17)	15.3	0.2364598(24)	30.9	0.06
15	1.1418460 (54)	6.1	0.5119666 (26)	0.3484036 (16)	0.6	0.2415842 (19)	-1.2	0.2364492 (25)	-14.0	0.10
16	1.1418486 (58)	8.4	0.5119664 (27)	0.3484064 (17)	8.6	0.2415833(20)	- 5.0	0.2364496 (27)	-12.3	0.03
17	1.1418320 (46)	-6.1	0.5119624 (20)	0.3484011 (13)	- 6.6	0.2415842 (15)	- 1.2	0.2364496 (20)	-12.3	0.10
18	1.1418482 (52)	8.1	0.5119675 (25)	0.3484026 (16)	- 2.3	0.2415833 (18)	- 5.0	0.2364520(23)	- 2.1	0.10
Average	1.1418390		0.5119647	0.3484034		0.2415845		0.2364525		
2RSD (ppm)	0.000089		0.0000070	0.0000085		0.0000235		0.0000420		

Table 5

Nd isotopic ratio data for Khariar samples analysed in this work.

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Sample ID	Method	¹⁴² Nd/ ¹⁴⁴ Nd	$\mu^{142}\text{Nd}$	¹⁴³ Nd/ ¹⁴⁴ Nd	¹⁴⁵ Nd/ ¹⁴⁴ Nd	¹⁴⁸ Nd/ ¹⁴⁴ Nd	¹⁵⁰ Nd/ ¹⁴⁴ Nd	¹⁴⁰ Ce/ ¹⁴² Nd	Av. Fr. Rate (ppm/s)
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	OD-8/1									
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	(1)	3- sequence	1,1418219 (38)	- 13.7	0.5116305 (12)	0.3484050 (9)	0.2415817 (11)	0.2364475 (13)	1.08E-04	0.02
$ \begin{array}{c} \text{Average} \\ (3) & 2 \text{-sequence} \\ 1.4 1825 (130) & -9.6 \\ 0.5116315 (27) & 0.3484049 (4) \\ 2 \text{-sequence} \\ 1.4 1830 (24) & -8.1 \\ 0.5116386 (19) \\ 0.3484049 (12) \\ 0.241580 (21) \\ 0.241580 (21) \\ 0.2264516 (20) \\ 2.072 65 \\ 0.06 \\ 0.2264516 (20) \\ 2.072 65 \\ 0.06 $	(2)	3- sequence	1.1418311 (41)	- 5.6	0.5116324	0.3484047 (8)	0.2415802 (11)	0.2364510 (13)	8.31E-05	0.08
					(146)					
	Average		1.1418265 (130)	- 9.6	0.5116315 (27)	0.3484049 (4)	0.2415810 (21)	0.2364493 (49)		
	(3)	2-sequence	1.1418298 (42)	-8.1	0.5116386 (19)	0.3484049 (12)	0.2415835 (14)	0.2364485 (19)	9.25E-05	0.05
Average 1.1418305 (20) -7.4 0.5116383 (8) 0.3484043 (17) 0.2415841 (17) 0.2364501 (14) OD-7.1 - - - - - - - 0.2415803 (12) 0.2364503 (13) 5.47E.05 0.08 (2) 3-sequence 1.1418329 (49) 1.2 0.5116776 (15) 0.3484044 (10) 0.2415580 (16) 0.2364546 (17) 1.25E.05 0.06 Average 1.1418331 (165) -7.5 0.51166758 (51) 0.3484046 (14) 0.2415580 (16) 0.2364559 (13) 3.58E.05 0.10 (4) 2-sequence 1.1418313 (25) -6.0 0.5116691 (21) 0.3484066 (14) 0.2415859 (16) 0.2364532 (73) 3.29E.05 0.07 Average 1.1418309 (45) -5.8 0.5116573 (14) 0.3484044 (12) 0.2415815 (16) 0.236453 (13) 6.67E.05 0.02 (2) 3-sequence 1.1418209 (45) -5.8 0.5116573 (14) 0.3484044 (12) 0.2415812 (15) 0.2364530 (12) 0.46463 (19) 0.48464 (12) 0.2415814 (13) 0.3264546 (13) 0.58E.05 0.01 (2) 3-sequence 1.1418269 (40) -8.	(4)	2- sequence	1.1418312 (45)	- 6.8	0.5116380 (21)	0.3484037 (13)	0.2415847 (15)	0.2364516 (20)	2.07E-05	0.06
OD-7/1 Sequence 1.141827 (41) - 9.0 0.5116740 (12) 0.3484036 (9) 0.24155803 (12) 0.2364536 (17) 1.25E-05 0.06 Average 1.1418331 (165) -3.9 0.5116776 (15) 0.3484040 (11) 0.2415590 (16) 0.2364536 (17) 1.25E-05 0.06 Average 1.1418331 (165) -3.9 0.5116758 (51) 0.3484040 (11) 0.2415580 (16) 0.2364504 (19) 3.56E-05 0.10 (4) 2.sequence 1.1418322 (47) -6.0 0.5116691 (21) 0.3484056 (14) 0.2415849 (58) 0.2364453 (19) 3.56E-05 0.07 Average 1.1418320 (41) -7.7 0.5116695 (18) 0.3484040 (10) 0.2415849 (58) 0.2364463 (19) 8.28E-05 0.01 (2) 3.sequence 1.1418206 (417) -9.4 0.5116595 (18) 0.3484044 (10) 0.2415815 (16) 0.2364463 (19) 8.28E-05 0.02 (3) 2.sequence 1.1418220 (417) -9.4 0.5116595 (18) 0.3484046 (11) 0.2415817 (13) 0.3264488 (18) 5.98E-05 0.02 Average	Average		1.1418305 (20)	- 7.4	0.5116383 (8)	0.3484043 (17)	0.2415841 (17)	0.2364501 (44)		
(1) 3-sequence 1.1418272 (41) -9.0 0.5116740 (12) 0.3484036 (9) 0.2415803 (12) 0.2364536 (13) 5.47E-05 0.08 (2) 3-sequence 1.1418339 (165) -3.9 0.5116776 (15) 0.3484040 (11) 0.2415799 (15) 0.2364526 (17) 1.25E-05 0.06 (3) 2-sequence 1.1418320 (47) -6.0 0.5116878 (13) 0.3484040 (11) 0.2415826 (14) 0.2364550 (12) 3.56E-05 0.10 (4) 2-sequence 1.1418322 (47) -6.0 0.5116808 (13) 0.3484044 (10) 0.2415850 (16) 0.2364550 (13) 3.56E-05 0.01 (4) 3-sequence 1.1418320 (47) -6.0 0.51165073 (14) 0.3484044 (12) 0.2415815 (16) 0.2364559 (12) 0.2364559 (12) 0.2364559 (12) 0.2364559 (12) 0.2364559 (12) 0.236458 (18) 5.98E-05 0.01 (2) 3-sequence 1.1418206 (17) -9.4 0.5116507 (14) 0.3484044 (10) 0.2415815 (16) 0.2364580 (12) 0.2364580 (12) 0.2364580 (12) 0.2364580 (13) 6.48E-05 0.02 (4) 2-sequence 1.1418209 (40) -9.3 0.5116612 (1	OD-7/1									
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	(1)	3- sequence	1.1418272 (41)	- 9.0	0.5116740 (12)	0.3484036 (9)	0.2415803 (12)	0.2364503 (13)	5.47E-05	0.08
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	(2)	3- sequence	1.1418389 (49)	1.2	0.5116776 (15)	0.3484044 (10)	0.2415799 (15)	0.2364546 (17)	1.25E-05	0.06
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Average		1.1418331 (165)	- 3.9	0.5116758 (51)	0.3484040 (11)	0.2415801 (6)	0.2364525 (61)		
(4) 2-sequence 1.1418322 (47) -6.0 0.5116812 (21) 0.3484056 (14) 0.2415869 (16) 0.2364559 (23) 3.29E-05 0.07 Average 0.06/1 -6.7 0.5116808 (13) 0.3484058 (24) 0.2415849 (56) 0.2364453 (19) 8.28E-05 0.01 (2) 3-sequence 1.1418206 (17) -9.4 0.5116595 (18) 0.3484044 (10) 0.2415815 (16) 0.2364453 (19) 8.28E-05 0.01 (3) 2-sequence 1.1418206 (117) -9.4 0.5116584 (31) 0.3484046 (10) 0.2415813 (13) 0.2364453 (18) 5.98E-05 0.10 (4) 2-sequence 1.1418206 (10) -8.8 0.5116601 (20) 0.3484056 (11) 0.2415811 (31) 0.2364583 (18) 7.68E-05 0.02 (4) 2-sequence 1.1418206 (40) -8.4 0.5116601 (20) 0.3484050 (11) 0.2415813 (11) 0.2364564 (13) 6.48E-05 0.02 (4) 3-sequence 1.1418206 (40) -9.3 0.5115282 (11) 0.3484051 (8) 0.2415841 (21) 0.2364566 (12) 1.20E-05 0.02 (1) 3-sequence 1.1418245 (42) -10.6 0.5	(3)	2-sequence	1.1418304 (41)	- 7.5	0.5116803 (19)	0.3484049 (11)	0.2415828 (14)	0.2364504 (19)	3.56E-05	0.10
Average1.1418313 (25) -6.7 $0.5116808 (13)$ $0.3484058 (24)$ $0.2415849 (58)$ $0.2364532 (78)$ DD-6/1 (1) 3 -sequence $1.1418226 (57)$ -13.0 $0.5116595 (18)$ $0.3484044 (12)$ $0.2415815 (16)$ $0.2364463 (19)$ $8.28E-5$ 0.01 (2) 3 -sequence $1.141830 (45)$ -9.4 $0.551657 (14)$ $0.3484044 (10)$ $0.2415809 (12)$ $0.236458 (14)$ $6.76E-05$ 0.02 (3) 2 -sequence $1.141826 (17)$ -9.4 $0.5116584 (31)$ $0.348404 (10)$ $0.2415811 (13)$ $0.2364583 (18)$ $7.68E-05$ 0.10 (4) 2 -sequence $1.1418382 (41)$ -0.7 $0.5116601 (20)$ $0.3484060 (11)$ $0.2415817 (14)$ $0.2364583 (18)$ $7.68E-05$ 0.02 Average $1.1418382 (41)$ -0.7 $0.5116601 (4)$ $0.3484060 (11)$ $0.2415817 (14)$ $0.2364581 (18)$ $7.68E-05$ 0.02 Average $1.141832 (37)$ -1.7 $0.5116601 (4)$ $0.3484061 (1)$ $0.2415814 (2)$ $0.2364536 (13)$ 0.02 (4) 3 -sequence $1.1418269 (40)$ -9.3 $0.5115282 (11)$ $0.348405 (17)$ $0.2364580 (12)$ $1.20E-05$ 0.02 (4) 3 -sequence $1.1418269 (42)$ -16.0 $0.511530 (17)$ $0.2415811 (16)$ $0.2364526 (7)$ $(1.20E-05)$ 0.02 (4) 3 -sequence $1.141826 (42)$ -16.0 $0.5115413 (19)$ $0.348405 (12)$ $0.2415817 (15)$ $0.2364526 (12)$ $1.20E-05$ 0.02 <t< td=""><td>(4)</td><td>2- sequence</td><td>1.1418322 (47)</td><td>- 6.0</td><td>0.5116812 (21)</td><td>0.3484066 (14)</td><td>0.2415869 (16)</td><td>0.2364559 (23)</td><td>3.29E-05</td><td>0.07</td></t<>	(4)	2- sequence	1.1418322 (47)	- 6.0	0.5116812 (21)	0.3484066 (14)	0.2415869 (16)	0.2364559 (23)	3.29E-05	0.07
OD-6/1 Image: Control of the sequence	Average	*	1.1418313 (25)	- 6.7	0.5116808 (13)	0.3484058 (24)	0.2415849 (58)	0.2364532 (78)		
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	OD-6/1									
(1) 3-sequence 1.1418209 (45) -5.8 0.5116573 (14) 0.3484044 (10) 0.2415810 (12) 0.2364554 (14) 6.76E-05 0.02 (3) 2-sequence 1.1418209 (40) -8.8 0.5116573 (14) 0.3484044 (10) 0.2415812 (8) 0.2364554 (14) 6.76E-05 0.02 (4) 2-sequence 1.1418320 (40) -8.8 0.5116601 (20) 0.3484064 (11) 0.24158176 (14) 0.2364583 (18) 7.68E-05 0.02 (4) 2-sequence 1.1418326 (13) -0.7 0.5116601 (17) 0.3484064 (11) 0.2415876 (14) 0.2364536 (13) 6.48E-05 0.02 (4) 2-sequence 1.1418269 (40) -9.3 0.5115282 (11) 0.3484064 (7) 0.2415813 (11) 0.2364536 (12) 1.20E-05 0.02 (4) 3-sequence 1.1418269 (40) -9.3 0.5115335 (11) 0.3484064 (7) 0.2415813 (11) 0.2364536 (12) 1.20E-05 0.02 (4) 3-sequence 1.1418269 (40) -9.3 0.5115313 (19) 0.3484050 (12) 0.2415813 (11) 0.2364536 (12) 1.20E-05 0.02 (4) 3-sequence 1.1418249 (32)	(1)	3- seguence	1 1418226 (57)	- 13.0	0 5116595 (18)	0 3484044 (12)	0 2415815 (16)	0 2364463 (19)	8 28E-05	0.01
Construction 1.1418268 (117) -9.4 0.5116584 (31) 0.3484044 (0) 0.2415812 (8) 0.23645509 (129) (3) 2-sequence 1.1418268 (117) -9.4 0.5116584 (31) 0.3484044 (0) 0.2415812 (8) 0.23645509 (129) (4) 2-sequence 1.1418382 (41) -0.7 0.5116606 (14) 0.3484064 (11) 0.2415876 (14) 0.2364583 (18) 7.68E-05 0.02 Average 1.141836 (130) -4.7 0.5116606 (14) 0.3484060 (11) 0.2415814 (12) 0.2364536 (13) 6.48E-05 0.02 OD-3/3 (1) 3-sequence 1.1418269 (40) -9.3 0.5115325 (11) 0.3484051 (8) 0.2415813 (11) 0.2364536 (12) 1.20E-05 0.02 (4) 3-sequence 1.1418259 (42) -10.6 0.5115309 (75) 0.3484050 (4) 0.2415809 (11) 0.2364580 (12) 1.20E-05 0.02 (4) 3-sequence 1.1418254 (42) -10.6 0.5115409 (75) 0.3484051 (2) 0.2415871 (5) 0.2364580 (20) 8.09E-05 0.01 (3) 2-sequence 1.1418245 (23) -5.1 0.5115408 (19) 0.3484023 (12) 0.2415853 (15)	(2)	3- sequence	1 1418309 (45)	- 5.8	0.5116573 (14)	0.3484044(10)	0.2415809(12)	0.2364554 (14)	6 76E-05	0.02
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Average	o bequence	1.1418268 (117)	- 9.4	0.5116584 (31)	0.3484044 (0)	0.2415812 (8)	0.2364509 (129)	01/02/00	0.02
(4) 2- sequence 1.1418382 (41) -0.7 0.5116611 (17) 0.3484064 (11) 0.2415876 (14) 0.2364583 (18) 7.68E-05 0.02 Average 1.1418336 (130) -4.7 0.511660 (14) 0.3484060 (11) 0.2415876 (14) 0.2364583 (18) 7.68E-05 0.02 OD-3/3 - - - - - 0.5115282 (11) 0.3484051 (8) 0.2415813 (11) 0.2364546 (13) 6.48E-05 0.02 (4) 3- sequence 1.1418239 (37) - 1.9 0.5115335 (11) 0.3484050 (12) 0.2415810 (11) 0.2364546 (13) 6.48E-05 0.02 Average 1.1418254 (42) - 1.06 0.5115309 (75) 0.3484050 (12) 0.2415817 (15) 0.2364580 (20) 8.09E-05 0.01 (3) 2-sequence 1.1418312 (39) - 6.9 0.5115413 (19) 0.3484050 (12) 0.2415853 (15) 0.2364580 (20) 8.09E-05 0.01 (3) 2-sequence 1.1418322 (30) - 6.0 0.5115411 (7) 0.3484051 (12) 0.2415856 (34) 0.2364523 (17) 7.60E-05 0.08 Average 1.1418326 (52	(3)	2-sequence	1.1418290 (40)	- 8.8	0.5116601 (20)	0.3484056 (11)	0.2415811 (13)	0.2364488 (18)	5.98E-05	0.10
Average1.1418336 (130) -4.7 0.5116606 (14)0.3484060 (11)0.2415844 (92)0.2364536 (134)OD-3/3(1)3 - sequence1.1418269 (40) -9.3 0.5115282 (11)0.3484051 (8)0.2415813 (11)0.2364546 (13)6.48E-050.02(4)3 - sequence1.1418239 (37) -11.9 0.5115335 (11)0.3484050 (4)0.2415809 (11)0.2364566 (12)1.20E-050.02(4)3 - sequence1.1418254 (42) -10.6 0.5115309 (75)0.3484050 (4)0.2415801 (6)0.2364526 (57)(2)2 -sequence1.1418311 (43) -6.9 0.5115413 (19)0.3484050 (12)0.2415877 (15)0.2364580 (20)8.09E-050.01(3)2 - sequence1.1418322 (30) -5.1 0.5115408 (19)0.3484037 (38)0.2415865 (34)0.2364566 (18)2.13E-050.08BHVO-2(C)3 -sequence1.1418246 (52) -11.3 0.5129695 (16)0.3484046 (12)0.2415865 (34)0.2364523 (17)7.60E-050.08(C)3 -sequence1.1418346 (52) -11.3 0.5129703(19)0.3484046 (12)0.2415805 (24)0.2364518(14)(B)2 - sequence1.1418345(279) -2.63 0.5129723(19)0.34840451(13)0.2415805(24)0.2364531(18)1.79E-050.04(B)2 - sequence1.1418365(49) -2.19 0.5129762(21)0.34840453(13)0.2415883(16)0.23645318(14)(2.70E-05)0.08(C)-22 - sequence1.1418305(49) -2.19 0.5129763(20)	(4)	2- sequence	1.1418382 (41)	- 0.7	0.5116611 (17)	0.3484064 (11)	0.2415876 (14)	0.2364583 (18)	7.68E-05	0.02
OD-3/3 (1) 3- sequence 1.1418269 (40) - 9.3 0.5115282 (11) 0.3484051 (8) 0.2415813 (11) 0.2364546 (13) 6.48E-05 0.02 (4) 3- sequence 1.1418239 (37) - 11.9 0.5115335 (11) 0.3484048 (7) 0.2415809 (11) 0.2364566 (12) 1.20E-05 0.02 Average 1.1418254 (42) - 10.6 0.5115309 (75) 0.3484050 (12) 0.2415811 (6) 0.2364526 (57) (2) 2-sequence 1.1418311 (43) - 6.9 0.5115413 (19) 0.3484050 (12) 0.2415877 (15) 0.2364580 (20) 8.09E-05 0.01 (3) 2- sequence 1.1418322 (30) - 5.1 0.5115408 (19) 0.3484037 (38) 0.2415865 (34) 0.2364563 (48) BHVO-2 (A) 3-sequence 1.1418246 (52) - 11.3 0.5129695 (16) 0.3484037 (38) 0.2415865 (34) 0.2364553 (17) 7.60E-05 0.08 (C) 3-sequence 1.1418246 (52) - 11.3 0.5129703(19) 0.3484034(13) 0.2415894 (15) 0.2364518(14) 0.2464513(18) 1.79E-05 0.04 Average 1.1418345(279) - 2.63	Average		1.1418336 (130)	- 4.7	0.5116606 (14)	0.3484060 (11)	0.2415844 (92)	0.2364536 (134)		
(1) 3- sequence 1.1418269 (40) - 9.3 0.5115282 (11) 0.3484051 (8) 0.2415813 (11) 0.2364546 (13) 6.48E-05 0.02 (4) 3- sequence 1.1418239 (37) -11.9 0.5115335 (11) 0.3484048 (7) 0.2415809 (11) 0.2364566 (12) 1.20E-05 0.02 Average 1.1418254 (42) -10.6 0.5115309 (75) 0.3484050 (12) 0.2415811 (6) 0.2364526 (57) (2) 2-sequence 1.1418311 (43) -6.9 0.5115413 (19) 0.3484050 (12) 0.2415877 (15) 0.2364580 (20) 8.09E-05 0.01 (3) 2-sequence 1.1418322 (30) -5.1 0.5115408 (19) 0.3484037 (38) 0.2415853 (15) 0.2364563 (48) 0.2364563 (48) BHVO-2 (A) 3-sequence 1.1418322 (30) -6.0 0.5119705 (16) 0.3484046 (12) 0.2415865 (34) 0.2364553 (17) 7.60E-05 0.08 (C) 3-sequence 1.1418246 (52) -11.3 0.5129703 (19) 0.3484046 (12) 0.2415871 (15) 0.2364513 (18) 1.79E-05 0.04 Average 1.1418345 (279) -2.63 0.5129702(19)	00.2/2									
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	(1)	3- sequence	1 1418269 (40)	- 9 3	0 5115282 (11)	0 3484051 (8)	0 2415813 (11)	0 2364546 (13)	6 48F-05	0.02
Average $1.1418246(42)$ -10.6 $0.5115309(75)$ $0.3484050(4)$ $0.2415811(6)$ $0.2364526(57)$ (2)2-sequence $1.141832(39)$ -6.9 $0.5115309(75)$ $0.3484050(4)$ $0.2415871(16)$ $0.2364526(57)$ (3)2-sequence $1.141832(39)$ -5.1 $0.5115408(19)$ $0.3484050(12)$ $0.2415851(16)$ $0.2364526(58)$ (3)2-sequence $1.1418322(30)$ -6.0 $0.5115411(7)$ $0.3484037(38)$ $0.2415853(15)$ $0.2364526(18)$ $2.13E-05$ 0.08 Average $1.1418322(30)$ -6.0 $0.5115411(7)$ $0.3484037(38)$ $0.2415865(34)$ $0.2364523(17)$ $7.60E-05$ 0.08 BHVO-2(A)3-sequence $1.1418246(52)$ -11.3 $0.5129723(19)$ $0.3484034(13)$ $0.2415897(17)$ $0.2364523(17)$ $7.60E-05$ 0.08 (C)3-sequence $1.1418345(279)$ -2.63 $0.5129723(19)$ $0.3484034(13)$ $0.2415895(24)$ $0.2364513(18)$ $1.79E-05$ 0.04 Average $1.1418345(279)$ -2.63 $0.5129702(21)$ $0.3484053(13)$ $0.2415805(24)$ $0.2364513(18)$ $1.79E-05$ 0.04 (B)2-sequence $1.1418339(42)$ -4.47 $0.5129732(19)$ $0.3484053(13)$ $0.2415805(24)$ $0.2364533(19)$ $2.70E-05$ 0.08 (C)-22-sequence $1.1418339(42)$ -4.47 $0.5129732(19)$ $0.3484057(13)$ $0.2415884(14)$ $0.2364533(19)$ $2.70E-05$ 0.08 (C)-22-sequence $1.1418339(42)$	(4)	3- sequence	1 1418239 (37)	- 11.9	0.5115232 (11)	0.3484048 (7)	0.2415809(11) 0.2415809(11)	0.2364506 (12)	1.20E-05	0.02
Intractor	Average	o bequence	1 1418254 (42)	- 10.6	0.5115309 (75)	0.3484050 (4)	0 2415811 (6)	0 2364526 (57)	11202 00	0.02
(3) 2- sequence 1.1418332 (39) -5.1 0.5115408 (19) 0.3484023 (12) 0.2415853 (15) 0.2364546 (18) 2.13E-05 0.08 Average 1.1418322 (30) -6.0 0.5115411 (7) 0.3484037 (38) 0.2415855 (34) 0.2364563 (48) 2.13E-05 0.08 BHVO-2 (A) 3-sequence 1.1418246 (52) -11.3 0.5129695 (16) 0.3484034 (13) 0.2415861 (15) 0.2364553 (17) 7.60E-05 0.08 (C) 3-sequence 1.1418246 (52) -11.3 0.5129723 (19) 0.3484034 (13) 0.2415897 (17) 0.2364513 (18) 1.79E-05 0.04 Average 1.1418345 (279) -2.63 0.5129709 (39) 0.3484034 (13) 0.2415805 (24) 0.2364513 (18) 1.79E-05 0.04 Average 1.1418345 (279) -2.63 0.5129709 (29) 0.3484040 (18) 0.2415805 (24) 0.2364518 (14) 1.49E-04 0.07 (B) 2- sequence 1.1418339 (42) -4.47 0.5129732 (19) 0.3484053 (13) 0.2415883 (14) 0.2364533 (19) 2.70E-05 0.08 (C)-2 2- sequence 1.1418339 (42) -4.47 0.5129	(2)	2-sequence	1.1418311 (43)	- 6.9	0.5115413 (19)	0.3484050(12)	0.2415877 (15)	0.2364580 (20)	8.09E-05	0.01
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BHV0-2 (A) 3-sequence 1.1418246 (52) - 11.3 0.5129695 (16) 0.3484046 (12) 0.2415814 (15) 0.2364523 (17) 7.60E-05 0.08 (C) 3-sequence 1.1418444(57) 6.04 0.5129723(19) 0.3484034(13) 0.2415797(17) 0.2364513(18) 1.79E-05 0.04 Average 1.1418345(279) - 2.63 0.5129709(39) 0.3484040(18) 0.2415805(24) 0.2364518(14) (B) 2- sequence 1.1418365(49) - 2.19 0.5129762(21) 0.3484053(13) 0.2415834(16) 0.2364518(14) (B)-2 2- sequence 1.1418339(42) - 4.47 0.5129732(29) 0.3484057(13) 0.2415834(16) 0.2364533(19) 2.70E-05 0.08 (C)-2 2- sequence 1.1418339(42) - 4.47 0.5129736(20) 0.3484036(12) 0.2415841(15) 0.2364533(19) 2.70E-05 0.08 (C)-2 2- sequence 1.1418309(64) 1.14 0.5129753(20) 0.3484036(12) 0.2415841(15) 0.2364532(0) 6.80E-05 0.20 Average 1.1418369(64)	Average		1.1418322 (30)	- 6.0	0.5115411 (7)	0.3484037 (38)	0.2415865 (34)	0.2364563 (48)		
Introduct Sequence 1.1418246 (52) - 11.3 0.5129695 (16) 0.3484046 (12) 0.2415814 (15) 0.2364523 (17) 7.60E-05 0.08 (C) 3-sequence 1.1418444(57) 6.04 0.5129723(19) 0.3484034(13) 0.2415797(17) 0.2364513(18) 1.79E-05 0.04 Average 1.1418345(279) - 2.63 0.5129709(39) 0.3484040(18) 0.2415805(24) 0.2364518(14) . (B) 2- sequence 1.1418365(49) - 2.19 0.5129762(21) 0.3484053(13) 0.2415834(16) 0.2364518(14) . 0.07 (B)-2 2- sequence 1.1418339(42) - 4.47 0.5129732(19) 0.3484057(13) 0.2415834(16) 0.2364533(19) 2.70E-05 0.08 (C)-2 2- sequence 1.1418339(42) - 4.47 0.5129736(20) 0.3484036(12) 0.2415841(15) 0.2364533(19) 2.70E-05 0.08 (C)-2 2- sequence 1.1418309(64) 1.14 0.5129753(20) 0.3484036(12) 0.2415841(15) 0.2364532(10) 0.3686050 (C)-2	BHVO 2									
(C) 3-sequence 1.1418444(57) 6.04 0.51297023(19) 0.3484034(13) 0.2415797(17) 0.2364513(18) 1.79E-05 0.04 Average 1.1418345(279) - 2.63 0.5129709(39) 0.3484034(13) 0.2415797(17) 0.2364513(18) 1.79E-05 0.04 (B) 2- sequence 1.1418345(279) - 2.63 0.5129702(21) 0.3484040(18) 0.2415805(24) 0.2364513(18) 1.79E-05 0.04 (B) 2- sequence 1.1418345(279) - 2.19 0.5129702(21) 0.34840453(13) 0.2415834(16) 0.2364533(19) 2.70E-05 0.08 (B)-2 2- sequence 1.141839(42) - 4.47 0.512973(20) 0.3484049(12) 0.2415841(15) 0.2364533(19) 2.70E-05 0.08 (C)-2 2- sequence 1.1418309(64) 1.14 0.5129753(20) 0.3484049(22) 0.2415841(15) 0.2364532(10) 0.2364531(169) 2.70E-05 0.08 (C)-2 2- sequence 1.1418369(64) 1.14 0.5129753(25) 0.3484049(22) 0.2415841(12) 0.23645310(169) 2.70E-0	(A)	3-sequence	1 1418246 (52)	- 11.3	0 5129695 (16)	0.3484046 (12)	0 2415814 (15)	0 2364523 (17)	7 60E-05	0.08
Average 1.1418345(279) - 2.63 0.5129702(39) 0.3484040(18) 0.2415805(24) 0.2364518(14) (B) 2- sequence 1.14183365(49) - 2.19 0.5129762(21) 0.348405(13) 0.2415805(24) 0.2364518(14) (B)-2 2- sequence 1.1418339(42) - 4.47 0.5129752(21) 0.3484057(13) 0.2415851(14) 0.2364513(19) 2.70E-05 0.08 (C)-2 2- sequence 1.1418403(45) 1.14 0.5129763(20) 0.3484057(13) 0.2415841(15) 0.2364526(20) 6.80E-05 0.20 Average 1.1418369(64) - 1.84 0.5129753(35) 0.3484049(22) 0.2415844(24) 0.2364510(69)	(C)	3-sequence	1 1418444(57)	6.04	0.5129723(19)	0.3484034(13)	0 2415797(17)	0 2364513(18)	1 79E-05	0.04
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Average	2 sequence	1.1418345(279)	- 2.63	0.5129709(39)	0.3484040(18)	0.2415805(24)	0.2364518(14)	, , 2 00	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	(B)	2- sequence	1.1418365(49)	- 2.19	0.5129762(21)	0.3484053(13)	0.2415834(16)	0.2364470(22)	1.49E-04	0.07
CD-2 2- sequence 1.1418403(45) 1.14 0.5129763(20) 0.3484036(12) 0.2415841(15) 0.2364526(20) 6.80E-05 0.20 Average 1.1418369(64) -1.84 0.5129753(35) 0.3484049(22) 0.24158441(24) 0.2364510(69)	(B)-2	2- sequence	1.1418339(42)	- 4.47	0.5129732(19)	0.3484057(13)	0.2415858(14)	0.2364533(19)	2.70E-05	0.08
Average 1.1418369(64) - 1.84 0.5129753(35) 0.3484049(22) 0.2415844(24) 0.2364510(69)	(C)-2	2- sequence	1.1418403(45)	1.14	0.5129763(20)	0.3484036(12)	0.2415841(15)	0.2364526(20)	6.80E-05	0.20
	Average	*	1.1418369(64)	- 1.84	0.5129753(35)	0.3484049(22)	0.2415844(24)	0.2364510(69)		

Note: 3-sequence and 2-sequence μ^{142} Nd values were determined using AMES Nd standard ¹⁴²Nd/¹⁴⁴Nd of 1.1418375 and 1.4148390, respectively. It should be noted that the 3-sequence data have been corrected for mass fractionation using a power- normalized exponential law, whereas that of 2-sequence using exponential law. The internal precision (2SE) is given in parentheses. For average values, 2 standard-deviations (2SD) are given in the parentheses. Av. Fr. Rate = Average Fractionate Rate = slope of the linear regression in a plot of ¹⁴⁶Nd/¹⁴⁴Nd from the first sequence versus time.

calculation of μ^{142} Nd of samples. For the 3-sequence data acquisition scheme, each run lasted for about 6–7 h and that for the 2-sequence data acquisition scheme, around 5 h. Isobaric interferences on Nd isotopes from Sm and Ce were monitored by measuring ¹⁴⁷Sm and ¹⁴⁰Ce, respectively. The ¹⁴⁰Ce/¹⁴²Nd for the analysed samples is given in Table 5. The maximum and minimum values of ¹⁴⁰Ce/¹⁴²Nd were 1.49 × 10⁻⁴ and 1.20 × 10⁻⁵, respectively. ¹⁴⁷Sm/¹⁴⁴Nd values never exceeded 7.65 × 10⁻⁷ and hence deemed insignificant for any correction. Nonetheless, interference corrections for Ce and Sm were applied for the standard and samples. We did not see any significant correlation between the ¹⁴⁰Ce/¹⁴²Nd and the corresponding fractionation corrected ¹⁴²Nd/¹⁴⁴Nd (Fig. S-3; Supplementary Information). This lack of correlation suggests that the interference corrections applied for Ce and Sm did not bias the final ¹⁴²Nd data, therefore were robust.

3. Results

In this study we have used Ames Nd standard for normalization of 142 Nd/ 144 Nd of samples, because it was routinely analysed along with the samples. We have also analysed JNdi-1 standard and Nd from rock standard BHVO-2 for accuracy check. All standards and samples of alkaline silicate rocks from Khariar were analysed using multi-dynamic scheme of data acquisition employing both 3- and 2-sequence modes. Fifteen and eighteen loads of Ames Nd were analysed for the 3-

sequence and 2- sequence modes, respectively. In the 3-sequence mode, isotopic ratios were corrected for mass fractionation using the *power* (*law*)-normalised exponential *law* as in Upadhyay et al. (2009) and our experiment yielded an average value of 1.1418375 for ¹⁴²Nd/¹⁴⁴Nd of Ames Nd with an external reproducibility of 7.1 ppm (Table 4-a). In the 2-sequence mode, the simple exponential fractionation *law* (as in Roth et al., 2014b) was used and an average value of 1.1418390 for ¹⁴²Nd/¹⁴⁴Nd was obtained with an external reproducibility of 8.9 ppm (Table 4-b). Our external precision (2 SD) is lower than that reported by most studies on such experiments (i.e., ~5 ppm), in spite of the fact that the within-run precisions are < 5 ppm (2 SE). The reason for the lower external precision could be because of the aging (> 12 years old) of the Faraday Cups.

Because we have used two different schemes of data acquisition for the samples and BHVO-2, the above two values of ¹⁴²Nd/¹⁴⁴Nd for Ames Nd have been used for determination of μ^{142} Nd (Figs. 1 and 2). μ^{142} Nd values of Khariar samples obtained through a 3-sequence method appear to be slightly negative, albeit unresolvable within 2SD, compared to those obtained through a 2-sequence method (Figs. 1 and 2). It should be noted that the average fractionation rates (r_a), irrespective of the number of sequences, are less than the threshold fractionation rates (r_t) (Table 5).

To understand the role of fractionation correction in the generation of analytical artefacts, the raw/uncorrected data for 67 Ames Nd



Fig. 1. μ^{142} Nd values of 1.48 Ga alkaline rocks from Khariar analysed in this study: (a) data acquired using a 3-sequence multi dynamic mode and corrected for mass fractionation using the *power-normalised exponential law*; (b) data acquired using a 2-sequence multi dynamic mode and corrected for mass fractionation using the *exponential law*; (b) data acquired using a 2-sequence multi dynamic mode and corrected for mass fractionation using the *exponential law*; (b) data acquired using a 2-sequence multi dynamic mode and corrected for mass fractionation using the *exponential law*. The average values of Ames Nd used for calculating μ^{142} Nd in (a) and (b) are 1.1418375 \pm 7.1 ppm (2RSD, *n* = 15) and 1.1418390 \pm 8.9 ppm (2RSD, *n* = 18), respectively. The grey bands encompass \pm 2RSD, external reproducibility, for Ames Nd standard.

aliquots (Table S-3), analysed during and prior to this experiment over a period of 3 years, were corrected for mass fractionation using the (1) *power-normalised exponential law*, and (2) *exponential law*. Data acquired using 2-sequence mode were not included in this exercise, because barring ¹⁴²Nd/¹⁴⁴Nd all other Nd isotopic ratios cannot be corrected for fractionation using the first law (i.e. 1; Tables 1 and 2). Figs. 3 and 4 show results of this exercise. The average values for ¹⁴²Nd/¹⁴⁴Nd, ¹⁴³Nd/¹⁴⁴Nd, ¹⁴⁵Nd/¹⁴⁴Nd, ¹⁴⁸Nd/¹⁴⁴Nd and ¹⁵⁰Nd/¹⁴⁴Nd are given in Table S-3 along with their respective 2SD values. Eleven aliquots of JNdi-1 were analysed along with six loads of Ames Nd (Table 6; Fig. 5). As can be seen in Fig. 5 all Nd isotopic ratios of JNdi-1, although overlap at 2SD with those of the Ames standard, show minor differences in the mean values. The average value of ¹⁴²Nd/¹⁴⁴Nd for JNdi-1 is lower by 6 ppm compared to that of the long term average of Ames Nd (Fig. S-4). Consequently, μ^{142} Nd values of Khariar samples calculated using 142 Nd/ 144 Nd of JNdi-1 lost their apparent deficit from normal (Fig. 6). It should be noted that for comparison we have used isotopic ratios of 142 Nd/ 144 Nd instead of μ^{142} Nd in Fig. 6.

4. Discussion

High precision isotopic ratio measurements by TIMS often requires data acquisition through a multi-dynamic mode, wherein differences in collector efficiencies/factors can be nullified by measuring individual ion beams in multiple Faraday Cups through peak jumping. In such a data acquisition method, the *power-normalised exponential law* is



Fig. 2. μ^{142} Nd of Khariar rocks and BHVO-2, analysed in this study, with respect to the Ames Nd. The data acquired in both 3- and 2-sequences are corrected offline for mass fractionation using both the *power-normalised exponential law* and the *exponential law*. The average values of four replicates for each sample are also plotted with errors; 2SE for individual analyses and 2SD for the average values (Table 5). The external reproducibility (2RSD) for the Ames Nd standard is 7.1 ppm for *power-normalised exponential law* (inter light grey band) and 8.9 ppm for *exponential law* (outer dark grey band).

deemed as the most appropriate method for correction of machine induced mass fractionation (Thirlwall, 1991; Supplementary Information). Whereas Upadhyay et al. (2009) followed the above fractionation correction method to discover μ^{142} Nd anomalies in Khariar alkaline rocks, Roth et al. (2014b) used the simple *exponential law*, generally used in static mode of data acquisition, and rejected the claim of Upadhyay et al. (2009). Our experimentation was aimed at comparing both the methods. Our results, presented above, are discussed below exploring the effects of (1) rate of mass fractionation, (2) choice of law of fractionation correction, and (3) choice of terrestrial standard.

4.1. Rate of mass fractionation

Following Roth et al. (2014b), we have calculated and compared threshold (r_t), average (r_a) and relative (r_f) rates of fractionation for both 3- and 2-sequence multi-dynamic modes. If the external precision for ¹⁴²Nd/¹⁴⁴Nd measurements were considered to be 5 ppm, then the respective r_t values would have been 0.22 ppm/s and 0.44 ppm/s for corresponding time durations of 22.8 s and 11.4 s, respectively. Our isotopic data from all the analyses of samples and standards, by both modes, show $r_a < 0.22$ ppm/s (Tables 4, 5 and S-3), suggesting $r_f < 1$. This is unlike what Roth et al. (2014b) observed in the 3-sequence data of Upadhyay et al. (2009), i.e., $r_f > 1$. Consequently, there was no need for the time correction in the data acquired in our 3-sequence mode to deal with any excess fractionation. Therefore, we infer that the time-gaps between successive sequences in a multi-dynamic mode do not affect the quality of the data acquired (when $r_a < r_t$).

4.2. Correction for mass fractionation

A comparison of the pattern of mass fractionation observed in our data with the theoretical patterns expected from various empirical fractionation laws (Habfast, 1998), with the help of ¹⁴²Nd/¹⁴⁴Nd versus ¹⁵⁰Nd/¹⁴⁴Nd, reveals that the *exponential law* best explains the observed pattern in each individual sequences (Fig. 7), which are equivalent to static mode of data acquisitions. The same method was utilized by Roth et al. (2014b) during the reanalysis of Upadhyay et al. (2009) samples in their 2- sequence mode of data acquisition. As mentioned in Section 3, we have corrected the raw data for Ames Nd, acquired through a 3sequence mode, using both the power-normalised exponential law and the exponential law (Table S-3; Figs. 3 and 4). The details of the laws and correction procedure adapted by us are discussed in detail in the Section-S2 in the Supplementary Information and Table 2, respectively. We observe that: (1) isotopic ratios corrected using the power-normalised exponential law do not show any significant inter correlation (Figs. 3a-d and 4a-d), whereas the exponential law correction method leaves behind substantial residual correlations, especially for ¹⁵⁰Nd/¹⁴⁴Nd and ¹⁴⁸Nd/¹⁴⁴Nd (Figs. 3e-h and 4e-h); (2) power-normalised exponential law noticeably improves precisions (2SD) for ¹⁴³Nd/¹⁴⁴Nd (5.1 ppm), ¹⁴⁵Nd/¹⁴⁴Nd (4.6 ppm) and ¹⁴⁸Nd/¹⁴⁴Nd (11.7 ppm) ratios, compared to those obtained through exponential correction (Table S-3; Figs. 3 and 4), which are 17.4 ppm, 11.7 ppm and 26.5 ppm, respectively. However, the 2SD values for ¹⁵⁰Nd/¹⁴⁴Nd are similar in both the methods because it is obtained from only one sequence (i.e., sequence-1), like that in a static mode but with different β values (Tables 1 and 2). Residual correlations as described above, in (1), are undesirable and



Fig. 3. Plots of Nd isotopic ratios (except for 143 Nd/ 144 Nd) for Ames Nd standard (n = 67) obtained during 3-sequence data acquisition method (data are in Table S-3 in *Supplementary Information*). Each datum (raw, corrected only for interference corrections) is corrected offline using the *power-normalised exponential law* (a–d) as well as the *exponential law* (e–h).

indicate insufficiency of the method/law used for mass fractionation (Andreasen and Sharma, 2009). We, therefore, infer that application of the *power-normalised exponential law* for correction of mass dependent fractionation in a multi-dynamic method is the most appropriate data reduction approach.

Using the *power-normalised exponential law* we corrected data for our samples acquired through both the 3- and 2-sequence modes (Fig. 2), but could not reproduce the anomalies of Upadhyay et al. (2009). We, however, observed that the mean μ^{142} Nd values of some of the sample-replicates plotted outside, on the negative side, the 7.1 ppm range defined for the standard (also corrected using the *power-normalised*)

exponential law). In contrast, sample data from both 3- and 2-sequence modes corrected using the *exponential law* plotted well within the 8.9 ppm range for the standard, corrected using the *exponential law* (Fig. 2). In addition to μ^{142} Nd, inter comparison was also done for stable Nd isotopic compositions acquired through 3-sequence mode and corrected using both the laws (Figs. S-5 and S-6). As can be seen data corrected using the *exponential law* show larger spread compared to those corrected using the *power-normalised exponential law* (Figs. S-5 and S-6). It is therefore evident that it is the method of fractionation correction and not the mode of data acquisition that controls the quality of data.

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Fig. 4. ¹⁴³Nd/¹⁴⁴Nd isotopic ratio of Ames Nd is compared with the other Nd isotopic ratios (n = 67). The data was acquired during 3-sequence method (Table S-3) and corrected offline for mass fractionation using both the laws, i.e. power-normalised exponential law (a - h) and exponential law (e - h).

y = 0.0984x + 0.298

 $R^2 = 0.0465$

0.511977

0.511977

-0.3209x + 0.4008 $R^2 = 0.103$

y = 0.0879x + 1.0968

 $R^2 = 0.0052$

0.511977

0.511977

y = 0.0402x + 0.221

 $R^2 = 0.0031$

0.511967

4.3. Choice of the terrestrial standard

Because the ¹⁴²Nd/¹⁴⁴Nd isotopic ratio of the terrestrial standard is key to the definition of μ^{142} Nd and therefore, to any discovery of anomalous compositions, it is essential that the standard should possess uniform isotopic ratio and truly represent the modern accessible mantle. Several terrestrial standards have been used over the years in ¹⁴²Nd studies- such as LaJolla Nd, JNdi-1, Ames Nd and many in-house standards. Although it is expected that all the stable Nd isotopic ratios and $^{142}\mathrm{Nd}/^{144}\mathrm{Nd}$ of these standards are identical, observations suggest otherwise (e.g., Brandon et al., 2009; O'Neil et al., 2008; Saji et al., 2016; Wakaki and Tanaka, 2012). This can lead to appearance or disappearance of anomalies depending on choice of the standard. We observed such a phenomenon in our data too, when ¹⁴²Nd/¹⁴⁴Nd of Khariar samples were normalised with respect to Ames Nd and JNdi-1. The slight negative μ^{142} Nd obtained using Ames Nd became normal with respect to JNdi-1 (Fig. 6). The mean values of μ^{142} Nd of BHVO-2 measured by us are different with respect to each standard; however, they overlap within the external reproducibility of each standard (Fig. 6).

It should be noted that Upadhyay et al. (2009) used La Jolla as reference whereas Roth et al. (2014b) used JNdi-1. La Jolla possesses higher ¹⁴²Nd/¹⁴⁴Nd with respect to JNdi-1 (Wakaki and Tanaka, 2012), similar to what we observe in the case of Ames Nd (Fig. 6; Table 6). We speculate that the conflicting results obtained from the same aliquots of the Khariar samples by Upadhyay et al. (2009) and Roth et al. (2014b) are a combined effect of the choice of fractionation correction law and terrestrial standard used for calculation of µ.

5. Conclusions

This work evaluates the effects of various analytical methods on the





Fig. 5. Comparison of various Nd isotopic compositions of JNdi-1 (n = 11) and Ames Nd (n = 6) in μ notation. $\mu^{i} = ((^{i}Nd)^{144}Nd)_{iNdi-1} / (^{i}Nd)^{144}Nd)_{Ames}) - 1) \times 10^{6}$, where i = 142, 145, 148 and 150.

Data are given in Table 6. Pink squares represent individual measurements of the JNdi-1and green square (cross - haired) represents average value for JNdi-1. The green shaded area shows external reproducibility (2RSD) for JNdi-1 whereas grey shaded area represents the same for Ames Nd. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 6. This plot shows¹⁴²Nd/¹⁴⁴Nd of the Khariar alkaline rocks and terrestrial standard BHVO-2 analysed by us, where raw data are corrected for mass fractionation using the *power-normalised exponential law* and the *exponential law*. The reference value for Ames Nd is 1.1418375, whereas for JNdi-1 it is 1.1418306. Pink shaded area shows external reproducibility for Ames Nd (2RSD) and yellow shaded area shows external reproducibility (2RSD) of JNdi-1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 7. (a) Plot of uncorrected ¹⁵⁰Nd/¹⁴⁴Nd versus ¹⁴²Nd/¹⁴⁴Nd isotopic ratios for Ames Nd standard acquired using a 3-sequence multi-dynamic mode. ¹⁴²Nd/¹⁴⁴Nd values are from all the three sequences and ¹⁵⁰Nd/¹⁴⁴Nd from the first sequence only. Each point is an average of 10 cycles (one block) and the plot contains data from 752 blocks for 14 analyses. Lines corresponding to different fractionation laws are also shown. (b) and (c) represent enlarged versions of the marked segments of the plot. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 6							
Neodymium	isotopic ratio	s of JNdi-1	and	Ames	analysed	with	JNdi-1.

Sample ID	¹⁴² Nd/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	¹⁴⁵ Nd/ ¹⁴⁴ Nd	¹⁴⁸ Nd/ ¹⁴⁴ Nd	¹⁵⁰ Nd/ ¹⁴⁴ Nd
JNdi-1					
091116	1.1418241 (49)	0.5120979 (17)	0.3484048 (11)	0.2415805 (16)	0.2364540 (19)
111116	1.1418328 (52)	0.5120989 (15)	0.3484037 (12)	0.2415789 (16)	0.2364452 (17)
131116	1.1418327 (54)	0.5121015 (16)	0.3484033 (12)	0.2415806 (16)	0.2364483 (17)
181116	1.1418313 (57)	0.5120997 (18)	0.3484048 (12)	0.2415809 (16)	0.2364513 (17)
191116	1.1418259 (53)	0.5120983 (17)	0.3484047 (11)	0.2415805 (15)	0.2364465 (18)
211116	1.1418377 (54)	0.5121003 (17)	0.3484050 (12)	0.2415792 (16)	0.2364503 (19)
181116	1.1418274 (48)	0.5120976 (15)	0.3484058 (12)	0.2415817 (14)	0.2364501 (17)
211116	1.1418328 (58)	0.5121000 (19)	0.3484044 (12)	0.2415818 (16)	0.2364546 (19)
101116	1.1418272 (52)	0.5120997 (17)	0.3484051 (10)	0.2415796 (15)	0.2364496 (16)
091116	1.1418300 (67)	0.5121006 (23)	0.3484047 (15)	0.2415799 (20)	0.2364483 (22)
221116	1.1418349 (69)	0.5121019 (21)	0.3484047 (14)	0.2415814 (19)	0.2364554 (23)
Average	1.1418306	0.5120997	0.3484046	0.2415805	0.2364503
2SD	0.0000082	0.0000028	0.0000013	0.0000020	0.0000066
Ames Nd					
081116	1.1418269 (54)	0.5119586 (17)	0.3484044 (14)	0.2415819 (17)	0.2364496 (17)
081116	1.1418324 (58)	0.5119571 (18)	0.3484036 (12)	0.2415801 (16)	0.2364490 (18)
101116	1.1418378 (45)	0.5119625 (14)	0.3484052 (11)	0.2415800 (14)	0.2364475 (16)
111116	1.1418339 (51)	0.5119573 (15)	0.3484045 (10)	0.2415816 (14)	0.2364491 (16)
141116	1.1418348 (51)	0.5119585 (17)	0.3484034 (11)	0.2415775 (16)	0.2364435 (17)
141116	1.1418460 (51)	0.5119606 (17)	0.3484039 (11)	0.2415784 (17)	0.2364524 (18)
average	1.1418353	0.5119591	0.3484042	0.2415799	0.2364485
2SD	0.0000127	0.0000042	0.0000013	0.0000035	0.0000059

The data is acquired using three sequence multi dynamic mode and corrected for the fractionation using power-normalised exponential law (normalised to $^{146}Nd/^{144}Nd = 0.7219$). Internal precision is given in brackets (2SE). For average values, 2standard deviation (2SD) is given.

accuracy of ¹⁴²Nd/¹⁴⁴Nd measurements by TIMS and extends this information for the determination of μ^{142} Nd of alkaline rocks from Khariar complex, India. The important report of the negative μ^{142} Nd anomalies in the 1.48 billion year old alkaline silicate rocks from Khariar complex by Upadhyay et al. (2009) needed independent verifications. Following identical analytical procedures on freshly collected samples from the same outcrops we were unsuccessful in reproducing these anomalies. However, we did observe slightly negative μ^{142} Nd, although unresolvable, when Ames Nd was the standard for normalization. These negative values became normal with respect to JNdi-1.

We explored the reasons for the appearance of μ^{142} Nd anomalies in the study of Upadhyay et al. (2009) by investigating the roles of fractionation correction method and choice of the terrestrial standard. Using various combinations of the most commonly employed methods, we observed that in a multi-dynamic mode of data acquisition, the power-normalised exponential law is the right method to correct for the mass fractionation. We also find that the suggested cause (by Roth et al., 2014b) for illusive appearance of negative μ^{142} Nd anomalies in Upadhyay et al. (2009)'s data, the time-gaps between the successive sequences in a multi-dynamic mode, had no role to play in the final corrected value of ¹⁴²Nd/¹⁴⁴Nd. However, the terrestrial standard used by Upadhyay et al. (2009), i.e., LaJolla, with its higher ¹⁴²Nd/¹⁴⁴Nd than that of the currently prevalent JNdi-1, could have been the main cause for appearance of the negative anomalies. We, therefore, propose that all studies on early silicate Earth differentiation using ¹⁴²Nd as a tracer should use a single and homogeneous terrestrial standard, such as JNdi-1, to avoid issues with reproduction of anomalous compositions.

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.chemgeo.2017.06.036.

Acknowledgements

We thank Anirban Chatterjee and Bivin Geo George for their help during the field trips. We greatly appreciate critical comments by R. Carlson on an earlier version of the manuscript. We sincerely thank Maud Boyet and an anonymous reviewer for their constructive comments and suggestions. This work was funded by the Department of Space, Government of India.

References

- Andreasen, R., Sharma, M., 2009. Fractionation and mixing in a thermal ionization mass spectrometer source: implications and limitations for high-precision Nd isotope analyses. Int. J. Mass Spectrom. 285, 49–57. http://dx.doi.org/10.1016/j.ijms.2009. 04.004.
- Bennett, V.C., Brandon, A.D., Nutman, A.P., 2007. Coupled 142Nd-143Nd isotopic evidence for Hadean mantle dynamics. Science 318, 1907–1910. http://dx.doi.org/10. 1126/science.1145928.

Boyet, M., Carlson, R.W., 2006. A new geochemical model for the Earth's mantle inferred

from 146Sm-142Nd systematics. Earth Planet. Sci. Lett. 250, 254–268. http://dx.doi. org/10.1016/j.epsl.2006.07.046.

- Boyet, M., Blichert-Toft, J., Rosing, M., Storey, M., Télouk, P., Albarède, F., 2003. 142Nd evidence for early earth differentiation. Earth Planet. Sci. Lett. 214, 427–442. http:// dx.doi.org/10.1016/S0012-821X(03)00423-0.
- Brandon, A.D., Lapen, T.J., Debaille, V., Beard, B.L., Rankenburg, K., Neal, C., 2009. Reevaluating 142Nd/144Nd in lunar mare basalts with implications for the early evolution and bulk Sm/Nd of the moon. Geochim. Cosmochim. Acta 73, 6421–6445. http://dx.doi.org/10.1016/j.gca.2009.07.015.
- Caro, G., Bourdon, B., Birck, J., 2003. 146Sm 142 Nd evidence from Isua metamorphosed sediments for early differentiation of the Earth's mantle. Nature 423, 428–432. http://dx.doi.org/10.1038/nature01639.1.
- Caro, G., Bourdon, B., Birck, J.L., Moorbath, S., 2006. High-precision 142Nd/144Nd measurements in terrestrial rocks: constraints on the early differentiation of the earth's mantle. Geochim. Cosmochim. Acta 70, 164–191. http://dx.doi.org/10.1016/ j.gca.2005.08.015.
- Habfast, K., 1998. Fractionation correction and multiple collectors in thermal ionization isotope ratio mass spectrometry. Int. J. Mass Spectrom. 176, 133–148. http://dx.doi. org/10.1016/S1387-3806(98)14030-7.
- Kinoshita, N., Paul, M., Collon, P., Deibel, M., DiGiovine, B., Greene, J.P., Henderson, D.J., Jiang, C.L., Marley, S.T., Nakanishi, T., Pardo, R.C., Rehm, K.E., Robertson, D., Scott, R., Schmitt, C., Tang, X.D., Vondrasek, R.Y.A., 2012. A Shorter 146Sm half-life measured and implications for 146Sm-142Nd chronology in the solar sysytem. Science 80 (335), 1614–1617.
- Marks, N.E., Borg, L.E., Hutcheon, I.D., Jacobsen, B., Clayton, R.N., 2014. Samariumneodymium chronology and rubidium-strontium systematics of an Allende calciumaluminum-rich inclusion with implications for 146Sm half-life. Earth Planet. Sci. Lett. 405, 15–24. http://dx.doi.org/10.1016/j.epsl.2014.08.017.
- O'Neil, J., Carlson, R.W., Francis, D., Stevenson, R.K., 2008. Neodymium-142 evidence for Hadean mafic crust. Science 321, 1828–1831. http://dx.doi.org/10.1126/science. 1161925.
- Rizo, H., Boyet, M., Blichert-Toft, J., Rosing, M., 2011. Combined Nd and Hf isotope evidence for deep-seated source of Isua lavas. Earth Planet. Sci. Lett. 312, 267–279. http://dx.doi.org/10.1016/j.epsl.2011.10.014.
- Rizo, H., Boyet, M., Blichert-toft, J., Neil, J.O., Rosing, M.T., Paquette, J., 2012. The elusive Hadean enriched reservoir revealed by 142Nd deficits in Isua Archaean rocks. Nature 490, 96–100. http://dx.doi.org/10.1038/nature11565.
- Roth, A.S.G., Bourdon, B., Mojzsis, S.J., Touboul, M., Sprung, P., Guitreau, M., Blichert-Toft, J., 2013. Inherited 142Nd anomalies in Eoarchean protoliths. Earth Planet. Sci. Lett. 361, 50–57. http://dx.doi.org/10.1016/j.epsl.2012.11.023.
- Roth, A.S.G., Bourdon, B., Mojzsis, S.J., Rudge, J.F., Guitreau, M., Blichert-Toft, J., 2014a. Combined 147,146Sm - 143,142Nd constraints on the longevity and residence time of early terrestrial crust. Geochem. Geophys. Geosyst. 15, 2329–2345. http://dx.doi. org/10.1002/2014GC005313.Received.
- Roth, A.S.G., Scherer, E.E., Maden, C., Mezger, K., Bourdon, B., 2014b. Revisiting the 142Nd deficits in the 1.48 Ga Khariar alkaline rocks. India. Chem. Geol. 386, 238–248. http://dx.doi.org/10.1016/j.chemgeo.2014.06.022.
- Saji, N.S., Wielandt, D., Paton, C., Bizzarro, M., 2016. Ultra-high-precision Nd-isotope measurements of geological materials by MC-ICPMS. J. Anal. At. Spectrom. 31, 1490–1504. http://dx.doi.org/10.1039/C6JA00064A.
- Thirlwall, M.F., 1991. Long-term reproducibility of multicollector Sr and Nd isotope ratio analysis. Chem. Geol. 94, 85–104. http://dx.doi.org/10.1016/0168-9622(91) 90002-E.
- Upadhyay, D., Raith, M.M., Mezger, K., Bhattacharya, A., Kinny, P.D., 2006. Mesoproterozoic rifting and Pan-African continental collision in SE India: evidence from the Khariar alkaline complex. Contrib. Mineral. Petrol. 151, 434–456. http://dx. doi.org/10.1007/s00410-006-0069-4.
- Upadhyay, D., Scherer, E.E., Mezger, K., 2009. (142)Nd evidence for an enriched Hadean reservoir in cratonic roots. Nature 459, 1118–1121. http://dx.doi.org/10.1038/ nature08089.
- Wakaki, S., Tanaka, T., 2012. Stable isotope analysis of Nd by double spike thermal ionization mass spectrometry. Int. J. Mass Spectrom. 323-324, 45–54. http://dx.doi. org/10.1016/j.ijms.2012.06.019.