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: ^{129}I-^{129}Xe ($T_{1/2}$ = 16 Ma); ^{247}Cm-^{235}U ($T_{1/2}$ = 15.6 Ma); ^{107}Pd-^{107}Ag ($T_{1/2}$ = 6.5 Ma); ^{53}Mn-^{53}Cr ($T_{1/2}$ = 3.7 Ma); ^{60}Fe-^{60}Ni ($T_{1/2}$ = 1.5 Ma); ^{26}Al-^{26}Mg ($T_{1/2}$ = 0.7 Ma); ^{41}Ca-^{41}K ($T_{1/2}$ = 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 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}I-^{129}Xe ($T_{1/2}$ = 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 ^{182}Hf 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 ^{182}Hf was extant, no anomalous composition of the radiogenic daughter ^{182}W should be observed in the mantle. Interestingly, however, ^{182}W anomalies are observed in the terrestrial mantle, which indicate that the core segregation process happened before all the ^{182}Hf had completely decayed to ^{182}W, 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 ^{146}Sm-^{142}Nd systematics. The ^{142}Nd 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 ^{142}Nd radiogenic daughter, indicating the formation of its mantle source at a time when ^{146}Sm 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.

1.2.1 ^{146}Sm-^{142}Nd 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 long-lived ^{147}Sm-^{143}Nd 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 ^{147}Sm ($T_{1/2}$ = 106 Ga) there is very little change in the isotope composition of daughter ^{143}Nd 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 $\varepsilon^{143}Nd = [((^{143}Nd/^{144}Nd)_{rock}/\ (^{143}Nd/^{144}Nd)_{CHUR}\ )-1)\times10^4]$. 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. ^{146}Sm 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 ^{142}Nd. The events that took place within the first few hundreds of millions of years can be easily distinguished using the change in the $^{142}Nd/^{144}Nd$ 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 ^{147}Sm-^{143}Nd systematics, the early differentiation events cannot be resolved within first 500Ma. This is explained in Figure 1.1. Since the initial abundance of $^{146}Sm/^{144}Sm$ was low (0.0085±0.0007;

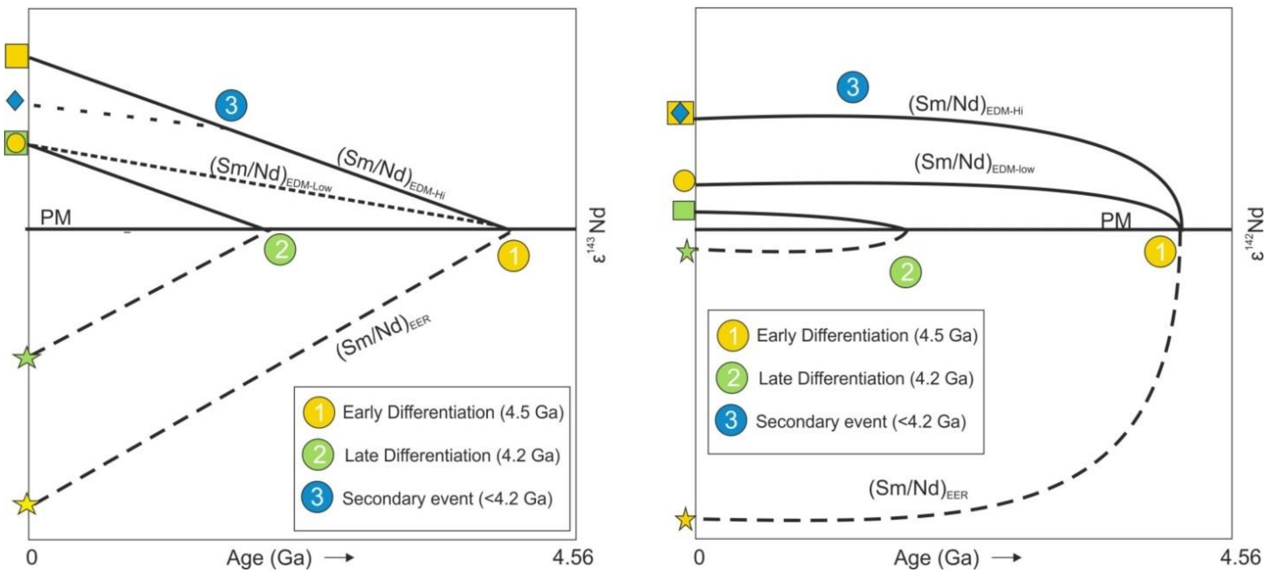

Figure 1.1 *A schematic illustration showing how short-lived ^{146}Sm-^{142}Nd isotopic systematics helps in differentiating early events (events 1 and 2, closely spaced in time) as compared to the long-lived ^{147}Sm-^{143}Nd isotopic systematics (after Caro, 2011). The event no. 3 is a late differentiation event. Using $\varepsilon^{142}Nd$ the early events can be distinguished which are not resolvable in time using $\varepsilon^{132}Nd$. 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. $\varepsilon^{142}Nd$ defined as $\varepsilon^{142}Nd = [((^{143}Nd/^{144}Nd)_{rock}/ (^{143}Nd/^{144}Nd)_{terrest\ std}$ $)-1)\times10^4]$.*

Boyet et al. 2010), the change in $^{142}Nd/^{144}Nd$ isotopic composition is very small and is usually expressed as $\mu^{142}Nd = [((^{142}Nd/^{144}Nd)_{rock}/(^{142}Nd/^{144}Nd)_{terrestrial\ standard}) - 1]\times10^6$, to magnify the variations in the sixth decimal place. Any deviation in the $^{142}Nd/^{144}Nd$ 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 ^{146}Sm 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 $\mu^{142}Nd$ anomalies reported till date. A positive anomaly represents a mantle source which had more Sm than Nd and hence, possesses higher amount of radiogenic ^{142}Nd 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 ^{142}Nd would have been lower than that in the undifferentiated source, thus leading to a negative $\mu^{142}Nd$. Whereas in the case of EDR, a positive value for $\mu^{142}Nd$ would be acquired over time.

Figure 1.2 shows most important results of the $\mu^{142}Nd$ studies plotted using La-Jolla/Ames Nd/JNdi-1 as the terrestrial standard (assuming all have identical $^{142}Nd/^{144}Nd$ 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 $\mu^{142}Nd$ 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.

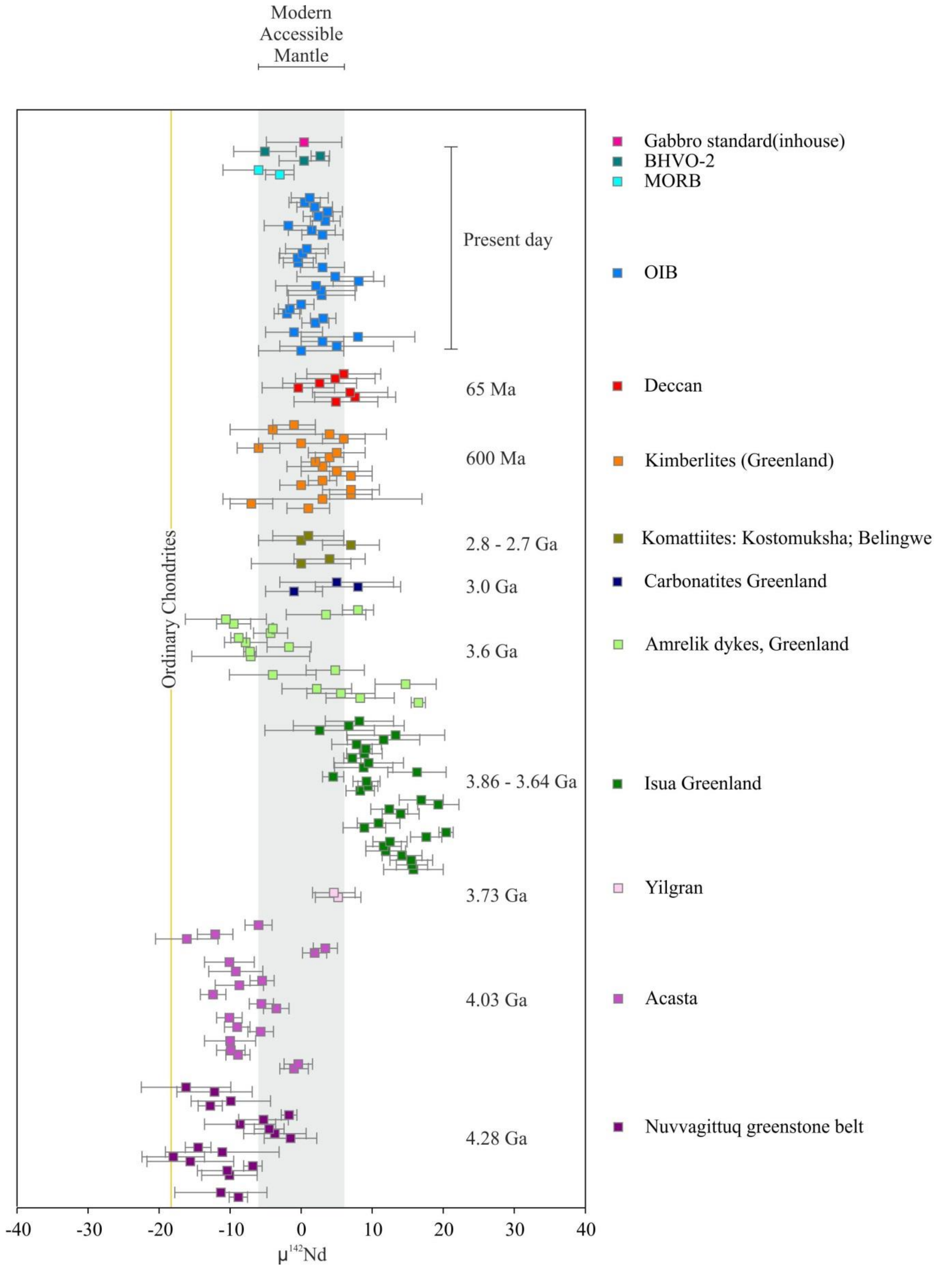

Figure 1.2 *The plot shows $^{142}Nd/^{144}Nd$ in ppm, defined as $\mu^{142}Nd = [((^{142}Nd/^{144}Nd)_{rock} / (^{142}Nd/^{144}Nd)_{terrestrial\ standard}) - 1] \times 10^6$, of mantle derived rocks of varying ages and from different tectonic settings* (Andreasen et al., 2008; Bennett et al., 2007; 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 $\mu^{142}Nd$, $^{142}Nd/^{144}Nd$ 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 $\varepsilon^{143}Nd$. This is done to make the present day value of $\mu^{142}Nd = 0$ for Earth's crust and present-day mantle (Caro, 2011). However, initially it was believed that the $^{142}Nd/^{144}Nd$ isotopic composition of the chondrites (Ordinary Chondrites-OC) is equivalent to that of the terrestrial standard, which represents $^{142}Nd/^{144}Nd$ isotopic composition of the accessible mantle. This assumption was proved wrong in 2005, when Boyet and Carlson (2005) showed that the OCs have $\mu^{142}Nd$ value of -20 ppm with respect to the terrestrial standard. This means that all the terrestrial rocks, except a few, have +20 ppm excess ^{142}Nd 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 non-chondritic $\mu^{142}Nd$ 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 $^{142}Nd/^{144}Nd$ 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 $^{143}Nd/^{144}Nd$ 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).

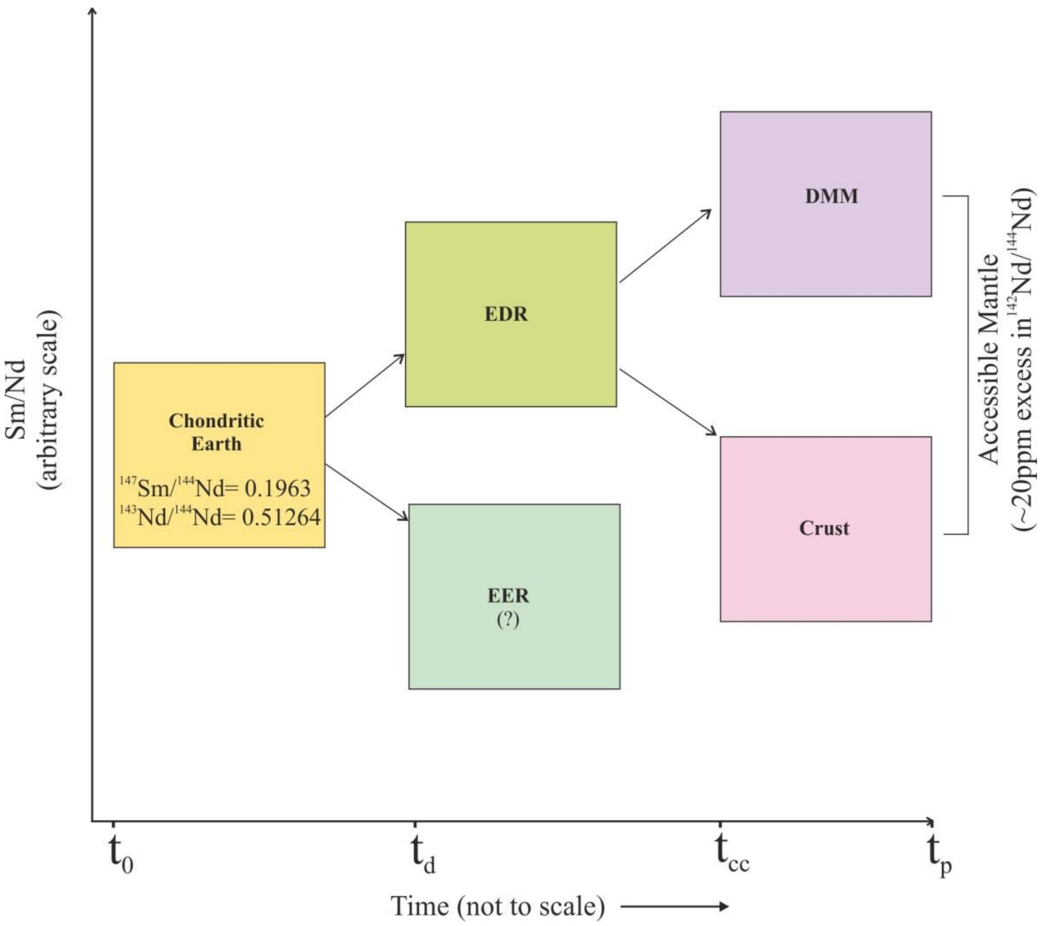

Figure 1.3 *A simplified illustrative representation for Scenario I, where Earth (BSE) starts with a chondritic composition at time t_0 (time of formation of the Solar System) and at a time t_d (time of early differentiation) it differentiates to form early formed mantle reservoirs which are chemically 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 $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ 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 $^{142}Nd/^{144}Nd$ 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 $^{143}Nd/^{144}Nd$ 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 $^{143}Nd/^{144}Nd$ of 0.513000 and $^{147}Sm/^{144}Nd$ of 0.2081 (Figure 1.4).

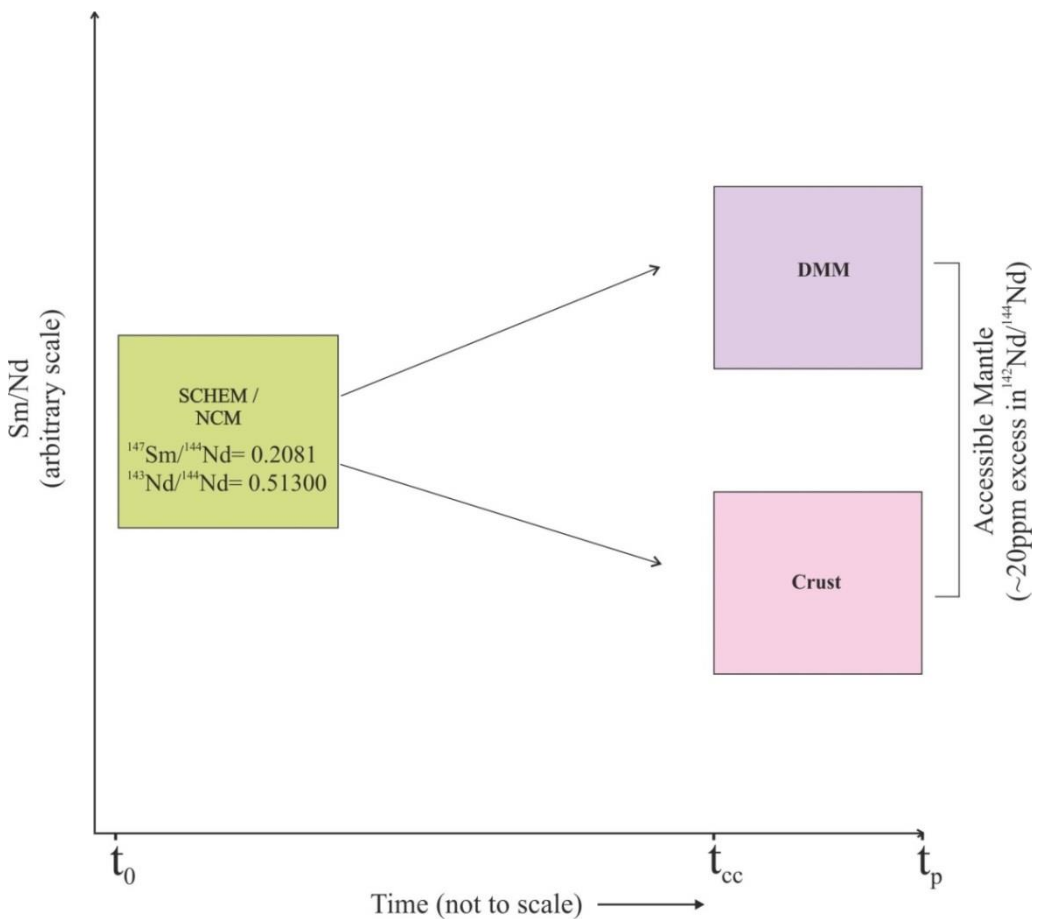

Figure 1.4 *A simplified illustrative representation for scenario II where Earth (BSE) starts with a non-chondritic or super-chondritic composition at time t_0 (time of formation of solar system). DMM = Depleted MORB Mantle; SCHEM = Super Chondritic Earth Model; NCM = Non-Chondritic Mantle; t_{cc} =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

Scenario III: Nucleosynthetic $^{142}Nd/^{144}Nd$ 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 ^{142}Nd offset between Earth and meteorites is due to excess of s-process contribution of ^{142}Nd (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 ^{142}Nd 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 $^{142}Nd/^{144}Nd$ 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.

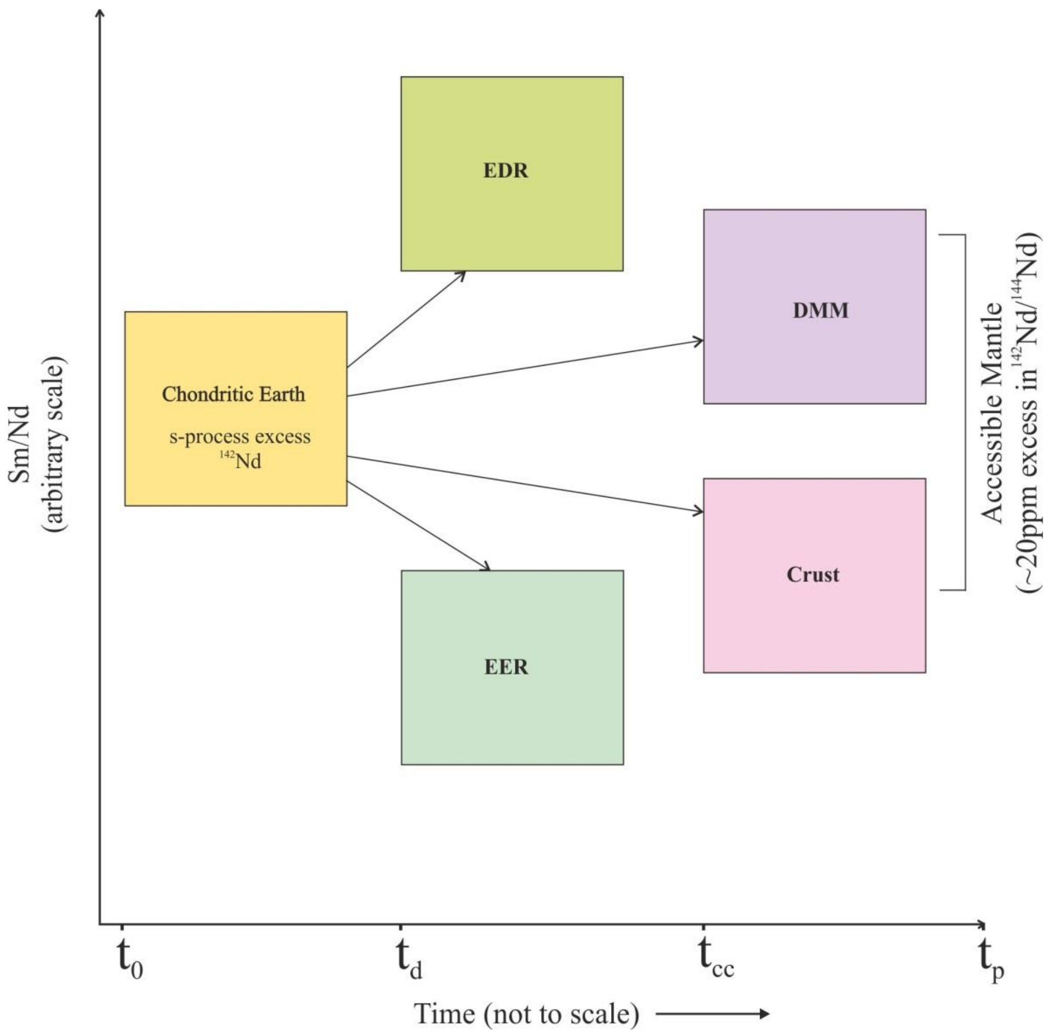

Figure 1.5 *A simplified illustrative representation for Scenario III, where Earth (BSE) starts with a chondritic composition. Symbols and definitions are as described in Figures 1.3 and 1.4.*

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 s-process nuclides like ^{142}Nd (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 ^{142}Nd isotopic anomalies in terrestrial rocks with respect to ^{142}Nd/^{144}Nd 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 ^{142}Nd 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 ^{142}Nd isotopes in mantle derived rocks from the Indian Shield. The main goals of my Ph.D. work were to determine:

1) The location and nature of the earliest LILE-enriched silicate reservoir in the mantle, and

2) 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.

1. *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 ^{142}Nd isotopic compositions.
2. *Develop an analytical protocol for chemical separation of Nd from rock matrix and its purification for accurate determination of ^{142}Nd/^{144}Nd using TIMS*. Nd isotopic investigations using TIMS (as Nd^{+} ions) are restricted by the isobaric interferences from Sm and Ce. In particular, for ^{142}Nd/^{144}Nd isotopic investigation a Ce – free Nd fraction from the rock sample is a must to avoid interference from ^{142}Ce.
3. *To understand the roles of methods of data acquisition and mass fractionation correction in accurate determination of ^{142}Nd/^{144}Nd 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 μ^{142}Nd on reporting of anomalous ^{142}Nd compositions.* I explored the possibility that different terrestrial standards used for ^{142}Nd study may possess different ^{142}Nd/^{144}Nd and thereby affect the reported μ^{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 ^{146}Sm ($T_{1/2}$ = 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 ^{142}Nd/^{144}Nd isotopic compositions, which would have different ^{142}Nd/^{144}Nd isotopic compositions from that of the undifferentiated (starting) bulk mantle. This would have resulted in anomalous ^{142}Nd 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). ^{142}Nd/^{144}Nd 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 $^{142}Nd/^{144}Nd$ isotopic compositions. Of these the Isua Supracrustal Belt (ISB), Greenland, carry the strongest evidence in the form of positive ^{142}Nd 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 $\mu^{142}Nd$ 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 $\mu^{142}Nd$ 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 $\mu^{142}Nd$ (Debaille et al. 2013). Four examples of negative $\mu^{142}Nd$ (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 ^{142}Nd 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 ^{142}Nd 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 ^{142}Nd 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 ^{142}Nd composition is evaluated in detail, which is one of the major findings of this work. This is followed by the information obtained from ^{142}Nd isotopic investigation of the Indian rocks. The implications of the results for ^{142}Nd 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 μ^{142}Nd anomalies.

Sr. No.	Year	Nd reference	Location	Samples	μ^{142}Nd
1)	1992	CIT Ndβ	Isua SW Greenland	IE 715-28, metasediment	+33 ppm for IE 715- 28
2)	1993	La Jolla or RSES (std of the day)	Greenland (Amitsoq & Akilia) and Northern Canada (Acasta)	Felsic gneiss, mafic gneiss and ultramafic rocks	In ε, not resolvable; unable to 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 2. NWT, Canada 3. Kaapval craton, S. Africa	1. (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 2. Gneisses (4.03 Ga; U-Pb zircon age) 3. Barberton Komatiites (3540± 30 Ma; Sm – Nd isochron age)	1.+8 to +15 ppm 2. No anomaly 3. No anomaly
6)	2007	Ames Nd	1.SW Greenland, Itsaq complex 2. Western Australia Yilgran craton, Narryer gneiss complex	1. Tonalites (3.64 to 3.85 Ga) 2. Tonalitic gneisses (3.73 Ga)	1. +9 to +20 ppm 2. +5 ppm
7)	2008	La Jolla	NGB, Northern Quebec, Canada	1.Faux amphibolites 2. Tonalites	1. -7 to -15 ppm 2. -12 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)	1. Hornblende amphibolites 2. cummingtonite amphibolites 3. tonalite gneiss 4. Trondhjemite gneisses	1. one sample -11.1 ppm 2. one sample -8.6 ppm

				5. granodiorite gneisses 6. quartzite	4. one sample -8.7 ppm 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), NorthWest territories, Canada	granitoid gneiss and plagioclase-hornblende schist	Ten out of thirteen samples show values from -6.0 to -14.1 ppm Average is -9. 6 ppm
15)	2016	JNdi-1	1. Ukaliq supracrustal belt, Canada 2. NSB and ISB	1. amphibolites 2. BIF	1. 0 to -10 ppm 2. no resolvable anomaly
16)	2016	Ames Nd (JNdi-1 at DTM)	Schapenburg, South Africa	Komatiites (3.55 Ga)	-5 ppm

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)