Review Article

Hunt for the Early Silicate Earth Differentiation Signatures

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The events that took place during the first few hundred million years of the Solar system formation have resulted into the differentiated structure of our planet. This is true for other terrestrial planets and differentiated meteorites as well. Of these early events, core formation (metal-silicate segregation) was one important event followed by the early differentiation of silicate Earth (mantle). Understanding early silicate Earth differentiation processes is vital in understanding how the Earth evolved to its present state. However, extracting information about these early silicate differentiation events is not easy from a convecting and tectonically active planet like Earth. This article discusses how the information about the early silicate Earth differentiation can be obtained using ^{142}Nd isotope and the analytical challenges involved. Using available data from the studies done so far, the implications for the Chondritic nature of Earth *vis-a-vis* early silicate differentiation is provided.

Keywords: Early Silicate Earth Differentiation; $^{142}\text{Nd}/^{144}\text{Nd}$ Isotopic Ratios; Thermal Ionization Mass Spectrometry (TIMS); Early Differentiated Reservoirs; Chondritic Earth

1. Introduction

Present is the key to the past – is a thumb rule that we follow in Geosciences. This is true for the larger part of the geological time scale and our understanding of the present day processes have largely helped us in understanding how our planet has evolved for so long. However, the first-order secular changes that took place during the first few hundred million years after the formation of the Solar system, like segregation of the core, affected the entire planet and resulted in the differentiated form of our planet. The forces operating after these changes took place have largely, but not entirely, been limited to modifying and recycling only a few hundreds of kilometers from the surface. It is therefore important to understand the early processes that resulted into a differentiated planet. Several studies focused on the different types of meteorites – chondrites (undifferentiated), achondrites (differentiated) and terrestrial rocks, have helped in deciding a geochemical reference for the Earth (and other terrestrial planets of the Solar system) and understanding the early and subsequent differentiation processes. The chondrites are taken

as geochemical reference to study the differentiation processes, using mass balance of certain elements (known as *Refractory Elements*) and its isotopes (explained in sections 3.1 and 3.2). Isotopic studies have also helped in obtaining the timing of these differentiation events like core sequestration and early mantle differentiation. The short-lived isotope systematics of certain refractory elements in particular, have assisted in obtaining information about these events. Short-lived nuclides, having half-life in range of a few million years like 0.705 Ma for ^{26}Al - ^{26}Mg systematics (as given in Guntre and Mensing (2004), were present during the early history of solar system when formation of first solid phases was taking place. The presence of decay products of these radionuclides gives an estimate about their presence in early formed solids and help in obtaining information about the early differentiation process(s). Likewise, the understanding about the core formation of Earth has largely come from elemental and isotopic study of ^{182}Hf - ^{182}W systematics in differentiated and undifferentiated meteorites. More details are given in section 5. In the sections that follow, it is detailed how, with the help of extinct radioactivity of ^{146}Sm -

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^{142}Nd isotopic systematics, the information about the early silicate Earth differentiation can be obtained. Silicate Earth or Bulk Silicate Earth (BSE) can be understood as Bulk Earth composition minus core composition. It includes the present day crust and mantle. Using this systematics critical information about the conditions that prevailed during early history of the Solar system is obtained. The interpretation of these signals has questioned the chondritic Earth model at various times and our understanding about the chemical composition of the Earth, the timing of early mantle differentiation, the scale of this differentiation has evolved with the subsequent studies. These are discussed in the following sections.

2. Understanding Early Silicate Earth Differentiation

‘Early’ here refers to the first five hundred million years after the formation of the Solar system. This time-span in geological time-scale is also known as Hadean Eon. Until recently, there was no report of any preserved rock record of this age on the Earth. However, there are two localities in Canada—Acasta Gneiss Complex (AGC), North West Territories and Nuvvagituuq Greenstone Belt (NGB), Quebec, where rocks older than 4.0 Ga are found (Bowring and Williams, 1999; O’Neil *et al.*, 2008). Due to a near absence of preserved rock record for this time, the timing and nature of the first differentiation event(s) was not well constrained. First indirect evidence of the early silicate differentiation - formation of crust came from the 4.4Ga cores of detrital zircons from Jack Hill, Australia (Cavosie *et al.*, 2005; Valley *et al.*, 2014; Valley *et al.*, 2005). This is an indirect evidence because the rock of which these detrital zircons were part of, is not preserved. The presence of rock is inferred from these zircons. Presence of a rock of that age is counted as direct evidence. The first direct evidence of early differentiation has come from study of Archean rocks from the Isua Supracrustal Belt (ISB) (Bennett *et al.*, 2007; Boyet *et al.*, 2003; Caro *et al.*, 2006, 2003; Harper and Jacobsen, 1992). These were studied for $^{142}\text{Nd}/^{144}\text{Nd}$ isotopic composition, which showed anomalies with respect to the terrestrial standard reference. Further details are in section 4. $^{142}\text{Nd}/^{144}\text{Nd}$ isotopic investigations are a ‘hot-topic’ of research at present, the field is developing and understanding is changing whenever a new paper is reported. It is important to

carry out these investigations to get a better and more evolved understanding of the earliest differentiation of the terrestrial mantle. It is because of these differentiation events that our planet has crust, which supports biosphere—all life forms on the Earth. Mantle dynamics controls the surface processes, which in turn affects all spheres. Therefore, it is important to study and understand Earth’s mantle.

3. How is the Study Conducted?

In this section it is discussed, how with the help of radioactivity in general and extinct radioactivity in particular, information about the timing of early differentiation events can be extracted. The essential qualities to be a proxy for early silicate Earth differentiation process(s) are provided. Having decided the proxy, the approach used to extract this information is discussed. This is followed by a discussion on the analytical techniques used, the challenges involved and the latest understanding and the implication of accurate data.

3.1. Essential Qualifications to be a Proxy for Early Silicate Earth Differentiation

To be a proxy for silicate differentiation, following are the qualifying criteria, each one being equally important:

- 1) The elements should be present in the silicate part of the Earth. Such elements having affinity for silicates are known as *Lithophile* elements, e.g. Li, Al, K, Cs, REEs etc. The affinity of certain elements for silicate phases (or metal phase in case of siderophile elements like Fe) as described by Goldschmidt is dependent on the free energies of formation of corresponding silicate (or sulphide phase), at a given temperature, pressure and oxygen fugacity. A metal-silicate segregation process like core formation ensures that all lithophile elements are sequestered in mantle. On the other hand the lithophile elements are re-distributed in the various geochemical reservoirs formed due to any process affecting the silicate part of the Earth.
- 2) To record differentiation event(s), the lithophile elements must get affected in terms of their concentrations in the melt-residue/crystallizing

phase. This is described in terms of *incompatibility* and defined in terms of partition coefficient between two phases, $D_i^{s/l}$ ($= C_i^s / C_i^l$; C is concentration; i is the element; s and l refer to solid and liquid phases respectively. This can be defined between any two mineral phases). $D_i^{s/l} < 1$ for incompatible elements whereas $D_i^{s/l} > 1$ for compatible elements. For example, in a clinopyroxene from basalt, partition coefficient value for Sm is 0.462 whereas for Nd is 0.277 (White, 2013). If lithophile elements are incompatible, following partial melting of the peridotitic mantle source, their concentration in the formed melt will be greater than in the residue as these elements are not compatible in the residue's solid crystal lattice. Compatible elements are favored in the crystal lattice of the residual solid (in case of partial melting) or crystallizing mineral phase (in case of fractional crystallization) and therefore cannot track the differentiation event(s). Typical concentrations of Sm and Nd in ppm (parts per million) vary in different rocks as: basalts- (Sm: 3.30, Nd: 10.3); rhyolite- (Sm: 4.65, Nd: 21.6). The Sm/Nd ratio in these varies from 0.32 to 0.215 (Guntre and Mensing, 2004).

- 3) Chondritic meteorites are one of the oldest and primitive rocks of solar system that did not undergo subsequent differentiation. The elemental composition of chondrites is therefore, taken as geochemical reference for Earth and other terrestrial planets, to understand its differentiation processes leading to planetary evolution, using chemical balance. However, within different classes of chondrites, there is a variation in the elemental make up, which is related to the temperature of the formation of the various components of these rocks. Certain elements were entrained in the phases forming from solar nebula at high temperature and others did not become part of the forming phases till the temperatures were low. This is described in terms of refractory and volatile nature of certain elements, which is defined in terms of condensation temperatures. As defined in Lodders *et al.* (2009), the thermal equilibrium between solids and a cooling gas of solar composition, temperature at which the 50 % of

an element is in the condensed phase, at total nebular pressure of 10^{-4} bars, is known as the 50 % condensation temperature. The elements which have 50 % condensation temperature varying between 1650 K to 1360 K at 10^{-4} bars pressure, are known as refractory elements, e.g. Ca, Al, REEs etc. It is observed that the elemental ratios of refractory elements and not their absolute concentrations are same in all chondrites and terrestrial planets including the Earth (Lodders, 2010; Lodders *et al.*, 2009; Palme *et al.*, 2013).

The elements having all the three mentioned properties are known as *Refractory Lithophile Elements (RLEs)*. RLEs are the proxy for understanding silicate Earth differentiation. There are various RLEs available of which, *Sm and Nd* are the best choice (as explained in the next section) to study differentiation of silicate Earth. In addition, the isotopic systematics of Sm-Nd helps in finding timing of differentiation events; Sm has radioactive isotopes, 147 and 146 which decay to radiogenic isotopes ^{143}Nd and ^{142}Nd , respectively, by emitting an alpha particle, where both parent and daughter nuclides are lithophile.

3.2 Sm and Nd as Differentiation Tracers

The *Sm/Nd* elemental ratio is used as a proxy for understanding silicate Earth differentiation. Both of them are incompatible, but Nd is relatively more incompatible as compared to Sm. This is because Nd ($Z=60$) has larger ionic radius (1.08 Å for Nd^{+3}) than Sm ($Z=62$, 1.04 Å for Sm^{+3}) due to lanthanide (La, $Z=57$) contraction resulting from filling of inner shell f electrons, rather than the d electrons. Since Nd is more incompatible, during any differentiation event its concentration is greater in the melt whereas concentration of Sm increases in the solid or residual phase. This does not mean that Sm is not incompatible and does not enter the melt phase, but its relative concentration in the melt is less compared to Nd. Since both Sm and Nd are Rare Earth Elements (REEs), their chemical properties are similar and the variation in Sm/Nd elemental ratio observed in natural systems is limited. This change in Sm/Nd ratio during a differentiation event is reflected in the isotopic composition of these elements over time, as radioactive isotopes of Sm decays to produce radiogenic isotopes of Nd. By studying the variations in their isotopic

ratios, information about the differentiation process(s) and its timing is obtained.

Whereas the long lived ^{147}Sm - ^{143}Nd systematics is a tracer of silicate differentiation over geologic history, it cannot be used to differentiate between early events that occurred within a few hundred million years. This is because of the long half-life of parent nuclide ^{147}Sm (103 Ga), there is a very little change in the isotope composition of daughter ^{143}Nd isotope. In fact, the measureable change is in fourth decimal and is denoted in a ϵ notation, defined as $\epsilon = [((^{143}\text{Nd}/^{144}\text{Nd})_{\text{rock}}/(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}}) - 1] \times 10^4$. This systematics is a robust chronometer and is used to date event in rocks.

To extract information about early events, opportunely in nature we find a short lived isotopic systematics of Sm-Nd as well. ^{146}Sm is now extinct because it decayed quickly (short half-life of 106 Ma or 68 Ma; Kinoshita *et al.*, 2012; this value is not acceptable as discussed in Marks *et al.*, 2014) to produce radiogenic ^{142}Nd with emission of an alpha particle, similar to the decay of ^{147}Sm to ^{143}Nd . The events taking place within a few hundred million years (five to up to ten half-lives) can be experimentally

distinguished using $^{142}\text{Nd}/^{144}\text{Nd}$ isotopic ratios. This is explained in Figure 1. Since the initial abundance of $^{146}\text{Sm}/^{144}\text{Sm}$ was low (0.0085 ± 0.0007 ; (Boyett *et al.*, 2010; Lugmair *et al.*, 1975), and there is limited fractionation in Sm/Nd ratio in nature, the change in ^{142}Nd isotopic composition is very small and is denoted in μ notation. μ is defined as, $\mu^{142}\text{Nd} = [((^{142}\text{Nd}/^{144}\text{Nd})_{\text{rock}}/(^{142}\text{Nd}/^{144}\text{Nd})_{\text{terrestrial standard}}) - 1] \times 10^6$. Any deviation in the $^{142}\text{Nd}/^{144}\text{Nd}$ isotopic composition of a rock from that of terrestrial standard shows that the Sm/Nd ratio of the rock was different and this change took place when ^{146}Sm was still extant (i.e. during first five hundred million years; five half-lives using 103 Ma). This deviation is known as anomaly and represents a chemical signature of early differentiation of silicate Earth.

As the title of this article says, a hunt for early Earth differentiation signatures, in terms of $\mu^{142}\text{Nd}$ anomaly, is on. Table 1 summarizes the report of anomaly in $\mu^{142}\text{Nd}$ reported so far. The positive anomaly in $\mu^{142}\text{Nd}$ represents a mantle source which had more Sm than Nd and hence more generation of radiogenic ^{142}Nd in time as compared to the undifferentiated mantle. Since this mantle reservoir was depleted in incompatible elements like Nd (and other large Ion Lithophile

Fig. 1: A schematic illustration showing how short-lived ^{146}Sm - ^{142}Nd isotopic systematics helps in differentiating between 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 $\epsilon^{142}\text{Nd}$ the early events can be distinguished which are not resolvable in time using $\epsilon^{143}\text{Nd}$. The slope of the lines showing evolution of EDR and EER (or any mantle reservoir for that matter) depends upon Sm/Nd ratio; EDR-Early Depleted Reservoir, EER-Early Enriched Reservoir (explained in Section 4.1)

Table 1: List of anomaly in $\mu^{142}\text{Nd}$ reported

Year	Nd reference	Location	Samples	$\mu^{142}\text{Nd}$
1992 (Harper & Jacobsen)	CIT Nd	Isua SW Greenland	IE 715-28, metasediment	+33 ppm for IE 715- 28
1993 (McCulloch <i>et al.</i>)	La Jolla or RSES (std of the day)	Greenland (Amitsoq & Akilia) and Northern Canada (Acasta)	Felsic gneiss, mafic gneiss and ultramafic rocks	In Å, not resolvable; to reproduce 1992 result of Harper & Jacobsen
2003 (Boyet <i>et al.</i>)	JMC Nd (MC-ICPMS)	SW Greenland, ISB	Metabasalts; metagabbros	+30 ppm
2003 (Caro <i>et al.</i>)	Ames Nd	West Greenland, IGB	Metasediments	+15 ppm
2006 (Caro <i>et al.</i>)	Ames Nd	1. SW Greenland 2. NWT, Canada 3. Kaapvalcraton, 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
2007 (Bennett <i>et al.</i>)	Ames Nd	1.SW Greenland, Itsaq complex 2. Western Australia Yilgrancraton, 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
2008 (O’Neil <i>et al.</i>)	La Jolla	NGB, Northern Quebec, Canada	1.Faux amphibolites 2. Tonalites	1. -7 to -15ppm 2. -12 to -16 ppm
2009 (Upadhyay <i>et al.</i>)	La Jolla	Khariar, Odhisha, India	Alkaline rocks-nepheline syenites	-13 ppm
2011 (Rizo <i>et al.</i>)	JNdi-1	Isua, Greenland	Amphibolites	+7 to +16 ppm
2012 (Rizo <i>et al.</i>)	JNdi-1	Ameralik dykes, Isua	Noritic dykes (3.4 Ga)	-10.6 ppm
2013 (Debaille <i>et al.</i>)	Average of Ames Nd and La Jolla	Abitibi Greenstone Belt (AGB), Canadian craton	Thoellitic lava flow (2.7 Ga)	+7 ppm
2013 (Roth <i>et al.</i>)	JNdi-1	NSB, Que’bec, Canada (a few samples are same aliquots of O’Neil <i>et al.</i> 2008)	1. Hornblende amphibolites 2. cummingtoniteamphibolites 3. tonalite gneiss 4. Trondjemite gneisses 5. granodiorite gneisses 6. quartzite	1. one sample -11.1 ppm 2. one sample -8.6 ppm 4. one sample -8.7 ppm Rest do not show resolvable anomaly but these results confirm results of O’Neil 2008
2014 (Roth <i>et al.</i>)	JNdi-1	Khariar, Odhisha, India	Same sample aliquots of Upadhyay <i>et al.</i> 2009	No anomaly
2014 (Roth <i>et al.</i>)	JNdi-1	Acasta Gneiss Complex (AGC), North West 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
2016 (Caro <i>et al.</i>)	JNdi-1	1. Ukaliqsupracrustal belt, Canada 2. NSB and BIF	1. amphibolites 2. ISB	1. 0 to -10 ppm 2. resolvable anomaly
2016 (Puchtel <i>et al.</i>)	Ames Nd (JNdi-1 at DTM)	Schapenburg, South Africa	Komatiites (3.55 Ga)	-5 ppm

Fig. 2: The plot shows $^{142}\text{Nd}/^{144}\text{Nd}$ in ppm, defined as $\mu^{142}\text{Nd} = [((^{142}\text{Nd}/^{144}\text{Nd})_{\text{rock}} / (^{142}\text{Nd}/^{144}\text{Nd})_{\text{terrestrial standard}}) - 1] \times 10^6$, of the mantle derived rocks (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.*, 2008; Rizo *et al.*, 2012, 2011; Upadhyay *et al.*, 2009) and the references therein. The rocks span a geological time from Hadean-Archean to recent (not to scale) and different tectonic settings. Rock standard, BHVO-2, and an in-house gabbro standard (Upadhyay *et al.*, 2009) is also shown. Grey shaded area represents variability (2-standard deviation) in the measurement of the terrestrial standard over time, which is 6 ppm in this plot. Any deviation from the terrestrial standard (positive and negative) gives information about the early differentiation event(s). These deviations are restricted to a few of the oldest rocks known. Ordinary chondrites are assumed to be the precursor for Earth (geochemical reference for Bulk Silicate Earth composition), do not lie on the zero line. Instead, they lie on the negative side (-18.3 ppm; Burkhardt *et al.*, 2016)

Elements), hence is called depleted reservoir. According to mass balance, a complimentary mantle reservoir which had budget of incompatible elements like Nd is called enriched reservoir. As this enriched reservoir has less Sm to begin with, the production of radiogenic ^{142}Nd will be less and over time develop a negative $\mu^{142}\text{Nd}$ value.

3.3. Approach – Where to Look for these Signatures

The best way to extract information about early differentiation event(s) would be to study rocks that formed when ^{146}Sm was extant. But unfortunately, Earth does not have a well preserved-abundant Hadean rock record. As mentioned already in section 2, only two examples of Hadean rocks are known till date. Therefore, the majority of the $^{142}\text{Nd}/^{144}\text{Nd}$ isotopic investigations are focused on Archean rocks. This is because these rocks have maximum likelihood of the preservation of the early differentiation signatures in terms of $\mu^{142}\text{Nd}$ anomalies. The chance of preservation of such subtle signatures reduces as we look at rock record younger than Archean because the Earth's mantle has been convecting and recycling the mantle materials over geologic time along with some crustal material also.

However, not all regions of the mantle participate in the convective mixing and hence non-convecting mantle domains are present. These non-convective mantle domains could be potential sites for the preservation of early differentiation signatures. There are two such regions viz., *core-mantle boundary*, also known as *D''-layer* and the *Sub Continental Lithospheric Mantle (SCLM)*. The convecting mantle is the source for Archean SCLM as a result of time-integrated growth. The rocks which are formed from the melt derived from these mantle domains could be investigated to search for anomaly in $\mu^{142}\text{Nd}$. Plume derived magmas are derived from deep mantle, some originating around core-mantle boundary. Alkaline rocks are understood to be derived from SCLM (Gwalani *et al.*, 2016; Ray *et al.*, 2013; Woolley and Bailey, 2012), some workers believe (Condie, 2012 and references therein) that alkaline rocks have association with the plume derived melts. In this regard, a few attempts by various workers have been made on alkaline rocks including carbonatites and some plume derived magmas, which are discussed in

section 4. An important and interesting fact for investigating non-convective mantle is that *the age of emplacement of rock derived from these mantle domains will not matter for the preservation of these signatures* and could be present in young rocks, for which Earth has abundant preserved rock record.

3.4. Analytical Procedures

Nd isotopic measurements are carried out using *Thermal Ionization Mass Spectrometer (TIMS)*. This requires a clean separation of the element of interest from the rock matrix. This is a time consuming process, done with the help of ion-exchange chromatography. $^{142}\text{Nd}/^{144}\text{Nd}$ isotopic investigations require an extremely clean separation as explained in the following section.

3.4.1. Chemical Procedures: Nd isotopic investigations are affected by isobaric interferences from Sm and Ce. Routine measurements of $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic investigations are easy as the only isobarically interfering element is Sm (mass 144). But for $^{142}\text{Nd}/^{144}\text{Nd}$ isotopic measurements, in addition to Sm, Ce has a major isobaric interference on ^{142}Nd (27.2 % relative natural abundance) from ^{142}Ce (11.1 % relative natural abundance). Since Ce is geochemically similar to Nd, and the average abundance of Ce is more than Nd (e.g., a basalt typically contains 38 ppm Ce and 25 ppm Nd), its chemical separation from the latter is difficult and time consuming. There are many established protocols for the chemical separation of Ce from Nd but only two are most commonly employed. These are (1) using α -HydroxyIsoButyric Acid (α -HIBA) chemistry (Lugmair *et al.*, 1975) and (2) two-phase solvent extraction technique (Rehkämper *et al.*, 1996). These two techniques with slight modifications are used in different labs (e.g. Saji *et al.*, 2016 and Gautam *et al.*, 2017).

3.4.2. Thermal Ionization Mass Spectrometry: With the advent of new generation of Thermal Ionization Mass Spectrometers like *Triton*, it has been possible to obtain very high precision ($< 5\text{ ppm}$ 2-Standard Deviations – external precision) on the measured isotope ratio data (an exception to this is by Ali and Srinivasan, (2011), but external precision in this case was $> 10\text{ ppm}$). This has helped in measuring the subtle difference in the isotopic composition like that

of $^{142}\text{Nd}/^{144}\text{Nd}$. Nd is measured as Nd^+ ions in TIMS using a double filament (Rhenium zone refined) assembly. To monitor isobaric interferences from Sm (on masses 144, 148 and 150) and Ce (on mass 142) on Nd isotope ratio measurements ($^{142}\text{Nd}/^{144}\text{Nd}$, $^{143}\text{Nd}/^{144}\text{Nd}$, $^{145}\text{Nd}/^{144}\text{Nd}$, $^{146}\text{Nd}/^{144}\text{Nd}$, $^{148}\text{Nd}/^{144}\text{Nd}$ and $^{150}\text{Nd}/^{144}\text{Nd}$), masses 147 (^{147}Sm is 14.99 % relative natural abundance) and 140 (^{140}Ce is 88.45 % relative natural abundance) are measured along with mentioned Nd isotopes. The data acquired is mass-fractionated and needs correction for fractionation that takes place during ionization of sample due to heating. There are various fractionation laws proposed to correct for mass fractionation like linear law, power-law, exponential law. The details can be found in Thirlwall, (1991) and the references therein. A fractionation correction factor per mass unit is calculated using $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$, since the abundance of these two isotopes is fixed in nature as they are not produced due to any radiogenic decay. Some studies have also reported using $^{148}\text{Nd}/^{144}\text{Nd}$ for internal normalization (e.g. Saji *et al.*, 2016). More details about mass spectrometry of $^{142}\text{Nd}/^{144}\text{Nd}$ isotopic ratio measurement can be found in (Andreasen and Sharma, 2009; Gautam *et al.*, 2017; Upadhyay *et al.*, 2008) and the references therein. Fractionation correction is critical to obtaining accurate data, which can in turn affect the interpretation of the data. This is discussed in detail in Gautam *et al.* (2017).

4. What is Known so Far?

Of all the work carried out and reported for $^{142}\text{Nd}/^{144}\text{Nd}$ by various workers, Table 1 summarizes the important reports of anomalous $\mu^{142}\text{Nd}$ (Bennett *et al.*, 2007; Boyet *et al.*, 2003; Caro *et al.*, 2006, 2003; Caro *et al.*, 2016; Debaille *et al.*, 2013; Harper and Jacobsen, 1992; Mcculloch and Bennett, 1993; O'Neil *et al.*, 2008; Puchtel *et al.*, 2016; Rizo *et al.*, 2012, 2011; Roth *et al.*, 2014(a), 2013; Roth *et al.*, 2014(b); Upadhyay *et al.*, 2009). This does not contain all the remaining non-anomalous (normal) reports of $\mu^{142}\text{Nd}$ isotopic data.

It is important to understand here that any report of the ^{142}Nd anomaly is required to be reproduced independently by other laboratories. It is only after this that the reported anomaly can be claimed as an unflinching discovery. This is required because of the critical implications these anomalies carry as a

signature of early differentiation event(s). The important information that has been derived from these reports is discussed in the following sub-sections.

4.1. Chondritic Versus Non-chondritic Earth

As explained already in section 3, Chondrites are taken as geochemical reference to understand the planetary evolution. The subsequent change in the isotopic composition of $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{142}\text{Nd}/^{144}\text{Nd}$ over time, due to change in Sm/Nd ratio resulting from differentiation, is expressed in ϵ and μ notations, respectively. Unlike using Chondritic Uniform Reservoir (CHUR) to normalize in the definition of $\epsilon^{143}\text{Nd}$ ($= [((^{143}\text{Nd}/^{144}\text{Nd})_{\text{rock}} / (^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}}) - 1] \times 10^4$), terrestrial standard is used for normalization in the definition of $\mu^{142}\text{Nd}$. This is done to make the present day value of $\mu^{142}\text{Nd} = 0$ for crust and present day mantle. However, initially it was believed that the $^{142}\text{Nd}/^{144}\text{Nd}$ isotopic composition of the chondrites (Ordinary Chondrites-OC) is equivalent to that of terrestrial standard, which represents $^{142}\text{Nd}/^{144}\text{Nd}$ isotopic composition of the *accessible mantle*. This assumption was proven wrong in 2005, when Boyet and Carlson (2005) showed that the OC have $\mu^{142}\text{Nd}$ value of -20ppm with respect to the terrestrial standard. This means that all the terrestrial rocks (except for that of ISB, Greenland) showed $+20\text{ppm}$ excess as compared to the chondrites. This important discovery has implications which can change our fundamental assumption about the chondritic geochemical reference for Earth (and other terrestrial planets) and is explained in the following scenarios:

Scenario 1: Change in $^{142}\text{Nd}/^{144}\text{Nd}$ isotopic composition due to decay of ^{146}Sm to ^{142}Nd

Scenario 1-a: Chondritic Earth undergoing a global scale differentiation event before 4.53Ga (Boyet and Carlson, 2005)

In this scenario, an early global differentiation event formed an Early Depleted Reservoir (EDR), which is sampled by all the terrestrial rocks analyzed so far. Mass balance requires formation of a complimentary Early Enriched Reservoir (EER). But so far there is no report of such a reservoir. It is also likely possible that it is seated deep in mantle and may not be sampled (also known as *hidden reservoir*), or this EER represented the earliest formed crust and was lost subsequently to space due to collisional erosion

(O'Neill and Palme, 2008). Depending upon the time of formation of this EDR, the amount of Sm/Nd required to explain present day $^{143}\text{Nd}/^{144}\text{Nd}$ for OIB (Ocean Island Basalts), MORBs (Mid Ocean Ridge Basalts) will change. According to Boyet and Carlson (Boyet and Carlson, 2006, 2005), this EDR is characterized by 6% higher Sm/Nd ratio than chondritic, if formed at 4.53 Ga. It is not only the timing of formation of EDR, but also the amount of extraction of continental crust from EDR and the part of mantle involved in the process, which can affect the estimates of Sm/Nd in EDR. Different estimates for the composition of EER are given in Carlson *et al.* (2015) and the references therein. It is interesting to note that in this scenario all mantle reservoirs (accessible mantle) are derived from EDR, which is super-chondritic in composition (Fig. 3). Super-chondritic here refers to Sm/Nd ratio higher for the BSE composition as compared to that of chondrites.

Fig. 3: A simplified illustrative representation for scenario I-a, 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 composition changes with variation in the t_d ; EDR-Early Depleted Reservoir; EER-Early Enriched Reservoir; DMM-Depleted MORB Mantle; t_{cc} -time of formation of continental crust; t_p -present day. DMM and crust together represent the accessible mantle of Earth, which shows 20 ppm excess in $\mu^{142}\text{Nd}$ with respect to Ordinary Chondrites. The $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic values for the CHUR are taken from (McDonough and Sun, 1995) and represent present day values for CHUR and not at t_0

Estimates of $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ for EER based on mass balance, depending upon the size of EER, is given by Carlson and Boyet (2008).

Scenario I-b: Non-Chondritic Earth

To explain the offset in $^{142}\text{Nd}/^{144}\text{Nd}$ isotopic composition between the terrestrial rocks studied so far and the chondritic meteorites, another possibility is that Earth did not start with a chondritic composition but with a super-chondritic Sm/Nd ratio. In this scenario, the present day values of $^{143}\text{Nd}/^{144}\text{Nd}$ observed for rocks derived from the various mantle reservoirs and budget for other elements and their isotopic ratios must be explained. This can be explained by more than one model, like EDR (in the absence of complimentary reservoir, EER, as shown in Fig. 4), Super Chondritic Earth Model (SCHEM) and Non-Chondritic Mantle (NCM). The details of these models are given in (Carlson *et al.*, 2015) and references therein. Due to limited fractionation of Sm-Nd observed in nature, the number of predicted models is limited. The SCHEM model (Caro and Bourdon, 2010) assumes present day $^{143}\text{Nd}/^{144}\text{Nd}$ to be 0.51299 for SCHEM instead of 0.512638 for Bulk Silicate Earth (BSE). The NCM (Jackson and Jellinek, 2013) assumes a value of 0.51300 instead of 0.51264.

Scenario II: Nucleosynthetic Origin for $^{142}\text{Nd}/^{144}\text{Nd}$ Isotopic Offset Between Earth and Chondrites

Different nuclides are formed by various nucleosynthetic processes (like s-, r-, p- processes) in solar nebula. These processes are specific to stellar sites and hence can result in certain degree of heterogeneity in composition of the material forming from solar nebula, which is dependent on the heliocentric distance from the Sun. As the Earth and parent bodies (meteorites) perhaps formed at different distances they could have inherited the differences in compositions depending upon the heliocentric distance. This can lead to different initial isotopic abundances between Earth and meteorites. This difference cannot be attributed to decay of radioactive isotopes over time following a change in elemental ratios due to a differentiation process. The contributions to various isotopes of Nd (142, 143, 144, 145, 146, 148, 150) by p, s and r process can be estimated and similarly for various isotopes of Sm. For example, galactic chemical evolution model by

Bisterzo *et al.* (2014) estimate s-process contribution. Using this model estimated abundances, a correlation in various isotopes can be estimated and compared with the measured values to estimate the extent of correction required in ^{142}Nd abundances to deconvolute the measured values for what is due to decay of ^{146}Sm and what is due to s-process contribution.

It is now known that the ^{142}Nd offset between earth and meteorites is due to excess of s-process contribution of ^{142}Nd (Andreasen and Sharma, 2007, 2006; Burkhardt *et al.*, 2016; Saji *et al.*, 2016). The s-process excess in terrestrial rocks has been confirmed for molybdenum isotopes as well (Render *et al.*, 2017). Figure 5 illustrates this scenario.

4.2. Early Differentiated Reservoirs

As described in the previous section (4.1-scenario II), the difference in the $^{142}\text{Nd}/^{144}\text{Nd}$ isotopic composition between terrestrial accessible mantle and Ordinary chondrites is not caused due to a global scale differentiation event within a first few million years of the formation of solar system, but rather shows heterogeneity in the Solar nebula in terms of s-process nuclides. This means Earth is still chondritic in composition in terms of Sm-Nd elemental ratio (RLEs) and the anomalies with respect to terrestrial standard carry an evidence of the early differentiation of the silicate Earth. The implication is that the differentiation events may be localized events and were not of global scale. The positive anomalies reported from Isua (Greenland) still means that the mantle source was a depleted mantle reservoir like EDR and a complimentary enriched reservoir (EER) must have formed, with respect to the terrestrial standard and not with respect to the Ordinary Chondrites (Fig. 5). The budget for EER and EDR has changed now and its (for EER) estimate cannot be made unless the extent/scales of these differentiation events are known.

4.3. Dependence of Anomalies on the Choice of Terrestrial Standard

So far the anomalies in $\mu^{142}\text{Nd}$ as the evidence for early differentiation event(s) for silicate Earth have been discussed. This anomaly is defined with respect to $^{142}\text{Nd}/^{144}\text{Nd}$ of the terrestrial standard, assuming the terrestrial standard represents equivalent $^{142}\text{Nd}/$

^{144}Nd isotopic composition of that of the accessible mantle. As can be seen in Table 1, various Nd standards have been used by different workers and it is assumed that isotopically they are all equivalent. This is however, not the case. Recent studies have shown that the Nd isotope composition of the commonly used Nd standards like La Jolla, JNdi-1, Ames and many others is not identical (Gautam and Ray, 2017; Saji *et al.*, 2016; Wakaki and Tanaka, 2012) as reflected in their $^{142}\text{Nd}/^{144}\text{Nd}$ isotopic ratios. This could be a result of the chemical purification processes which are used to prepare pure (more than 99.99 %) metal/metal oxides. In this scenario, it is likely that the anomalies with respect to one standard may disappear with respect to the other. This is observed for a few of the rocks analyzed by Gautam and Ray (2017). It is therefore important to fix a standard for $^{142}\text{Nd}/^{144}\text{Nd}$ isotopic studies in future. This will facilitate comparison of the $^{142}\text{Nd}/^{144}\text{Nd}$ data among various laboratories if $^{142}\text{Nd}/^{144}\text{Nd}$ for this standard could also be fixed through inter-laboratory analyses like it is available for $^{143}\text{Nd}/^{144}\text{Nd}$ (Tanaka *et al.*, 2000). By doing this, an isotopic reference material for $^{142}\text{Nd}/^{144}\text{Nd}$ will be available.

5. Future Studies

This summarizes the exciting field of understanding early silicate Earth (mantle) differentiation. The hunt for these signatures, in various rocks, indicating early Earth melting/differentiation events is still on. There are numerous future prospects in this area of research; after overcoming the technical difficulties involved in the analyses.

1. Inter-laboratory $^{142}\text{Nd}/^{144}\text{Nd}$ isotopic ratio analyses of Nd standard(s).
2. Combined ^{142}Nd - ^{182}W isotopic studies of the oldest rocks in each continent.

^{182}W is radiogenic daughter product of radioactive decay of ^{182}Hf by emitting a beta particle, with a half-life of 9 Ma (Guntre and Mensing, 2004). Hf is a lithophile element whereas W is siderophile. ^{182}Hf - ^{182}W isotope systematics has helped in constraining the timing of core formation event(s) (Kleine *et al.*, 2009; Kruijer *et al.*, 2012; Jacobsen *et al.*, 2002). During core formation, W was segregated into the core whereas Hf remained in the silicate

Fig. 4: A simplified illustrative representation for scenario I-b, where Earth (BSE) starts with a non-chondritic or super-chondritic composition at time t_0 (time of formation of solar system), unlike scenario I-a, an early differentiation event is not required to explain the chemical composition of the accessible mantle; 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. DMM and crust together represent the accessible mantle of Earth, which shows 20 ppm excess in $\mu^{142}\text{Nd}$ with respect to Ordinary Chondrites

Earth. With time, due to decay of ^{182}Hf , there was radiogenic growth of ^{182}W in the silicate Earth, which reflects that the core formation process(s) were over before ^{182}Hf completely decayed, that is within first 50 Ma (around five half-lives of ^{182}Hf). Any silicate differentiation event taking place during this time, will have additional effect on the ^{182}W isotopic composition of the mantle domains affected due to the event(s). Therefore, combined studies of these two isotopic systematics like in the Archean terranes, can give a better understanding of the early Earth events.

3. Study of Mantle Xenoliths for $^{142}\text{Nd}/^{144}\text{Nd}$ Isotopic Composition

Since mantle xenoliths directly sample the mantle which is otherwise inaccessible, it provides an opportunity to directly study it. These

Fig. 5: A simplified illustrative representation for scenario II, where Earth (BSE) starts with a chondritic composition at time t_0 (time of formation of solar system), unlike scenario I-a, an early differentiation event is not required to explain the isotopic composition of the accessible mantle. The 20 ppm excess in $\mu^{142}\text{Nd}$ with respect to Ordinary Chondrites (OC) is due to excess in s-process generated ^{142}Nd nuclide in Earth at t_0 as compared to the OC; EDR-Early Depleted Reservoir; EER-Early Enriched Reservoir; DMM-Depleted MORB Mantle; t_d -time of early differentiation; t_{cc} -time of formation of continental crust; t_p -present day

are yet another best proxy to understand the mantle and can provide insights about the early events too. So far attempts have not been successful as the typical Nd concentrations of Nd in these peridotites are low (around 0.1-0.01 ppm).

4. $^{142}\text{Nd}/^{144}\text{Nd}$ isotopic studies on rocks of other terrestrial planets and/or their moons.

This will help in understanding the ^{142}Nd makeup of the terrestrial planets and also help in a better understanding of nucleosynthetic origin of isotopic offset between these planetary bodies and meteorites. Overall, it will aid in acquiring a better understanding of planetary evolution. A few studies exists like (Brandon *et al.*, 2009; Debaille *et al.*, 2013, 2007; Nyquist *et al.*, 1995).

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