

# Early Earth: insights from the meteorites

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**The evolution of planetary bodies like 4 Vesta and terrestrial planets (e.g. Earth, Moon, Mars) involved accretion, melting, differentiation, formation of silicate mantle and metallic core, and mantle differentiation. Determination of the time scales of these processes forms the fundamental basis for understanding the early evolution of the Earth. The decay of  $^{182}\text{Hf}$  (half-life  $\sim 9$  Ma) to  $^{182}\text{W}$  and  $^{146}\text{Sm}$  (half-life  $\sim 103$  Ma) to  $^{142}\text{Nd}$  has been used to determine time scales of metal-silicate differentiation leading to core formation of planets and mantle differentiation resulting in eruption of basalts on planetary bodies which are preserved even today on 4 Vesta, but not preserved on the Earth. By using the meteorite data as a baseline, one can establish a time frame for early evolution of Earth.**

**Keywords:** Chondrules, early Earth, meteorites, planetesimals.

## Introduction

THE Sun, a low mass star, perhaps formed in a cluster of stars, similar to what is observed in star-forming regions in our galaxy (the Milky Way) and other galaxies. Astronomical observations of star-forming regions, e.g., Orion nebula, show that stars are generally born in clusters in ‘molecular clouds’ which are vast, cold volumes of gas, mostly molecular hydrogen and helium, complex organic molecules, and very importantly they also contain dust grains which include heavy elements in the form of silicates, hydrocarbons and various ices. The masses of molecular clouds typically range from  $10^6$  to  $10^8$  solar masses within which denser regions with embedded objects have been observed. The free fall of molecular clouds is inhibited by internal pressure, turbulence and magnetic pressure. The velocity distribution in the gas suggests that the cloud is in a state of turbulence. The gaseous eddies of different length scales exchange energy, and dissipation of energy on the smallest scale size inevitably results in collapse. A neighbouring supernova or powerful outflows of matter from young stars could provide energy to sustain turbulence in the gas preventing its collapse<sup>1</sup>. The dissipation of energy at the smallest scales results in the formation of smallest cloud structures, which in turn leads to collapse of small cloud structure to form stars (e.g. ref. 2). The Sun and the sys-

tem of planetary bodies around it formed nearly 4.5 billion years ago in such an environment, which is mimicked by the young stellar objects in the Orion nebula<sup>3</sup>.

## Mass and chemical balance in disks around stars

The disks surrounding new born stars in the Orion nebula are comprised of gas and dust<sup>4</sup>. The disk radii are comparable to solar system’s planetary radii at its outer limits ( $\sim 50$ – $100$  AU) and some contain sufficient mass to make up all the planets in our solar system<sup>5</sup>. The disks around such new born stars have pan-cake like or flattened structure, and thus resemble the geometry of the planetary orbits of our solar system. In astronomical literature these disks are called ‘protoplanetary’ disk or nebula, whereas in meteorite literature they are generically called the solar nebula. As the disk is made up of the same material from which the central star formed, the proportional distribution of dust and gas (hydrogen, helium, water and carbon monoxide) in both star and the disk is similar. Subsequent evolution of the disk could alter the proportion of gas and dust, if the gas is preferentially blown away by young Sun’s stellar winds. If the mass in planetary system is about  $\sim 150$  Earth mass, and assuming that a significant fraction of this is rock-forming material, we can estimate the amount of H and He required to make the composition of the disk similar to the Sun. The mass of the disk from which planets formed is significant compared to the rock mass in the inner solar system. More than the mass of the planet, the chemical and isotopic evolution of various reservoirs while interacting with one another holds the key to understanding the current state of the Earth. In order to decipher the chemical and isotopic data we need a baseline for comparison, and this is provided by meteorites.

## *Anatomy of a chondrite*

Much of our knowledge about early history of the solar system and formation times of planetary bodies is derived from the meteorites. Most of these rocks are fragments of asteroid from the asteroid belt. Meteorites are divided into two types, primitive and differentiated. The primitive meteorites sample asteroids which have escaped complete melting, on the other hand the differentiated meteorites sample asteroids which experienced a high temperature regime resulting in planet-scale melting. The primitive

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meteorites are also called chondrites, and derive their name from the ubiquitous chondrules, once free-floating molten spheres in the nebula which solidified in the nebula prior to incorporation in a planetary body. Chondrites are generally considered to represent the oldest and most primitive rocks of the solar system. They represent chemically least processed material of the solar system because their non-volatile chemical composition is broadly similar to that of the solar photosphere<sup>6</sup>. Chondrules range in size from sub-millimetre to several millimetre, and are composed of rock-forming silicates like olivine  $[(\text{Mg,Fe})_2\text{SiO}_4]$ , pyroxene  $[(\text{Mg,Fe,Ca})\text{SiO}_3]$ , Fe–Ni metal and glass or quenched silicate melt. Experimental results on chondrule properties suggest that dust aggregates and/or broken fragments of previous generation chondrules were flash-heated to very high temperatures of 1700–2100 K in the solar nebula<sup>7</sup>. The thermal environment experienced by these individual objects exceeded the liquidus and a majority of the chondrules underwent complete or partial melting. The presence of relict grains suggests that melting was not always complete but nearly complete<sup>8</sup>. Subsequently they cooled very rapidly with cooling rates of 10–1000 K/h (ref. 9). The conventional wisdom was that during its formation and evolution each chondrule evolved as a chemically closed system, and the bulk chemical composition was a function of its precursors, i.e. dust aggregate from which they formed. The petrographic features of chondrules are a function of their initial bulk composition of the dust aggregate, peak temperature, cooling rates and presence of seed nuclei (e.g. relict grains).

### Chondrules and accretion of planetesimals

Nearly 20–80 volume% of most chondrites are made up of chondrules. The physically and chemically distinct properties of chondrules<sup>10</sup> together with distinct formation ages of chondrules<sup>11</sup> from different chondrite groups suggest that they formed in localized environments spanning 1–4 million years following solar system formation. This necessarily demands a lack of mixing in chondrule population from different locales in the nebula before their accretion to form parent bodies of primitive meteorites. The formation of chondrules at high temperature with rapid cooling in a conventional low density solar nebula (total pressure  $\approx 10^{-6}$ – $10^{-3}$  bars) and the cooling at rapid rates, experiments<sup>9</sup> and calculations (e.g. refs 12, 13) suggested that chondrules would experience extensive evaporative loss of elements, both major and minor, as a function of volatility. Systematic isotopic fractionation is not exhibited by the fractionated elements as expected<sup>14</sup>. Analyses of several chondrules from primitive meteorite Semarkona<sup>15</sup> showed that abundance of the volatile element, sodium, remained relatively constant during chondrule formation. This result is in conflict with

chondrule synthesis experiments mimicking low density conditions in the solar nebula. Therefore the only way out of this conundrum is that chondrule formation took place in regions with much higher solid densities than predicted by nebular concentration mechanisms<sup>15</sup>. On the basis of the lack of isotopic fractionations in chondrules, it has been estimated that chondrule-forming regions were at least 150–6000 km in radius<sup>16</sup>. Calculations<sup>15</sup> suggest that regions with radius  $> 4000$  km would produce chondrules that would cool at rapid rates as measured for chondrules. These regions would contain enough mass that would make them self-gravitate to produce parent bodies of chondrites with a radius of  $\sim 50$  km and density of  $\sim 3$  g/cc which can ultimately accrete to form large planetesimals. Sodium distribution and cooling rates of chondrules have provided a constraint for mass distribution in chondrule-forming region, which is intimately connected with planetesimal formation<sup>17</sup>.

### Chondrules and refractory inclusions – connection?

Chondrules do not carry evidence of nucleosynthetic anomalies and they have low abundance of short-lived radionuclides (SLRs) compared to refractory inclusions (see below). Apart from chondrules, the carbonaceous chondrites also consist of inclusions enriched in Ca, Al and other rare earth elements (REEs) compared to bulk meteorite chemical composition. In early 1970s thermodynamic calculations suggested that the Ca–Al-rich inclusions (CAIs), probably condensed at high temperatures, form a gas of approximately solar composition<sup>18</sup>. CAIs are enriched in refractory elements (e.g. Ca, Al, Ti) and trace elements  $\sim 20\times$  chondrite or more, and formed at high temperatures ranging from 1400 to 1800 K, and experienced slow cooling compared to chondrules. CAIs are rich in high temperature minerals, silicates like, melilite, fassaite (Ti-rich pyroxene), and oxides (like, spinel, hibonite). CAIs are not size-sorted between different meteorite classes and range in size from a few centimetres to sub-millimetres, sometimes too small to be identified as a composite object. They are unevenly distributed between different meteorite classes, ranging from  $\sim 5\%$  in CV3 meteorites to nearly absent in ordinary chondrites. They also have a high abundance of SLRs (e.g. <sup>26</sup>Al, <sup>41</sup>Ca, <sup>10</sup>Be, etc.), and have nucleosynthetic anomalies in neutron rich isotopes, e.g. <sup>50</sup>Ti, <sup>48</sup>Ca and <sup>54</sup>Cr. The chondrites also consist of broken fragments of the chondrules and CAIs, matrix material<sup>19</sup>, opaques objects such as Fe–Ni, FeS<sup>20</sup> and very importantly pre-solar grains<sup>21</sup>. From the time CAIs were found in Allende CV3 meteorite it was obvious to researchers that CAIs were a unique class of objects, and therefore, their formation required specific physical, chemical and thermal conditions. The conventional idea was that CAIs formed in a monotonically

cooling solar nebula as the first condensates (e.g. Grossman<sup>18</sup>) seemed less viable as more and more data became available. The distinction between the chemical and isotopic composition of both the chondrules and CAIs was noticeable, however, given that both formed in the solar nebula the specifics of astrophysical processes responsible for their formation with such uniquely different characteristics was not obvious. Until 1996 no specific idea for CAI and chondrule formation was put forward which was rooted in astrophysical models of disk evolution. Shu *et al.*<sup>22</sup> postulated the X-wind model for formation of CAIs and chondrules. The relationship between a 'astrophysical process' or its variants resulting in formation of CAIs and chondrules remains outstanding.

### *Evolution of small planetary bodies*

The iron meteorites and basaltic achondrites (e.g. eucrites) represent samples of rocks from differentiated planetary bodies. The parent bodies of these meteorites were assembled sufficiently early and experienced planet wide melting because of heat generated by decay of <sup>26</sup>Al and perhaps even <sup>60</sup>Fe. This resulted in separation of silicate from metal and paved the way for formation of metallic core and silicate mantle. The iron meteorites sample the core and the basaltic achondrites sample the mantle. The basaltic achondrites resemble terrestrial basalts and are composed of silicates (e.g. feldspar and pyroxene). A group of basaltic achondrites identified as HEDs (howardites, eucrites and diogenites) probably originated from a large differentiated asteroid 4 Vesta<sup>23</sup>.

### *Timelines for small body evolution*

The crystallization ages of chondrites and its components show that chondrules and CAIs are the oldest rocks in the solar system which formed through an igneous event. Several of these objects formed nearly ~4.567 billion years ago, establishing a time marker for birth of solar system. Furthermore, a relative age difference of a few million years between CAIs and chondrules is inferred on the basis of U–Pb data<sup>24</sup>. If chondrules and CAIs are primary products of nebular processes, then locales within the nebula with suitable environment (temperature, pressure and material composition) need to be identified in the context of disk structure around young stellar objects. This establishes fundamental connection between meteorites analysed in laboratories and astronomical observations of young stars with disks around them with the potential to form planets. The meteorites can also be studied for the presence of SLRs in early solar system. The half-lives of SLRs found in meteorites range from 0.1 to 103 million years. The abundance of the now extinct SLRs can be determined using their daughter isotope abundance variation as a proxy. By anchoring the forma-

tion time of one group of objects (e.g. CAIs) with absolute chronometers (U–Pb system), and using the measured relative difference in abundance of an SLR (e.g. <sup>26</sup>Al) between CAI and a chondrule or basaltic achondrite we can establish a framework for formation and evolution of several early solar system objects both at nebular scale and planetary scale. The underlying assumption is that the distribution of SLRs is homogeneous and that minerals did not exchange parent or daughter after crystallization. Because of their short half-lives, SLRs are capable of resolving short-time intervals which helps to resolve early evolution of chondrules, CAIs and planetary bodies. This degree of resolution is not feasible using absolute chronometers.

For example, based on the differences in abundances of <sup>26</sup>Al in CAIs and chondrules, it is estimated that the latter formed at least few million years after CAIs<sup>25,26</sup>. The CAI-forming event was short, whereas the chondrule formation stretched over a period of time and the assembly of planetesimals took place over several million years (see e.g. Russell *et al.*<sup>25</sup>).

The presence of <sup>26</sup>Al in eucrites like Piplia Kalan shows that eucrites crystallized very early when <sup>26</sup>Al was still alive. Furthermore, the difference in abundance between eucrites like PK and CAIs suggests that eucrite crystallized within 3.5 million years of formation of CAIs. Basalt formation time on the eucrite parent body (EPB) suggests rapid accretion and differentiation of planetesimals<sup>27</sup>. The formation of basalts requires the proto-planet to evolve through metal–silicate differentiation to produce a silicate mantle and a metallic core. This resulted in the separation of lithophile and siderophile elements into the silicate mantle and metallic core, respectively, and further differentiation of the silicate mantle would give rise to basalts like PK. The chemical composition of the protoplanet on which eucrites evolved had chondritic abundances for refractory elements but not for volatile elements<sup>28</sup>, and therefore, the eucrite parent body prior to differentiation had chondrules, CAIs and the pot-pourri of material observed in chondrites.

### *Thermal evolution of planetesimals*

We began our discussion by stating that chondrites escaped planetary heating and melting. The moot point is what governs small body melting? It was postulated in 1955 by Urey<sup>29</sup> that decay of <sup>26</sup>Al generates 3 Mev of energy. Because Al is a major rock-forming element, sufficient abundance of <sup>26</sup>Al could produce enough heat to melt asteroids. The extent of heating of such a protoplanet is directly proportional to the abundance of <sup>26</sup>Al and the characteristic thermal diffusivity  $\eta = (\kappa t / \rho C_p r^2)$ , where  $\kappa$  thermal conductivity,  $\rho$  the density,  $C_p$  the specific heat,  $r$  the planetary radius and  $t$  is time after accretion. In the limiting case of  $\eta \ll 1$ , the centre of the planet

is effectively insulated and most of the heat is retained (e.g. Schramm *et al.*<sup>30</sup>). If the planet accreted with an initial  $^{26}\text{Al}/^{27}\text{Al} \sim 2 \times 10^{-6}$ , the temperature of the planet would not have exceeded  $\sim 500^\circ\text{C}$ , insufficient to melt a planetary body for differentiation and core–mantle formation. If the parent-body of PK had accreted with a  $^{26}\text{Al}/^{27}\text{Al} \sim 8 \times 10^{-6}$  the central temperatures would be close to  $\sim 1100^\circ\text{C}$  but only small volume of the central region of the planet would have been close to melting temperatures making it difficult for differentiation to succeed. A planet with radius  $> 80$  km and initial  $^{26}\text{Al}/^{27}\text{Al} \sim 2 \times 10^{-5}$  would undergo large-scale melting with temperatures exceeding  $1100^\circ\text{C}$  for the dominant volume of the planet<sup>31</sup>, resulting in the formation of metallic core and silicate mantle, followed by the eruption of basalts.

### Dating core–mantle formation in planets

The accretion of the parent bodies of differentiated meteorites (e.g. eucrites), Mars, Moon and Earth was quickly followed by large-scale melting and metal–silicate differentiation, resulting in core–mantle formation. Basaltic eucrites are a group of differentiated meteorites that formed as lava flows or as shallow intrusions following metal–silicate differentiation on the EPB. Asteroid 4 Vesta is identified as a plausible EPB<sup>28</sup>. Time constraints on the processes of melting, metal–silicate separation leading to core formation and subsequent mantle differentiation that produced precursors to basaltic eucrites are critical to models of the thermal evolution of EPB which also help to understand similar processes on the Earth, albeit on a smaller scale size. The proto-Earth, the precursor of the current Earth, was assembled along similar time scales as the other inner planets; however there are no traces of the rocks from this era to be examined. If the process of planetary differentiation had followed soon after accretion then dating the differentiation serves as proxy or a lower limit for the Earth's accretion time. The Earth, Mars, Moon and asteroid 4 Vesta experienced a common stage in their evolution, all these planetary bodies underwent large-scale melting, resulting in the formation of metallic core and silicate mantle. This major 'geophysical event', which stratifies the planets into different chemical layers, marks an important change in the life cycle of planetary evolution because the formation of major planetary reservoirs, atmosphere, hydrosphere, lithosphere and biosphere (on the Earth only) that we see today postdates differentiation. When planets containing bulk solar proportions of elements are melted and differentiated, lithophile elements (e.g. Ca, Mg) and siderophile elements (e.g. Fe, Ni) are chemically fractionated and redistributed into the silicate mantle and metallic core respectively. This process also chemically fractionates and redistributes trace elements like lithophile (Hf) and siderophile (W) into the silicate mantle and metallic

core respectively<sup>32</sup>. The extinct  $^{182}\text{Hf}$ – $^{182}\text{W}$  decay system has proven to be useful as a chronometer for the early planetary processes, viz. core–mantle separation because the  $^{182}\text{Hf}$  half-life of 9 Myr is sufficiently long to resolve the time scales of planetary accretion and differentiation. The decay of  $^{182}\text{Hf}$  to  $^{182}\text{W}$  has been used to determine time scales of metal–silicate differentiation leading to core formation of planets<sup>33</sup> and mantle differentiation resulting in eruption of basalts on EPB<sup>33,34</sup>. Moreover, the refractory nature of the elements Hf and W ensures that their bulk abundance in planetary bodies is in chondritic proportions, making comparisons across different planetary bodies meaningful. For example, if one of these elements were volatile and the other refractory, the bulk abundances in a planetary body would not necessarily be chondritic. The radial distance of zone of accretion from the Sun could play an important role in the relative enrichment or depletion of the parent over daughter in the planetary body. The total daughter isotope budget would be influenced by this factor making comparisons between different planetary bodies unreliable. Numerical calculations of planetary accretion time are in the range of few tens of million years (e.g. Wetherill<sup>35</sup>). Large bodies like the Earth grow by accretion of smaller bodies, making the process a function of population of interacting small bodies. The end-point for Earth's mass prior to differentiation is not easy to estimate. It can however be anticipated that core formation of a well mixed large planetary body like the proto-Earth would have required large-scale melting for separation of metal and silicate and the energy source for the same remains outstanding, although impacts are favoured candidates<sup>36</sup>. If the core formation is very early in the history of the solar system before any of the  $^{182}\text{Hf}$  has decayed then the isotopic abundance of  $^{182}\text{W}$  of the core would reflect the starting composition of the solar nebula prior to addition of radiogenic  $^{182}\text{W}$  inventory from the decay of  $^{182}\text{Hf}$ . The decay of  $^{182}\text{Hf}$  present in the mantle would increase the inventory of  $^{182}\text{W}$  in the silicate reservoir. The timing of the core–mantle formation in a planetary body relative to solar system formation would determine the abundance of live  $^{182}\text{Hf}$  in the mantle, and together with the enrichment of Hf/W ratio over and above the chondritic values would govern the increase in radiogenic  $^{182}\text{W}$  in the mantle. The terrestrial standards, representative of bulk silicate Earth (BSE), have  $^{182}\text{W}/^{184}\text{W}$  isotopic composition higher than primitive chondrites by  $2\varepsilon$  units (2 parts in 10,000) whereas the iron meteorites have  $^{182}\text{W}/^{184}\text{W}$  less by  $2\varepsilon$  units. The chondritic meteorites sampled the bulk solar nebula and the  $^{182}\text{W}$  isotopic composition evolved because of complete decay of  $^{182}\text{Hf}$ . The Fe-meteorites sample cores of differentiated planetesimals and their lower  $^{182}\text{W}$  values compared to chondrites reflect the non-radiogenic  $^{182}\text{W}$  in the cores prior to decay of  $^{182}\text{Hf}$ . This necessarily demands an early formation of cores in asteroids which experienced differentiation. The higher  $^{182}\text{W}$

in BSE as sampled (i) reflect the higher Hf/W ratios in silicate mantle compared to chondrites and (ii) the core formation event occurred prior to complete decay of  $^{182}\text{Hf}$ . On the basis of these considerations, Kleine *et al.*<sup>37</sup> and Yin *et al.*<sup>38</sup> estimated that core formation took place in  $\sim 30$  Myr after the start of solar system. The eucrites which sample the mantle of asteroid Vesta<sup>23</sup> show high excess of radiogenic  $^{182}\text{W}$ , typically on the order of 20–40 $\epsilon$  units, and yield a whole-rock isochron corresponding to an initial  $^{182}\text{Hf}/^{180}\text{Hf}$  of  $(7.96 \pm 0.34) \times 10^{-5}$  (ref. 34). The high  $^{182}\text{W}$  anomalies require early differentiation processes on Vesta while  $^{182}\text{Hf}$  was still alive. Based on the estimate of initial  $^{182}\text{Hf}/^{184}\text{Hf}$  in chondrites  $\sim 1 \times 10^{-4}$  (ref. 37), this yields an age for differentiation on Vesta of  $\sim 4.2$  Myr after the beginning of the Solar System. This time scale is consistent with the result from other isotope systems  $^{87}\text{Rb}$ – $^{87}\text{Sr}$  (ref. 39);  $^{53}\text{Mn}$ – $^{53}\text{Cr}$  (refs 40, 41) and  $^{26}\text{Al}$ – $^{26}\text{Mg}$  (ref. 27). The SNC meteorites are most likely derived from Mars (e.g., McSween<sup>42</sup>) and show W values ranging from 0 to 3 $\epsilon$  units, requiring core formation and silicate differentiation during the life-time of  $^{182}\text{Hf}$  (refs 33, 43).

SNC meteorites are representative samples from Mars<sup>42</sup> and terrestrial samples are representative of terrestrial silicate mantle and both do not show excess in  $^{182}\text{W}$  similar to the levels exhibited by eucrites which are products of silicate differentiation of the mantle from Vesta. This implies preservation of  $^{182}\text{W}$  effects on Vesta without significant dilution from non-radiogenic W added by impacts or without  $^{182}\text{W}$  being removed to the core by a prolonged magma ocean. The tungsten isotopes reveal that within first 5 Ma of the solar system, accretion and core formation in asteroids was complete, and the accretion of Earth and Mars was completed in 33 Ma and 15 Ma, respectively after CAI formation<sup>37,38,44,45</sup>. Given that smaller planetesimals had accreted and differentiated much before Mars and Earth, accretion of these two inner planets involved pre-differentiated planetesimals, partially if not completely. One possibility is that cores of Mars and Earth are products of accumulation of previously formed cores. In this scenario the re-equilibration of metallic cores with existing silicate mantle is limited, and one would expect to see substantially higher  $^{182}\text{W}/^{184}\text{W}$  ratios for bulk Martian and terrestrial mantles. Kleine *et al.*<sup>33</sup> predict that the bulk mantle composition of Mars and Earth should have  $^{182}\text{W}/^{184}\text{W}$  ratios ranging from 2–4 $\epsilon$  to 14–23 $\epsilon$   $^{182}\text{W}$ , however, this is not observed. Therefore some workers<sup>33</sup> suggest a scenario of metal–silicate equilibration during accretion (e.g. Rushmer *et al.*<sup>46</sup> and Yoshino *et al.*<sup>47</sup>). The low values of  $^{182}\text{W}$  of 0.4 $\epsilon$  for Mars and 0 for silicate Earth are attributed to magma ocean environment (e.g. Ballhaus and Ellis<sup>48</sup>) for efficiently scavenging radiogenic  $^{182}\text{W}$  into the cores of Mars and Earth<sup>33</sup>. However, unlike the Moon we do not have evidence for a magma ocean environment on Earth and Mars (e.g. Walter *et al.*<sup>49</sup>). If W isotope composition

requires such a scenario, then impacts of planetesimals appear to be most viable source of energy for such a process because of late core formation process which renders the SLRs  $^{26}\text{Al}$  and  $^{60}\text{Fe}$  ineffective as heat sources. Numerical calculations suggest that large impacts were common occurrence in the late stages of accretion (e.g. Wetherill<sup>35</sup>; Canup and Agnor<sup>50</sup>) and the energy released by them is sufficient to melt large portions of the silicate mantle (e.g. Benz and Cameron<sup>51</sup>; Tonks and Melosh<sup>52</sup>). The early segregation of metal core and silicate mantle in planetesimals was energized by the decay of short-lived nuclides (i.e.  $^{26}\text{Al}$ ,  $^{60}\text{Fe}$ ) whereas in the inner terrestrial planets it was related to large impacts.

### Early differentiation of mantle

The Sm–Nd radiogenic decay system includes the coupled  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  and  $^{146}\text{Sm}$ – $^{142}\text{Nd}$  chronometers which are useful for geochemical and cosmochemical studies. Sm–Nd radiogenic system is one of the most robust chronometers utilized to trace the long-term chemical evolution of the silicate portion of the Earth via long-lived radioisotope  $^{147}\text{Sm}$  ( $T_{1/2}$  (half-life)  $\sim 106$  Ga) as well as short-lived  $^{146}\text{Sm}$  ( $T_{1/2} \sim 103$  Ma) isotope. Both parent (Sm) and daughter (Nd) are refractory lithophile elements, and are therefore, unaffected either by volatile loss or core formation event in the early history of the Earth. Radiogenic isotope tracers such as  $^{142}\text{Nd}$  and  $^{143}\text{Nd}$  isotopes find useful applications in understanding the chemical evolution of planetary bodies. The long-lived  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  system is used extensively to understand chemical differentiation of the BSE into crust and mantle over the Earth's history of 4.6 Ga. The early differentiation of mantle is better investigated with the short-lived chronometer  $^{146}\text{Sm}$ – $^{142}\text{Nd}$ . The low initial abundance of extinct  $^{146}\text{Sm}$  in the solar system,  $^{146}\text{Sm}/^{144}\text{Sm} \sim 0.0085$  (e.g. Boyet *et al.*<sup>53</sup>), and the small differences in compatibility of Sm and Nd result in extremely small variations in Sm and Nd abundances and as a consequence the differences in  $^{142}\text{Nd}$  abundance<sup>51,52</sup> between different planetary reservoirs are also small. Application of  $^{146}\text{Sm}$ – $^{142}\text{Nd}$  systematics therefore requires determination of small variations in  $^{142}\text{Nd}$  abundance through measurement of  $^{142}\text{Nd}/^{144}\text{Nd}$  ratio with an external precision of  $< 10$  ppm.

Recently from the 3.8 Ga Isua Supracrustal Belt, Greenland<sup>54,55</sup>, a small number of samples with  $^{142}\text{Nd}/^{144}\text{Nd}$  excesses were detected, which is the first evidence for such excesses in the silicate portion of Earth. This suggests that formation of material on Earth is similar to differentiated samples on Moon<sup>56</sup> and Mars (e.g. Harper *et al.*<sup>57</sup>).

Measurements of chondritic meteorites show a 20 ppm deficit in  $^{142}\text{Nd}/^{144}\text{Nd}$  (ref. 58) compared to the terrestrial samples. For the longest time,  $^{142}\text{Nd}/^{144}\text{Nd}$  ratio measurements of bulk terrestrial samples and the chondrites

were similar, and the only exceptions were samples from Isua Greenland. With the advent of new generation mass spectrometer and improved techniques, it has become evident that elevated  $^{142}\text{Nd}$  in terrestrial samples compared to chondrites is widespread. This ubiquitous excess is possible if the Earth has higher Sm/Nd compared to chondrites; or assuming Earth is chondritic, all terrestrial rocks are derived from a source which is enriched in Sm/Nd compared to chondrites. This source formed within 300 Ma for the Earth's history and resulted from differentiation of silicate mantle following core–mantle formation. Assuming that bulk Earth is chondritic, the early formation of source depleted in incompatible elements like Nd compared to compatible Sm (Early Depleted Reservoir, EDR), mass balance would automatically require formation of rock reservoirs which are enriched in Nd and depleted in Sm (also called Early Enriched Reservoir, EER). The rocks derived from EDR would have  $^{142}\text{Nd}$  excess and rocks from EER would have deficit of  $^{142}\text{Nd}$  compared to chondrites. On the basis of model calculations, Boyet and Carlson<sup>58</sup> suggested that the excess of  $^{142}\text{Nd}$  is indicative of a planetary scale differentiation around  $\sim 4.53$  Ga ago, which is within 30 Ma of Earth's creation and formation of solar system. They also suggested that difference indicates that 70–90% of the Earth's mantle is compositionally similar to the incompatible element-depleted source of MORB.

From measurements of Sm–Nd isotope system, Rankenburg *et al.*<sup>59</sup> estimated that lunar samples have a  $^{142}\text{Nd}/^{144}\text{Nd}$  ratio that is 20 parts per million less than most samples from Earth and indistinguishable from chondrites. This data requires formation of the lunar mantle in  $\sim 215$  million years after initiation of formation of solar system. Because both the Earth and the Moon formed in the same region of the solar nebula, the Earth would be expected to have a chondritic bulk composition like the Moon, but it does not. The alternative explanation is that the measured Nd composition of the terrestrial rocks is balanced by a complementary reservoir with a lower  $^{142}\text{Nd}/^{144}\text{Nd}$  value that resides in Earth's mantle, which formed with lower Sm/Nd ratio while  $^{146}\text{Sm}$  was still alive.

The complementary mantle reservoir, with lower Sm/Nd composition, has recently been discovered at Nuvvuagittuq greenstone belt, Quebec, Canada<sup>60</sup> and some of the rock types have  $^{142}\text{Nd}/^{144}\text{Nd}$  values in the range of  $-70$  to  $-150$  ppm and  $^{146}\text{Sm}$ – $^{142}\text{Nd}$  isochron gives an age of  $4280 \pm 81$  million years. These rocks are derived from incompatible-element-enriched reservoir which formed soon after Earth's differentiation and may represent the oldest crustal component<sup>60</sup>.

A third alternative is that  $^{142}\text{Nd}$  difference between Earth and chondrites is due to nebular heterogeneity<sup>61</sup>. Investigation of Ba, Sm and Nd isotopic composition of several chondrites, terrestrial samples and lunar rocks revealed distinct stellar nucleosynthetic contributions to early solar nebula. After correcting for deficiencies in s

process, isotopes which affect  $^{142}\text{Nd}$ , chondrite samples had  $^{146}\text{Sm}$ – $^{142}\text{Nd}$  isochron consistent with previous estimates of the initial solar system abundance of  $^{146}\text{Sm}$ , and a  $^{142}\text{Nd}/^{144}\text{Nd}$  for average chondrite Sm/Nd ratio is lower than measured values in terrestrial rocks by  $21 \pm 3$  ppm. The possibility of nebular heterogeneity for  $^{142}\text{Nd}$  composition of Earth was ruled out.

The fourth alternative is that the budget of Sm and Nd in the silicate mantle and the isotopic evolution of  $^{143}\text{Nd}$  and  $^{142}\text{Nd}$  could be affected by later accretion of parts of differentiated planetesimals, a scenario which does not necessitate<sup>62</sup> the existence of hidden reservoirs as postulated previously<sup>58,60</sup>. The debris generated by impact of a Mars-sized object with proto-Earth is thought to be the source material for the Moon<sup>63</sup>. The formation and crystallization timelines for the lunar rocks can be determined using  $^{182}\text{Hf}$ – $^{182}\text{W}$  and  $^{146}\text{Sm}$ – $^{142}\text{Nd}$  (refs 64–66), however results from these studies do not converge.

Earlier studies<sup>65,67</sup> used the assumption that  $^{182}\text{Hf}$  is the primary source of  $^{182}\text{W}$  anomalies in lunar rocks, and estimated the solidification time for Moon, as  $\leq 60$  million years since the beginning of solar system. As the Moon is exposed to cosmic rays, neutron capture by  $^{181}\text{Ta}$  plays a significant role in the production of cosmogenic  $^{182}\text{W}$ , making it difficult to separate the cosmogenic from radiogenic part and thus rendering age calculations unreliable<sup>68</sup>. By analysing metals from KREEP-rich samples (KREEP, samples enriched in potassium (K), rare earth elements (REE) and phosphorus (P)), low-Ti and high-Ti mare basalts with low exposure corrections<sup>69</sup> demonstrated that samples with insignificant cosmogenic correction for  $^{181}\text{Ta}$  derived  $^{182}\text{W}$  reveal that lunar metal W isotope composition is identical to that of the Earth. This suggests that lunar magma ocean did not crystallize within 60 Ma of the Solar System formation. Since the accretion of the Earth was incomplete till the moon-forming giant impact was over, this age estimate of Moon formation is inconsistent (30 million years) for the differentiation of Earth's mantle<sup>58</sup> based on the  $^{142}\text{Nd}$  excess in bulk Earth compared to chondrites.

The  $^{182}\text{W}/^{184}\text{W}$  of any planetary mantle reflects the time scale of accretion, differentiation, core–mantle formation, mobilization and re-equilibration of W in mantle during core formation<sup>45</sup>. Following the giant impact and formation of Moon, the subsequent evolution of Earth and Moon is apparently not influenced by one another. Simulations of the giant impact suggest that significant fraction of material for Moon formation,  $\sim 80\%$  is derived from impactor material<sup>63</sup>. The compositional difference between impactor and proto-Earth should reflect the current composition of mantle of Moon and Earth, therefore only obvious explanations for the identical W isotope composition<sup>69</sup> is because Moon is derived from Earth material or W isotopes of Moon and Earth re-equilibrated after the giant impact. A parallel situation exists in case of stable isotopes of oxygen where the Moon and Earth

have identical composition, and this is perhaps reflective of the parent material for Earth and Moon being out-sourced from the same region in the nebula<sup>70</sup>. It is not clear if re-equilibration was responsible for identical W isotope composition of Earth and Moon, the nature of the operating mechanism remains unclear.

In conclusion, the formation of the Earth is constrained by the experimental data obtained from SLRs systems <sup>182</sup>Hf–<sup>182</sup>W and <sup>146</sup>Sm–<sup>142</sup>Nd. It is now obvious from these data that the Earth formed very early and its time scales of accretion, differentiation and mantle differentiation all occurred within few tens of million years and impacts played a significant role in the evolution of terrestrial planets like Earth. The possibility of hidden reservoir in the Earth enriched in compatible elements cannot be ruled and it is perhaps a direct consequence of the <sup>142</sup>Nd differences between the chondrites and terrestrial samples.

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