# Study on non-traditional isotopes in meteorites: Implications to core formation and planetary differentiation

A Thesis

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By

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# Dedícated to

# Baptu, Mammí and Lado

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## LIST OF ABBREVIATIONS

- BSE Bulk Silicate Earth
- BE Bulk Earth
- EC Enstatite Chondrite
- OC Ordinary Chondrite
- CC Carbonaceous Chondrite
- HED Howardite-Eucrite-Diogenite
- MC-ICPMS Multi Collector Inductively Coupled Plasma Mass Spectrometer
- ICPMS Inductively Coupled Plasma Mass Spectrometer
- ICP-AES Inductively Coupled Plasma Atomic Emission Spectrometer
- EPMA Electron Probe Micro Analyzer
- SEM Scanning Electron Microscope

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#### PHYSICAL RESEARCH LABORATORY

High precision Si isotope analyses in meteorites and terrestrial samples are recently being used as a tracer of Si content in Earth's core and to identify the building blocks of Earth (Georg *et al.*, 2007; Fitoussi and Bourdon, 2012). The presence of Si in the core of Earth has been argued since a long time from the superchondritic Mg/Si of terrestrial rocks (Ringwood, 1959). A strong proof for the presence of Si in Earth's core comes from the observed heavier Si isotopic composition of Bulk Silicate Earth (BSE: silicate reservoir of the Earth, excluding metallic core) compared to chondrites. It is suggested that preferential partitioning of lighter Si isotopes in the core of Earth has enriched the silicate reservoir of Earth in heavier isotopes of Si (Georg *et al.*, 2007). Based on Si isotopic offset between ordinary-carbonaceous chondrites and BSE, the presence of ~6-12 wt% Si in the core of Earth has been estimated by a number of authors in the recent past (Georg *et al.*, 2007; Zieglar *et al.*, 2010; Armytage *et al.*, 2011; Zambardi *et al.*, 2013).

The validity of using  $\delta^{30}$ Si differences between chondrites and BSE to estimate the Si content in Earth's core lie on the assumption that observed  $\delta^{30}$ Si offset result solely from equilibrium Si isotopic fractionation between metal and silicate during high temperature core formation. However, the idea of invoking equilibrium Si isotope fractionation between metal and silicate during core formation to explain isotope offset between BSE and chondrites faces a major hurdle since the estimated amount of Si in Earth's core varies with the choice of the representative proxy for bulk Earth composition (Armytage *et al.*, 2011). Due to significant difference in  $\delta^{30}$ Si value between enstatite chondrite and BSE, the estimated amount of Si in Earth's core turns out to be ~23 wt% when enstatite chondrites are taken as a proxy of bulk Earth composition. Since the presence of such a high concentration of light elements in the core is impossible based on geophysical estimates (Badro *et al.*, 2007), it is suggested

that not more than 15% of Earth's precursor material could be of enstatite chondritic origin (Fitoussi and Bourdon, 2012).

However, enstatite chondrite shows similarity with BSE in a number of isotopic systematics such as, O, N, Cr, Ni, Mo, Ti, Ca, Os and Nd; which indicates a generic connection of enstatite chondrite with the Earth (Javoy *et al.*, 2010). Although Si is an exception to this observation but Si isotopes are itself heterogeneously distributed within enstatite chondrite as the non-magnetic phases of enstatite chondrite have heavier Si isotope composition than its bulk composition (Savage and Moynier, 2013). Therefore, it is extremely important to accurately estimate the extent of Si isotope heterogeneity within enstatite chondrite before excluding this group of meteorites as a significant precursor of Earth. To estimate the  $\delta^{30}$ Si variation within enstatite chondrites, we have carried out Si isotopic analyses in different pre-characterized phases (metals, silicates and matrices) of unequilibrated EH3 chondrites that were obtained after micro milling.

In general, the processes responsible for isotopic discrepancy between terrestrial rock samples and chondrites have always been debated between two most probable causes: high-energy impacts versus core partitioning. Therefore, apart from Si isotope fractionation during core formation; preferential evaporation of Si relative to Mg during giant impacts is also known to have induced Si isotope fractionation and Mg/Si ratio enrichment in crustal rocks compared to chondrites (Pringle et al., 2014; Boujibar et al., 2015). In case of objects that have experienced high degree of evaporation, the degree of Mg isotope fractionation has been found to be twice of Si isotope fractionation (Clayton et al., 1983, 1988; Davis et al., 1990; Grossman et al., 2000; Sugiura et al., 2004). Therefore, it is reasonable to expect a higher extent of Mg isotope fractionation than Si isotopes during any large-scale planetary processes that are governed by impact related volatilization and evaporation. To better understand the role played by impacts in generating the heavier  $\delta^{30}$ Si composition of BSE compared to chondrites, we have investigated the fractionation pattern of both Si and Mg in bulk meteorites, terrestrial rock samples and phase separates (silicates, metals and matrices) of EH3 chondrites.

The Si and Mg isotope measurements were made using Thermo Neptune MC-ICPMS in pseudo high-resolution mode. The long-term reproducibility assessed by repeated

measurements of reference materials was found to be better than  $\pm 0.09\%$  ( $\pm 2\sigma$ ) for  $\delta^{30}$ Si and  $\pm 0.08\%$  ( $\pm 2\sigma$ ) for  $\delta^{26}$ Mg<sub>DSM-3.</sub> The Si and Mg isotopic analyses carried out in a wide range of meteorites indicate that homogenous stable Mg isotopic composition prevails in the solar system but Si isotopes are fractionated among planetary bodies. The observed trend of  $\delta^{30}$ Si variation among meteorites and terrestrial rock samples suggests the presence of three broad types of planetary materials that have been sampled by the presently known meteorites: (i) Enstatite meteorites, characterized by the lightest  $\delta^{30}$ Si value (<-0.64±0.11‰), (ii) Carbonaceous-ordinary chondrites and HEDs characterized by  $\delta^{30}$ Si values ranging from -0.41 to -0.47‰, (iii) Terrestrial samples, lunar meteorites and angrites, characterized by a heavier Si isotopic composition ( $\delta^{30}$ Si > -0.29\pm0.11‰).

Si isotope analyses among different micro-phases (silicates, matrices and metals) of primitive enstatite chondrite (EH3) reveals an enrichment of light isotopes of Si in its metallic phases whereas the silicates were found to possess a heavier Si isotopic signature that matches with BSE within analytical uncertainties. Thus, Si becomes the latest addition to the list of elements (O, N, Ni, Cr, Ti, Mo, Nd, Ca) where a closer isotopic similarity between enstatite chondrite and BSE has been already documented. The similarity in Si isotope composition of silicate reservoir of Earth, the Moon and silicate fractions of EH3 chondrite provides a strong evidence for the formation of enstatite chondrite, bulk Earth and Moon in similar reduced isotopic reservoir of inner protoplanetary disc. We have shown that condensation of extremely light Si isotopes in early-condensed metals ( $\delta^{30}$ Si < -6.94±0.09‰ with 1-3wt% Si) can alter the residual silicate reservoir to heavier  $\delta^{30}$ Si value, which is observed in silicate fractions of enstatite chondrite and BSE.

We propose that during the initial stages of Earth's formation when environmental conditions were extremely reduced, enstatite chondrite like precursor materials accreted together to form proto-Earth. In this stage, most of the metals (containing up to 5wt% Si) segregated into the center to form the core without much equilibration with silicate mantle. In the subsequent stages when the massive core of the Earth and a substantial layer of silicates had already formed, the nebula got relatively oxygenated and the chemical pathway of proto-Earth became different from highly reduced enstatite chondrite although their isotope characteristics remained the same. With the

further drop in temperature, forsterite was condensed from the altered silicate gas reservoir. But unlike enstatite chondrite parent bodies, quantitative formation of enstatite via reaction between forsterite and SiO gas could not go to completion in the partially reduced planetesimals that eventually accreted together to form BSE. This explains the distinct chemical differences between enstatite chondrite and Earth's upper mantle.

Although large mass-dependent Si isotopic fractionation is evident among different phases of enstatite chondrite, Mg isotopes in its silicate and matrix fractions ( $\delta^{26}$ Mg = - 0.29±0.12‰, 2 SD) is found to be uniform and indistinguishable from  $\delta^{26}$ Mg of bulk chondrite and BSE. This observation rules out the hypothesis of generation of heavier Si isotopic signature of BSE by impact volatilization and vaporization. Therefore, we conclude that the Earth has inherited its Si and Mg isotope composition during its accretionary stage from a reduced nebula and negligible alteration in Si and Mg isotope composition has been made during any post accretion event of the Earth.

Overall, this research work provides very important constraints on the nature of building blocks of Earth, the sequence associated with Earth accretion and the type of core segregation event that the Earth underwent during its early evolutionary stages.

**Keywords**: Silicon isotope, Magnesium isotope, Meteorites, Enstatite chondrites, MC-ICPMS, Earth and core formation.

# CHAPTER 1 INTRODUCTION

Understanding the early evolutionary history of Earth and its bulk chemical composition are the two fundamental problems in the field of Earth and planetary sciences. Since primitive meteorites (chondrites) are presumed to be the best proxy for undifferentiated bulk Earth composition, a comparative study of the chemical and isotopic properties of various types of chondrites and terrestrial rock samples provide a wealth of information on the formation and subsequent evolution of Earth. If we can decipher how Earth was formed, then the concept can be extended to the understanding of the formation scenario of other planets as well (more specifically terrestrial planets). The current research work aims to answer some of the very fundamental problems associated with formation scenario of Earth and its core by analyzing Si and Mg isotopic signatures that have remained preserved in meteorites.

This chapter introduces the basic concept of various planet-forming processes and provides a brief review on the current understanding of Earth's formation and its bulk composition from the perspective of meteorite studies. The recent developments in high precision Si and Mg isotopic data acquisition from terrestrial rock samples and meteorites to trace the building blocks of Earth are highlighted in this chapter. The studies carried out to understand the composition and physico-chemical conditions of Earth's core from Si isotopic discrepancy between chondrites and terrestrial rock samples have been discussed. Importance of determining isotopic fraction pattern of both Si and Mg from varied groups of meteorites has been highlighted followed by the objectives of this research work.

**CHAPTER 1: INTRODUCTION** 

### 1.1 Origin of the solar system and planet formation

The solar system was formed 4.56 billion years ago by gravitational collapse of a cold (T = 10-100 K) and dense ( $\rho = 10^3 \cdot 10^6$  particles/cm<sup>3</sup>) molecular cloud; which was primarily made up of hydrogen, helium and metals (elements heavier than He) from earlier generations of stars (Zeilik *et al.*, 1998; Montmerle *et al.*, 2006; Pfalzner *et al.*, 2015 and references therein). Subsequently, most of the collapsed matters were agglomerated in the center of the cloud to form the proto-Sun. A protoplanetary disk was immediately formed radially outward surrounding the proto-Sun to conserve angular momentum of the in-falling cloud material. The protoplanetary disk served both as channel for the in-falling material to eventually accrete into the Sun and also as locus for the formation of planets. The disk is expected to have a uniform chemical and isotopic composition 'referred as cosmic composition' due to turbulent mixing, thermal processing and evaporation of pre-existing dust grains (Suess and Urey, 1956; Clayton, 1981; Anders and Grevesse, 1989).

As the nebula cooled further, micron-sized grains condensed from the reprocessed nebular gas and dust, which later coagulated to form millimeter to centimeter sized objects (Wood and Morfill, 1988; Weidenshilling, 1988 and references therein). The accretion of planets from nebular gas and dust is considered to be a gravitational process and is generally divided into four prominent stages (Johansen *et al.*, 2007; Weidenschilling, 2000, 2003; Youdin and Shu, 2002; Chamber, 2014; Rufu *et al.*, 2017):

- (i) First stage involves coagulation of nebular dust grains by low velocity collisions and subsequent accretion of kilometer sized planetesimals triggered by gravitational perturbations.
- (ii) Second stage marks the runway growth of planetary embryos via collisions among the planetesimals (Wetherill and Stewart, 1993; Weidenschilling, 2000).
- (iii) In the third stage, there occurred slower oligarchic growth during which the larger planetary embryos were formed by the accretion of remaining planetesimals.

(iv) The final stage is represented by chaotic growth characterized by catastrophic collisions due to crossing orbits of planetary embryos. In this stage, the planetary embryos gradually started increasing its size at the rate of centimetres per year due to mutual collisions (Chamber, 2014; Ganghoffer *et al.*, 2016).

Highly energetic collisions and heat produced by the decay of short-lived radionuclides provided sufficient energy for global scale melting and metal-silicate differentiation in planetary bodies (Baker *et al.*, 2005; Srinivasan *et al.*, 2007). The last episode of giant impacts is known to have lasted for ~100 Myr before culminating in the final accretion stage of terrestrial planets and formation of their respective moons (Morbidelli *et al.*, 2012; Chamber, 2014). For example, the formation of Moon due to a giant impact of Mars-sized planetary body (Theia) with the proto-Earth is known to mark the last major accretion event in Earth's evolutionary history (Canup and Asphaug, 2001; Banerdt *et al.*, 2014; Dauphas and Schauble, 2016; Rufu *et al.*, 2017). It is believed that in this period, "late veneers" delivered the main source of noble metals to the Earth and might also have bought water and organic materials, which constituted the prerequisite for the development of life (Maher and Stevenson, 1988; Chyba and Sagan, 1992).

At present the solar system consists of a central star - the Sun, surrounded by four terrestrial rocky planets, four giant gas planets, and a multitude of smaller moons, comets, asteroids and dwarf planets. The Sun makes up more than 99.8% of the solar system's mass, whereas >98% of its angular momentum resides in the orbital motions of (mostly the giant) planets. Since the region of the solar system inside 4 AU was too warm, the volatile molecules like water and methane could not condense in the nearby regions of the Sun. Therefore, compounds with high melting points such as metals (iron and nickel) and rocky silicates are predominantly present in the planetesimals that accreted in inner solar nebula (Fischer and Ciesla, 2014 and references therein). The gaseous giant planets (Jupiter, Saturn, Uranus, Neptune) were formed beyond the frost line, where temperature is lower enough to allow volatile icy compounds to remain solid. Therefore, the objects that formed in the outer solar nebula were composed mainly of ices and presumably also a larger amount of unprocessed, primordial dust (Irwin, 2003 and references therein). A significant number of the

smaller planetary bodies with radii mostly ~1-100 km resides in the asteroid belt, which is located between Mars and Jupiter (2-3.3 AU). The asteroid belt initially contained enough matter to form Earth or Mars like planets, which could not accrete due to gravitation perturbation of giant Jupiter (Redd, 2012). These asteroids therefore represent the remaining planetesimals that were formed in the initial stages of solar system history and could not accrete enough materials to form planets (Davis *et al.*, 1979; Chambers and Wetherill, 2001; O'Brien *et al.*, 2007; Halliday, 2014).

Most of the meteorites are known to originate as part of the asteroid belt with the exception of Lunar and Martian meteorites. Meteorites are extra-terrestrial objects that are huge enough to survive the frictional heating of Earth's atmosphere and land on the surface of Earth. Due to sampling of the unaltered remnants of planetesimals, meteorites preserve a direct record of processes or events that occurred in early evolutionary history of solar system and thus provides vital information on the building blocks of planets (Steven *et al.*, 2016; Heng *et al.*, 2016 and references therein). Therefore, chemical and isotopic analyses of meteorites serve as a unique tool to reconstruct the history of various processes that operated during solar system formation and planet accretion process.

### 1.2 Meteorites and the early solar system

The processes involved in solar system and planet formation are generally elucidated through astronomical observations of star forming regions, circumstellar disks and extrasolar planets in combination with astrophysical models of planet formation. Cosmochemistry, which involves the physical, petrographic, chemical and isotopic analyses of meteorites provides an essential complement to astronomy and theoretical astrophysics by placing constraints on fundamental issues of solar system and planet forming processes. Some of the applications of cosmochemistry are listed below:

 (i) Comparing the distribution of elements and their isotopic abundances in terrestrial rock samples and meteorites provide vital information on physical, chemical and thermodynamic conditions that prevailed in different regions of the protoplanetary disk (Clayton, 1993; Trinquier *et al.*, 2009). It helps us in understanding the dynamics of material transport, mixing processes in the solar protoplanetary disk (Trinquier *et al.*, 2007) and also provides unique insight on the nature of building blocks of planets and their satellites (Javoy, 1999; Fitoussi and Bourdon, 2012; Valdes *et al.*, 2014, Trinquir *et al.*, 2007, 2009; Dauphas *et al.*, 2014; Dauphas, 2017).

- (ii) The isotopic abundances of various short-lived radionuclides preserved in meteorites (*e.g.*, <sup>10</sup>Be, <sup>26</sup>Al and <sup>60</sup>Fe;  $t_{1/2} < 100$  Myr) provide precise timescale of events starting from the formation of first solids of solar system (CAIs) to the processes that occurred within meteorite parent bodies, such as core-mantle differentiation, planetary magmatism and crustal formation etc (Halliday, 2003; McKeegan and Davis, 2007, and references therein).
- (iii) Isotopic study and trace element composition of presolar grains present in primitive meteorites provides constraints on the relative contributions of stellar nucleosynthesis vs. spallation inputs to parent molecular cloud from where the solar system was formed (Wasserburg *et al.*, 2006).

### **1.2.1 Classification of meteorites**

Meteorites are broadly divided into two groups based on texture and chemical composition: undifferentiated and differentiated meteorites, where differentiated are further subdivided into achondrites, irons and stony irons. Undifferentiated meteorites, also known as chondrites, are considered to be the most primitive meteorites that are essentially mechanical mixtures of components such as chondrules, CAIs (Calcium Aluminium and titanium rich Inclusions), metals and matrices (Scott and Krot 2005, 2007; Wang *et al.*, 2013). The CAIs are known to be the first formed solids of the solar system and hence the absolute age of the solar system is defined by the formation age of CAI, which has been dated back to ~4567-4568 Ma (Amelin *et al.*, 2002, 2010; Bouvier and Wadhwa, 2010).

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Chondrites are further classified as *carbonaceous chondrites* (divided broadly into eight groups: CI, CM, CR, CO, CV, CK, CB, and CH), *enstatite chondrites* (divided into EH and EL based on their iron content), *ordinary chondrites* (consist of three groups: LL, L and H, where LL to H reflect the abundances of metal from low to high) and R-K chondrites (Scott and Krot 2005, 2007). The parent bodies of chondrites accreted during the earliest stages of solar system formation and were never heated sufficiently high enough to induce global scale melting and differentiation with the exception of some sort of thermal processing or aqueous alterations in their parent bodies (Hutchison, 2004; Kleine *et al.*, 2009; Steven *et al.*, 2016; Goderis *et al.*, 2016). Therefore chondrites preserve a direct record of pristine chemical composition of our solar nebula and various processes that operated during the initial stages of solar system formation (Scott and Krot, 2003).

In contrast to chondrites, differentiated meteorites (the achondrites) originate from parent bodies that have experienced various degrees of melting and chemical differentiation (Weiss and Tanton, 2013 and references therein). The most evolved achondrites are products of crust-mantle differentiation and share similar texture and composition with terrestrial basalts. Following are the main types of achondrites present in meteorite inventory (Burbine *et al.*, 2002; Wasson, 2012 and references therein):

- The Howardite-Eucrite-Diogenite (HED) suite of meteorites is the largest group of differentiated meteorites known to originate from asteroid 4-Vesta (Binzel and Xu, 1993).
- Meteorites from Mars, Moon and other asteroids provide direct samples from these planetary bodies.
- Iron meteorites represent remnants of metallic cores of small planetesimals that melted and differentiated to form Fe-Ni cores and silicate mantles (Poitrasson *et al.*, 2005).
- Stony-iron meteorites (composed of roughly equal amounts of silicate and metal along with minor sulphides) are known to originate from the core-mantle boundary of small planetesimals (Wasson and Kimberlin, 1967).

Therefore, the differentiated meteorites provide a near complete suite of samples formed during various stages of planetary differentiation (Dodd, 1981). Since these extraterrestrial bodies were formed under a wide range of temperature, pressure and redox conditions, they provide valuable samples to understand the physical and chemical conditions that prevailed during various stages of accretion and differentiation of a planetary body.

### **1.3 Composition of bulk Earth from meteoritic perspective**

The question of the bulk chemical composition of Earth is one of the central problems in geochemistry and cosmochemistry (Allegre et al., 2001). An estimation of the initial bulk Earth composition is important to evaluate the condition and dynamics of coremantle differentiation, formation of crust and other planetary scale processes (Tackley, 2012; Kaminski and Javoy, 2013). The solid Earth is divided into crust, mantle and core (Burbine and O'Brien, 2004). The oceanic crusts are dominated by basalt whereas granites predominate the continents (Ehlers and Blatt, 1982). The mantle is mostly represented by peridotites, which are ultramafic rocks composed mainly of olivine and pyroxene (Jagoutz et al. 1979; McDonough and Sun 1995; McDonough and Rudnick 1998; Burbine and O'Brien, 2004; Khan, 2008). The crust and mantle together represents the silicate reservoir of the Earth, known as the Bulk Silicate Earth (BSE). The composition of BSE is estimated by analyzing crustal rocks and magmas derived from deep-seated volcanoes that samples mantle composition (Palme and O'Neill, 2014). However, the chemical composition of the bulk Earth, which refers to the composition of both silicate and metallic reservoir of Earth, has remained uncertain till date. It is because the core (constituting  $\sim 32\%$  of Earth's total mass) is the most inaccessible part of Earth and ultrahigh pressure (~130-360 GPa), temperature (~3500-4500°C) and density (9,900-13,000 kg/m<sup>3</sup>) prevails inside Earth's core (McDonough, 2003, 2014; Wood, 2008). Since direct sampling of core is impossible, therefore the knowledge of its composition and structure comes from indirect avenues of investigation such as studies of seismic waves and their analogy to iron meteorites.

One of the commonly used methods to elucidate the composition of Earth's core is through comparative study of the composition of BSE and chondrites. The elemental abundances in some of the primitive chondrites matches well with that of solar photosphere (except for some volatile elements), therefore chondrites are considered as precursors of all solar system solids including the planets. Furthermore, chondrites are the one of the earliest accreted objects of the solar system that has not undergone major alterations since its formation. This makes chondrites a good proxy for the undifferentiated bulk Earth composition (Jagoutz *et al.*, 1979; Allegre *et al.*, 1995, 2005; McDonough and Sun, 1995) and therefore it is commonly presumed that Earth's accreting material is compositionally similar to chondrites.

However, chondrites are of varied types and degree to which different kinds of chondrites represent the chemical composition of bulk Earth has remained an extensively debated issue, since none of the chondrites provide an exact compositional match to terrestrial samples (Drake and Righter, 2002; Halliday, 2014).

In the simplest scenario, Earth is considered to be compositionally similar to CI carbonaceous chondrites because this class of meteorites has the closest elemental composition to that of solar photosphere (McDonough and Sun, 1995; Fitoussi and Bourdon 2012), with the exception of highly volatiles elements such as H, C, N, O, Li (Anders and Grevesse, 1989, Lodders, 2003). Since the Sun comprises 99.9% of the total mass of Solar System, it is generally considered that primitive carbonaceous chondrites are the best proxy for bulk elemental and isotopic composition of our Solar System (Wang et al., 2013). But the degree to which carbonaceous chondrites represent bulk Earth composition has always remained doubtful. In the last decade, the determination of stable isotopic variations in solar system materials (meteorites) relative to terrestrial mantle (BSE) has emerged as a new tool to search for the material that accreted to form the Earth. Although carbonaceous chondrite provides a good match with BSE in terms of relative abundances of refractory lithophile elements (Al, Ca, and Sc), but it can not explain the isotope variations among most of the elements analyzed so far, such as O, Ca, N, Mo, Ru, Os and Ti (Javoy et al., 2010; Dauphas et al., 2014a; Fitoussi and Bourdon, 2012). Moreover, on oxygen three-isotope plot, carbonaceous chondrites plots away from the terrestrial fractionation line and form a distinct mass-independent trend *i.e.*, the carbonaceous chondrite anhydrous mineral

(CCAM) line (Clayton, 1984, Fig. 1.1). Studies of Nd isotope nucleosynthetic anomalies in refractory elements have shown that a major portion of the Earth's material cannot be explained by the accretion of carbonaceous chondrite like planetary bodies (Carlson *et al.*, 2007; Warren, 2011; Fitoussi *et al.*, 2016). Stable Sr and Cr isotopes also speak against CV, CO or CI chondrites as a possible precursor of Earth (Moynier *et al.*, 2010; Trinquier *et al.* 2007). In terms of stable isotope systematics, meteorite groups other than carbonaceous chondrites appear to be the better representative of the primary buildings blocks of the Earth. In general, isotope anomalies in BSE with respect to chondrites have been found to be the largest in carbonaceous chondrites and decrease from ordinary to enstatite chondrites (Godde and Kleine, 2017).

Birch, (1961); Simon and DePaolo, (2010) envisioned that Earth is compositionally similar to ordinary chondrite since it is the most common type of meteorite observed to fall on the Earth. But Allègre *et al.* (2001) have shown that ordinary chondrites fail to match the trace element composition of bulk Earth. Therefore, some researchers use mixture of different chondrite groups to determine the composition of Earth (Fitoussi and Bourdon, 2012; Fitoussi *et al.*, 2016).

In terms of oxygen isotopic compositions, enstatite chondrites are the only chondrite group that plot on terrestrial mass fractionation line, Fig. 1.1 (Clayton and Mayeda, 1984; Newton *et al.*, 2000). The reduced nature of enstatite chondrites and its isotopic similarity with BSE has been used to argue that enstatite chondrite-like materials were the major building materials of the Earth (Javoy, 1995; Javoy *et al.*, 2010). The existence of Mars at 1.5 AU with a distinctly different oxygen-isotopic composition compared to Earth suggests that patches of distinct oxygen reservoirs have been preserved across small heliocentric distances (Drake and Righter, 2002). The composition of enstatite chondrite shares similarity with the composition of BSE in not only oxygen isotope systematics but also with respect to a number of other stable isotopic systematics (Savage and Moynier, 2013) such as N (Javoy *et al.*, 1986), Mo (Dauphas *et al.*, 2002), Ru (Dauphas *et al.*, 2004, Gödde and Kleine, 2017), Ni (Regelous *et al.*, 2008), Cr (Trinquier *et al.*, 2007), Ti (Trinquier *et al.*, 2010, 2012), Ca

(Valdes *et al.*, 2014) and Nd (Gannoun *et al.*, 2011), which suggest a generic relationship between enstatite chondrites and the Earth.



**Figure 1.1:** Oxygen three-isotope plot of different groups of meteorites revealing the existence of discrete oxygen reservoirs in the solar system. The Earth-Moon-enstatite meteorites fall on same terrestrial fractionation line whereas other meteorites cluster around in distinct regions of the plot based on its origin. Image credit: Clayton *et al.* (1983). Drake and Righter, (2002).

Similar to oxygen, Si is also one of the most abundant elements of the solar system (Chakrabarti, 2015). As such, the distribution of Si isotopes among chondrites and terrestrial samples plays important constraints on the building blocks of Earth. Although enstatite chondrite shows similarity with BSE for a number of isotope systematics but they show large discrepancy from terrestrial rocks with respect to Si isotopes, which precludes enstatite chondrite as a potential building block of Earth (Fitoussi and Bourdon, 2012). Being formed under extremely reducing environment, enstatite chondrite is composed of varied rare minerals that are not found on Earth (Keil, 1968; Savage and Moynier, 2013). Also, enstatite chondrites have undergone extensive refractory liphophile element (RLE) fractionation that has substantially lowered its Mg/Si ratio (0.65-0.75) compared to BSE (1.05, Jagoutz *et al.*, 1979). The unique mineralogy of enstatite chondrite, its different oxidation state (Mason, 1966;

Keil, 1989), its lighter  $\delta^{30}$ Si value and lower Mg/Si and Al/Si ratio compared to superchondritic Mg/Si of BSE suggest that enstatite chondritic materials did not contribute a major fraction of Earth's accreting material (Fitoussi and Bourdon, 2012; Savage and Moynier, 2013).

Moreover, there is another school of thought who believes that bulk composition of Earth is non-chondritic (O'Neill and Palme, 2008; Caro *et al.*, 2008; Bonsor *et al.*, 2015). It is also argued that the major building blocks of the Earth are some type of meteorites that is currently not available in our meteorite inventory (Drake and Righter, 2002). Therefore, the nature of the building blocks of Earth have remained hypothetical till date and different Earth forming models have been proposed from time to time requiring the accretion of either carbonaceous chondrites (Allegre *et al.*, 1995, 2001; Palme and O'Neill, 2003) or enstatite chondrites (Javoy, 1995; Trinquier *et al.*, 2007; Javoy *et al.*, 2010) or ordinary chondrites (Carlson *et al.*, 2007; Leya *et al.*, 2008; Simon and DePaolo, 2010) or a mixture of different types of chondrites (Schonbachler *et al.*, 2010; Fitoussi and Bourdon, 2012; O'Neill and Palme, 2008). Although it is widely believed that Earth was made up of some sort of chondritic materials, but a major dilemma in the planetary science community is regarding the choice of chondrite types that can be efficiently taken as a representative for bulk Earth composition.

### 1.4 Geochemical evidences for core-forming event of Earth

The accurate estimation of bulk Earth composition has very important implications on the dynamics and evolution of Earth's core. The differentiation of planetary embryos into silicate mantle and a metallic core during the first few million years (Ma) of solar system history represents one of the most fundamental event towards building terrestrial planets like the Earth (Rubie *et al.*, 2003; Khan and Deschamps, 2015). In any planetary body, the segregation of highly dense metal (Fe, Ni, Co) towards the center and migration of less-dense elements (Si, Mg, Ca) to the crust takes place once a critical size of the body is reached and the melt fraction becomes high enough. The

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necessary heat for this density driven process is provided by the decay of short-lived radionuclides (<sup>26</sup>Al, <sup>56</sup>Fe), kinetic energy delivered by impacts and reduction in gravitational potential energy (MacPherson *et al.*, 1995).

In case of Earth, the core represents a major portion of planet constituting  $\sim 32\%$  of Earth's total mass and 16% of its volume. The <sup>182</sup>Hf-<sup>182</sup>W isotope systematics suggest that core–mantle differentiation took place within first 30 Ma years of Earth's evolutionary history (Kleine *et al.*, 2002; Yin *et al.*, 2002; Halliday, 2014). Earth was discovered to have a solid inner core distinct from its liquid outer core by Lehmann, (1936). Eddy currents produced by turbulent convection in the nickel iron rich fluid of outer core generates the Earth's magnetic field, which shields us from the lethal solar wind. The solid inner core is believed to crystallize from the liquid outer core at the rate of 1 mm per year radially, thus transferring heat outward towards the mantle. The heat released drives almost all geological processes of the Earth; including plate tectonics, volcanism and earthquakes. Since the dynamics of core is intimately associated with Earth's surficial and life sustaining processes, a sound knowledge of the composition and evolution of Earth's core is of fundamental importance (Morard *et al.*, 2013; McDonough, 2014).

The physico-chemical conditions prevalent inside Earth's core are mostly studied by comparing the physical properties of liquid iron alloys under pertinent pressure (P) and temperature (T) conditions with geophysical models of the Earth such as the Preliminary Reference Earth Model, PREM by Dziewonski and Anderson, (1981), (Morard *et al.*, 2013). The formation of Earth's core has left behind various geochemical signatures in the mantle rock that has remained preserved till date. Scientists measure different physical and chemical properties of mantle-derived rocks using state of art instruments to decipher the preserved signatures and thus try to unravel the mystery of core forming event. For example, the geochemistry of mantle-derived rocks reveals extensive depletion of siderophile elements relative to chondrites, which suggests that highly siderophilic elements were scavenged from the silicate mantle and sequestered into metallic core during the differentiation process (Li *et al.*, 1996; Rubie *et al.*, 2003). The environmental conditions that prevailed during core formation are constrained by experimentally determining the elemental distribution coefficients between metal-silicate and the variations in concentrations of

minor and trace elements in BSE. These important parameters give idea about the nature of elements that are likely to get partitioned into metals and also helps in establishing pressure, temperature and oxygen fugacity under which these elements were extracted from the mantle (Righter and Drake, 1996; Righter, 2003; Wood *et al.*, 2006; Rubie, 2007; Warren *et al.*, 2011; Halliday, 2014).

From the `stair-step' distribution pattern of siderophile elements in rocks that are representative of upper mantle (Fig. 1.2), it was suggested that initial ~80-90% of the Earth's accreting material was extremely reduced in nature (Wanke, 1981; Drake and Righter, 2002).



**Figure 1.2:** Stair-step pattern in the elemental abundances of Earth's primitive mantle. Image credit: Drake and Righter, (2002).

In reduced conditions, apart from refractory lithophile elements (RLE) and rare earth elements (REE), all other elements got quantitatively sequestered into the core (Drake and Righter, 2002). Relatively more oxidized components were contributed by the next 10-20% of Earth's accretionary material. At this stage, most of the highly siderophile elements (Ir, Os, Au and so on) were again quantitatively extracted into the core whereas other elements remained in the mantle (Wanke, 1981; 1988). The last ~1% of the accreting materials were added by the `late veneers', which was so oxidizing that
metallic Fe did not exist. The siderophile elements delivered by the `late veneer' at the end stage of Earth's accretion could not enter the core and therefore remained homogeneously distributed in the mantle. This heterogeneous accretion model of multi-stage core formation indicates that the material accreting to the Earth gradually kept on changing its composition and oxidation state with time (Drake and Righter, 2002 and references therein; Schönbächler *et al.*, 2014).

In contrast, homogenous model of Earth's accretion suggest that the Earth was accreted from homogeneous materials and subsequent internal differentiation led to creation of the core, mantle and crust (Ringwood, 1979; Righter, 2003).

It is believed that upon melting of an undifferentiated homogeneous planetary body, the metal portion – due to its high density segregated towards the center of the planet whereas the less dense magma floated upwards to form the mantle and crust of Earth (Wade and Wood, 2005). Earth's core is thought to have reached a state of equilibrium with the mantle near the base of a silicate magma ocean as immiscible liquid of Fe–Ni metal coalesced from surrounding silicates (Wood *et al.*, 2006; Wood, 2008; Frost *et al.*, 2004, 2008; Zeigler *et al.*, 2010). Fig. 1.3 provides an illustration of homogenous and heterogeneous accretion model of the core.



**Figure 1.3:** Schematic representation of heterogeneous *vs.* homogenous accretionary scenario of differentiated planetary bodies.

#### **1.5 Silicon in the core of Earth**

Based on seismic wave velocities, it is long being proposed that the core of Earth is made up predominantly of iron and nickel alloy along with ~10% light elements, which is required to explain core's density deficit relative to pure Fe-Ni alloy (Birch, 1952, 1968; Badro *et al.*, 2007). Partitioning experiments have shown that Si becomes siderophilic with increasing temperature-pressure and decreasing oxygen fugacity (Gessmann *et al.*, 2001; Wade and Wood, 2005; Armytage *et al.*, 2011; Kempl *et al.*, 2016). Therefore, Si has been suggested to be one of the principal low-density diluent element of Earth's core since long time (Ringwood, 1959; Birch *et al.*, 1964; MacDonald and Knopoff, 1958; Allegre *et al.*, 1995; Georg *et al.*, 2007; Ziegler *et al.*, 2010). Other candidates that are speculated to have entered the Earth's core during metal-silicate differentiation event are sulfur, nitrogen, oxygen, carbon and hydrogen (Birch, 1964; Poirier, 1994; Corgne *et al.*, 2007; Cote *et al.*, 2008; Chabot *et al.*, 2008; Badro *et al.*, 2014; Zhang and Yin, 2012; Zhang *et al.*, 2016).

The method of estimating the composition of Earth's core by analyzing primitive meteorites relies on the concept of mass-balance, *i.e.* the budget of elements not present in the silicate crust and mantle is expected to be present in the core. By analyzing various crustal and mantle-derived rock samples, the composition of the silicate reservoir of Earth or the Bulk Silicate Earth (BSE) is generally estimated (Khan and Deschamps, 2015). On the other hand, the composition of bulk Earth is often presumed to be similar to that of primitive meteorites called chondrites (Jagoutz et al., 1979; Allegre et al., 1995; McDonough and Sun, 1995). Thus by knowing the composition of bulk silicate Earth (BSE) and Bulk Earth (BE), the composition of core is constrained from the difference BE-BSE (Kempl et al., 2016). Using this concept, it has been argued that the higher Mg/Si ratio of BSE (~1.24) compared to chondrites (~1) reflects that the missing Si resides in core of the Earth (MacDonald and Knopoff, 1958; Allegre et al., 1995; Fitoussi et al., 2009). Allegre et al. (2001) demonstrated that the apparent depletion of Si in the mantle could be balanced by the incorporation of 7.3 wt% Si in the Earth's core. Geophysical investigations and high temperaturepressure experimental constraints suggest that a maximum of 2.5% of sulfur and 4-5wt% of silicon can be incorporated in the core of Earth (Shahar et al., 2011; Gessman

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et al. 2001; Morard et al., 2013; Huang et al., 2014).

#### 1.5.1 Physico-chemical conditions during core formation

The presence of silicon in Earth's core provides very important implications for physico-chemical conditions under which metal segregrated to form the core. Incorporation of Si into molten iron metal is primarily dependent on temperature (T) and oxygen fugacity (fo<sub>2</sub>), with a smaller dependency on pressure (P) (Gessmann et al., 2001; Shahar et al., 2009, 2011; Zeigler et al., 2010). Under oxidizing conditions prevalent in Earth's surface, Si is not stable in its atomic state and always occurs in combination with oxygen as silicate ion  $(SiO_4^{4-})$ . Only in reducing environments, silicon starts behaving siderophilic and gets incorporated into metallic phases. Different types of meteorites display a broad range of Si contents in metals based on the extent of reduction they underwent in their respective parent bodies (Kempl et al., 2013, 2016). Partially reduced planetary bodies such as magmatic and non-magmatic iron meteorites contain ppm levels of Si (Pack et al., 2011). Enstatite meteorites, being formed under extremely reduced conditions contain a high concentration (on the order of 5 wt%) of silicon in their metallic phases (Ringwood, 1960, 1961; Kempl et al., 2016). Since incorporation of significant amount of Si in metals is possible only under very low oxygen fugacity, the presence of Si in Earth's core requires that the environmental condition prevailing during core formation must have been extremely reducing. The corollary of the above statement is that the Earth's mantle must have subsequently evolved to its current more oxidized state from an initially reduced condition (Javoy et al., 2010). According to Javoy, (1995) the chemical mechanism of core differentiation couples the FeO concentration in the mantle to the Si content of the core following Eqn. 1.1.

$$2Fe_{metal} + SiO_2 \rightarrow 2FeO + Si_{metal}$$
(1.1)

This exchange mechanism can explain the augmentation of mantle FeO and oxygen fugacity ( $fo_2$ ) and does not require the accretion of increasingly oxidized material to explain the increase in oxygenation level of Earth (Javoy *et al.*, 2010). Thus Eqn. 1.1

provides an extremely likely mechanism for the increase in oxygen level of Earth from an initially reduced environment. Based on elemental partitioning studies, it is believed that fO<sub>2</sub> during Earth's core formation has gradually increased from  $\Delta IW = -6$  to present state during different stages of accretionary processes (Javoy, 1995; Gessmann *et al.*, 2001; Wade and Wood, 2005; Corgne *et al.*, 2008; Frost *et al.*, 2008; Wood, 2008; Zeigler *et al.*, 2010). This inferred oxidation level is consistent with the fO<sub>2</sub> of ~ $\Delta IW$ -6 that is recorded by enstatite meteorites (Berthet *et al.*, 2009). The extent of oxidation in terrestrial Si–Fe system is given by the atomic ratio of exchangeable oxygen to that of total Fe + Si, defined as EXOR value

$$EXOR = \frac{2nSiO_2 + nFeO}{nSi + nFe}$$
-----(1.2)

where,  $nSiO_2$  and nFeO are the mole fractions of  $SiO_2$  and FeO, whereas nSi and nFe represents the total Si and total Fe respectively (Javoy *et al.*, 2010). The value of EXOR is restricted to  $1.03 \pm 0.03$  for bulk Earth models (Ringwood, 1979; Allègre *et al.*, 1995; Javoy, 1995). Among all meteorites, only Fe rich enstatite chondrites display similar EXOR value (Javoy *et al.*, 2010). Therefore, enstatite chondrites are considered to serve as a good proxy for investigating the physico-chemical conditions that prevailed during Earth's initial stages of evolution.

In the last decade, advances in non-traditional stable isotope studies have emerged as a new tool to investigate planetary accretion and core segregation process. Accurate and precise measurements of stable isotopic composition of different elements in terrestrial rock samples and meteorites provide fingerprints of various planet-forming processes (Poitrasson *et al.*, 2004; Wiechert and Halliday, 2007). With the advent of high resolution MC-ICPMS (multi-collector inductively coupled plasma mass-spectrometry) in the last decade, a number of studies have been made to understand planet formation, accretion and metal-silicate segregation event through high precision stable isotope measurements of Si, Mg, Ca, Ti, Cr and Fe etc (Poitrasson *et al.*, 2004; Weyer *et al.*, 2005; Schoenberg and von Blanckenburg, 2006; Georg *et al.*, 2007; Teng *et al.*, 2010a; Wiechert and Halliday, 2007; Fitoussi *et al.*, 2009; Moynier *et al.*, 2012; Schiller *et al.*, 2010; Young and Galy, 2004; Bourdon *et al.*, 2010; An *et al.*, 2014; Bonnand *et al.*, 2016). Out of various non-traditional isotopes, determination of

isotopic variations of Si and Mg among meteorites and terrestrial rock samples to decipher the formation and differentiation event of Earth are the main focus of this research work, which is detailed in the subsequent paragraphs.

#### 1.5.2 Si isotopic variation in bulk meteorites

Si is the third most abundant element of the Earth after oxygen and iron (Savage *et al.*, 2011; Baskaran, 2012). It has three stable isotopes: <sup>28</sup>Si, <sup>29</sup>Si and <sup>30</sup>Si with relative abundances of 92.23%, 4.67% and 3.10% (Faure and Mensing, 2004). The variations in silicon isotope ratios are expressed in delta notation relative to reference standard NBS-28 (Reynolds *et al.*, 2007; Kempl *et al.*, 2013) in per mil (‰), where  $\delta^{i}$ Si is represented using Eqn. 1.3.

where, i = 29 or 30 for Si.

Si isotopic studies in meteorites are recently being used as a fingerprint to trace the composition of Earth's core and find any generic link between varied types of chondrites and the Earth. Although Molini-Velsko *et al.* (1986) presented a large compilation of Si isotopic composition in meteorites but it was the work by Georg *et al.* (2007), which has initiated the current interest of using Si isotopic composition in terrestrial and extra-terrestrial materials to trace the building blocks of the Earth and the composition of its core. Georg *et al.* (2007) have demonstrated that terrestrial rocks display a slightly heavier  $\delta^{30}$ Si value compared to undifferentiated meteorites, with a measureable difference of  $\Delta^{30}$ Si= $\delta^{30}$ Si<sub>BSE</sub> -  $\delta^{30}$ Si<sub>CHONDRITE</sub> =  $\geq 0.15\pm 0.11\%$  (1SD) between the Si isotopic composition of chondrites and BSE. Subsequent work by Fitoussi *et al.* (2009); Ziegler *et al.* (2010); Armytage *et al.* (2011) also found offsets in the Si isotope composition between chondrites and terrestrial samples. From an extensive study of mantle-derived rocks, Savage *et al.* (2010) have estimated the average  $\delta^{30}$ Si of BSE (bulk silicate Earth) to be  $-0.29\pm 0.04\%$  whereas the average

 $δ^{30}$ Si value for carbonaceous, ordinary and enstatite chondrites was measured to be – 0.49±0.15‰ (Armytage *et al.*, 2011, 2012). It is suggested that if Earth accreted from chondritic material (Palme and O'Neill, 2003 and references therein), the preferential partitioning of Si isotopes during metal-silicate equilibration have left the silicate portion of Earth with a heavier Si isotopic signature compared to primitive meteorites due to incorporation of lighter Si isotopes in metals (Georg *et al.*, 2007; Fitoussi *et al.*, 2009; Shahar *et al.*, 2009, 2011; Ziegler *et al.*, 2010; Armytage *et al.*, 2011; Savage and Moynier, 2013). Thus, the Si isotope differences observed between terrestrial samples and meteorites are best explained by the presence of lighter research to constrain the amount of Si residing in Earth's core and to estimate the building blocks of Earth (Chakrabarti and Jacobsen, 2010b; Ziegler *et al.*, 2010; Armytage *et al.*, 2011; Fitoussi and Bourdon, 2012; Zambardi *et al.*, 2013; Savage *et al.*, 2013; Dauphas *et al.*, 2015).

#### 1.5.3 Concentration of silicon in Earth's core

The differences in the relative abundances of Si isotopes between metal (core) and silicate (mantle and crust) are largely being used to estimate the amount Si in the core and elucidate the physic-chemical conditions that prevailed during core segregation. The isotopic difference between two phases ( $\delta^{30}$ Si<sub>silicate</sub> –  $\delta^{30}$ Si<sub>metal</sub>) is often expressed in terms of  $\Delta$  (Big delta), which provides the fractionation factor such that  $\Delta^{30}$ Si<sub>silicate</sub> –  $\delta^{30}$ Si<sub>silicat</sub> –  $\delta^{30}$ Si<sub>si</sub> –  $\delta^{30}$ Si<sub>silicat</sub> –  $\delta^{30}$ Si<sub>si</sub> –  $\delta^{30}$ Si<sub>silicat</sub> –

$$\delta^{30} \text{Si}_{\text{BSE}} - \delta^{30} \text{Si}_{\text{CHONDRITE}} = \Delta^{30} \text{Si}_{\text{silicate-metal}} \times \text{f}_{\text{Si,CORE}} - \dots - (1.4)$$

where,  $f_{Si,CORE}$  is the mass fraction of silicon in Earth's core,  $\delta^{30}Si_{BSE}$  and  $\delta^{30}Si_{CHONDRITE}$  are the isotopic composition of silicon in BSE and chondrites relative to NBS-28 and  $\Delta^{30}Si_{silicate-metal}$  is the equilibrium silicon isotope fractionation between Si in metal and silicate phases respectively. Based on Si isotopic offset between BSE and

ordinary/carbonaceous chondrites (OC/CC) ( $\Delta^{30}Si_{BSE-OC/CC} = \delta^{30}Si_{BSE}-\delta^{30}Si_{OC/CC}$ =0.15± 0.10‰) and an appropriate metal silicate fractionation factor ( $\Delta^{30}Si_{silicate-metal}$ = 0.89), an estimation of ~2.5-12 wt% Si in the Earth's core has been suggested by a number of authors in the recent past (Armytage *et al.*, 2011; Georg *et al.*, 2007; Fitoussi and Bourdon, 2012; Zieglar *et al.*, 2010; Zambardi *et al.*, 2013; Dauphas *et al.*, 2015).

These models to estimate the Si content in Earth's core are based on assumption that the bulk Earth has a chondritic  $\delta^{30}$ Si value (Hawkesworth and Schersten, 2007; Palme and O'Neill, 2014). However, there occurs variation in the Si isotopic composition among different groups of chondrites. Although there is no systematic  $\delta^{30}Si$ differences between carbonaceous ( $\delta^{30}$ Si<sub>CC</sub> = -0.43 ± 0.05‰, 2SE, n=3, Zambardi *et al.*, 2013), ordinary chondrites ( $\delta^{30}$ Si<sub>OC</sub> = -0.47 ± 0.01‰, 2SE, n=6, Zambardi *et al.*, 2013) and achondrites ( $\delta^{30}$ Si = -0.47 ± 0.11‰, 2SD, Armytage *et al.*, 2011), but enstatite chondrites are characterized by lighter Si isotopic composition ( $\delta^{30}$ Si = -0.63  $\pm$  0.07‰, 2SD, Armytage *et al.*, 2011) compared to other meteorite groups (Georg *et* al., 2007; Fitoussi et al., 2009; Savage and Moynier, 2013). Accordingly, if enstatite chondrites are taken as a proxy for bulk Earth composition then core of Earth should contain >23 wt% Si, which is unrealistically high based on geophysical estimates (Badro, 2007). Thus one of the major hurdles in estimating Si content in Earth's core based on  $\delta^{30}$ Si offset between BSE and chondrites is the uncertainty in accurate Si isotopic composition of the starting material that formed the Earth (Zambardi et al., 2013). In order to optimize the applicability of Si isotopic data to unravel the Si content in Earth's core, more studies should be carried out to constrain the initial Si isotopic composition of the bulk Earth.

Despite the isotopic similarities between bulk Earth and enstatite chondrite for a large number of elements (O, N, Mo, Ru, Ni, Cr, Ti, Fe, Os, Sr Ca and Nd), the significant Si isotopic offset between enstatite chondrites and BSE led Fitoussi and Bourdon, (2012) to conclude that enstatite chondrites cannot be a significant source of Earth's precursor material. The significant Si isotopic offset between BSE and enstatite chondrites ( $\Delta^{30}$ Si<sub>BSE-E-chond</sub> = ~0.30permill) led Fitoussi and Bourdon, (2012) to

suggest that only <15% of Earth's accreting material should be of enstatite chondritic nature. However, Savage and Moynier, (2013) have shown that the non-magnetic phases of enstatite chondrites have heavier Si isotope composition compared to bulk enstatite chondrite, suggesting the possibility of light Si isotopic enrichment in its metallic phases and therefore a heterogeneous distribution of Si isotopes within different phases of enstatite chondrite (Fig. 1.4).



**Figure 1.4:** Si isotopic composition of ordinary, carbonaceous and enstatite chondrite relative to BSE. Variation in  $\delta^{30}$ Si for bulk and non-magnetic (silicate) fractions of EH, EL and aubrite samples suggest a heterogeneous distribution of Si isotopes within enstatite chondrites. Image credit: Savage and Moynier, (2013).

Further studies on Si isotope systematics needs to be done on different micro-phases of enstatite chondrite to estimate the extent of Si isotopic heterogeneity within enstatite chondrite before concluding these group of chondrites as a negligible component of Earth's precursor material.

The proper estimation of equilibrium fractionation factor at relevant temperature and pressure is very crucial for optimizing the applicability of results obtained from stable isotope studies to constrain the core formation event of Earth. As mantle-core differentiation occurred under ultra high temperature and pressure conditions, it is likely that temperature (T) and pressure (P) might have influenced Si isotope fractionation. Theoretical calculations performed by Shahar *et al.* (2009) suggest that the effect of high pressure is only secondary. Isotope fractionation is known to be critically dependent on temperature (T) and typical equilibrium fractionations scale with  $1/T^2$  for high temperatures (Schauble, 2004). Assuming that there is full metal-silicate equilibration, the difference in  $\delta^{30}$ Si between BSE and the core provides the equilibration fractionation factor ( $\epsilon$ ) of Si. The relationship between equilibration fractionation factor and Si isotopic composition of BSE and meteorites at specific temperature is given by Eqn. 1.5.

$$\varepsilon_{Si}(T) = \delta^{30} \text{Si}_{\text{silicate}(T)} - \delta^{30} \text{Si}_{\text{metal}(T)} = \Delta^{30} \text{Si}_{\text{BSE-CORE}}(T) = \frac{A*10^6}{T^2} - --(1.5)$$

where, T is the temperature of metal-silicate equilibration in kelvin (K). A is a constant and its value has been estimated from natural samples (7.64  $\pm$  0.47, Ziegler *et al.*, 2010) and from metal–silicate fractionation experiments (7.45  $\pm$  0.41, Shahar *et al.*, 2011).

Till date a number of attempts have been made to estimate the <sup>30</sup>Si/<sup>28</sup>Si fractionation factor between silicate phases and silicon-bearing iron metal alloy [ $\Delta^{30}$ Si<sub>silicate-metal</sub> =  $\delta^{30}$ Si<sub>silicate</sub> –  $\delta^{30}$ Si<sub>metal</sub>] at different ranges of pressure (1-34 GPa), temperatures (1800– 3000°C) and at varying oxidation conditions using lattice-dynamics models (Georg *et al.*, 2007; Schauble *et al.*, 2009; Fitoussi *et al.*, 2009; Shahar *et al.*, 2009; Ramananda and Chakrabarti, 2010b). Georg *et al.* (2007) used olivine-Fe<sub>3</sub>Si pair to estimate the  $\Delta^{30}$ Si<sub>silicate-metal</sub> of 1.5-1.6‰ at 10<sup>5</sup> Pa and 2000 K. From experimental studies in perovskite-Fe<sub>3</sub>Si pair, Shahar *et al.* (2009) have estimated the  $\Delta^{30}$ Si<sub>silicate-metal</sub> to be 2.0‰ at 1 GPa and 2073 K, which reduces down to 0.65‰ at higher pressures and temperatures (3000 K). Zieglar *et al.* (2010) used metal-rich enstatite achondrites to investigate Si-isotope fractionation between metal and silicate and documented 5-6‰ difference in the <sup>30</sup>Si/<sup>28</sup>Si ratio between Si in metal and Si in silicates. By anchoring the Si isotopic composition of silicate and metals in aubrite to the experimental results by Shahar *et al.* (2009), the value of  $\Delta^{30}$ Si<sub>silicate-metal</sub> was estimated to be 1.2‰ at 2500K, with fractionation factor of  $\varepsilon = (8.04*10^6 \pm 0.47)/T^2$  (Zieglar *et al.*, 2010).

Although a number of studies have been carried out to estimate the amount of Si in Earth's core using different values of equilibrium fractionation factor but none of these studies have attempted to apply the  $\Delta^{30}$ Si<sub>silicate-metal</sub> derived from primitive enstatite chondrites, which provide the best proxy for initial physico-chemical conditions that prevailed during Earth's metal segregation event. Estimating the value of  $\Delta^{30}$ Si<sub>silicate-metal</sub> from Si isotopic composition of metal and silicate separates in enstatite chondrite could provide better constrains on the amount of Si that has been incorporated into Earth's core.

#### 1.5.4 Equilibrium vs. nebular Si isotope fractionation

The validity of using  $\delta^{30}$ Si offset between BSE and chondrites to estimate the Si content in Earth's core lie on the assumption that the observed  $\delta^{30}$ Si offset results solely from equilibrium Si isotopic fractionation during silicate-metal segregation event. Partitioning of Si between metal and silicate as a likely cause to fractionate silicon isotopes has been supported by many theoretical and experimental studies (Georg *et al.*, 2007; Zeigler *et al.*, 2010; Shahar *et al.*, 2011). The metal-silicate equilibrium Si isotope fractionation was experimentally determined to be 0.8 at 3000 K (Shahar *et al.*, 2009; 2011). But the more recent experiments by Hin *et al.* (2014) provided Si isotope fractionation factor of 0.5 at 3000 K. It was shown that the later results were deviated from the previous one because equilibrium was never completely reached in the experiments carried out by Shahar *et al.* (2009; 2011). Therefore, Hin *et al.* (2014) have shown that difference in  $\delta^{30}$ Si between bulk Earth (chondrites) and bulk silicate Earth (BSE) generated by equilibrium Si isotope fractionation during core formation is smaller than what was previously believed.

Moreover, the long-standing belief of equilibrium silicon isotope fractionation during high temperature core-mantle segregation has been recently questioned after it was found that  $\delta^{30}$ Si composition of angrites ( $\delta^{30}$ Si = -0.21±0.03‰, Pringle *et al.*, 2014; Dauphas *et al.*, 2015) is even heavier than terrestrial rock samples ( $\delta^{30}$ Si = -0.29±0.04‰, Savage *et al.*, 2010). The heavy Si isotopic composition of angrites speaks against of the significant incorporation of Si in the Earth's core as a likely explanation for heavy Si isotope signature of terrestrial mantle. This is because unlike Earth, core formation in the angrite parent-body (APB) occurred under oxidizing conditions at relatively lower pressure/temperature and a significant incorporation of silicon in metallic phases is very unlikely in oxidizing environment (Dauphas *et al.*, 2015).

Instead, it has been suggested that nebular fractionation associated with mixing between gaseous SiO (Mg/Si=0;  $\delta^{30}$ Si= -1.59‰) and solid forsterite (Mg/Si=2;  $\delta^{30}$ Si= 0.71‰) at ~1370 K in the solar nebula could have produced the observed Si isotope variations among planetary bodies (Dauphas *et al.*, 2015). Therefore, there exists another school of thought who believes that nebular fractionation and not equilibrium Si isotope fractionation during core formation have generated the observed Si isotope offset between BSE and chondrites (Hin *et al.*, 2014; Dauphas *et al.*, 2014a, 2015)

Since meteorites are nebular condensates, it is likely that the condensing phases have undergone various degrees of kinetic fractionation in nebula whereas only equilibrium fractionation (if any) is possible in the high temperature-pressure and closed system environment prevalent in the interior of a planetary body. Therefore, it is very essential to understand the extent of kinetic isotope fractionation that the planetary bodies might have undergone in nebular stage before anchoring any isotopic differences between chondrites and BSE to high temperature equilibrium Si isotope fraction in core-mantle boundary.

#### **1.6 Magnesium stable isotope systematics**

Similar to silicon, magnesium is also one of the major elements in the solar system (Lodders, 2003). It has three stable isotopes: <sup>24</sup>Mg, <sup>25</sup>Mg, and <sup>26</sup>Mg with natural abundances of 78.99%, 10.00%, and 11.01% respectively (Rosman and Taylor, 1997;

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Huang *et al.*, 2015). Mg isotope data are reported as  $\delta^{25}$ Mg and  $\delta^{26}$ Mg (‰) relative to DSM-3. Stable isotopes of Mg are known to be an excellent tracer to study various geological and cosmological processes (Wiechert and Halliday, 2007; Bourdon *et al.*, 2010; Chakrabarti and Jacobsen, 2010a; Teng *et al.*, 2007, 2010a, 2015, 2017).

Mg is found to be coexisting with Si in the most widely occurring minerals of the solar system such as forsterite (Mg<sub>2</sub>SiO<sub>4</sub>) and enstatite (MgSiO<sub>3</sub>). Since difference in volatility of elements was one of the major criteria that governed isotope fractionation in early solar nebula, the nearly similar condensation temperature of Si and Mg (50% condensation temperature of Si and Mg are 1311 and 1340 K respectively at 10<sup>-4</sup> atm, Lattimer, 1978) ensures that they should undergo fractionation in similar direction during any particular physico-chemical processes. This has been experimentally confirmed from the Si and Mg isotope fractionation pattern in coarse-grained calciumaluminum-rich inclusions, CAIs - the first formed objects of the solar system (Clayton et al., 1988; Davis et al., 1990). It is found that CAIs incorporate heavy isotopes of both Si and Mg, which are known to be potential indicators of various degrees of evaporation processes experienced by these objects. Moreover, the extent of isotopic fractionation for magnesium isotopes has been found to be larger than silicon isotopes in CAIs (up to ~5 ‰/amu for Si and ~11 ‰/amu for Mg; Clayton et al., 1988; Davis et al., 1990; Grossman et al., 2000; Sugiura et al., 2004). Therefore, in any large-scale planetary processes that are governed by impact related volatilization and evaporation, it is reasonable to expect that the extent of fractionation for Mg isotopes should be higher than that of Si isotopes.

The processes that caused the enrichment of Mg relative to Si in bulk silicate Earth (BSE) and its heavy Si isotopic signature compared to chondrites has been debated between two most probable causes: preferential evaporation of Si compared to Mg during high-energy impacts *versus* incorporation of Si in Earth's core. In order to better understand the role played by any impact related processes in causing Si isotopic variation among planetary bodies, it is important to determine the extent of both Si and Mg isotope fractionation in a single aliquot of meteorite and terrestrial rock samples. This is because large-scale evaporation should ideally cause Mg isotopes to fractionate more than Si isotopes as evinced by Si and Mg isotope composition in CAIs and

evaporative residues from CMAS melt (Grossman *et al.*, 2000; Sugiura *et al.*, 2004). Thus, simultaneous study of Si and Mg isotopic fractionation in meteorites and in various phases of meteorites could direct the origin of isotopic fractionation to impact volatilization or core formation (Sikdar and Rai, 2016).

#### **1.7 Objectives of Thesis**

The primary objectives of this research work are as follows:

(i) To determine the Si and Mg isotopic variation among different groups of meteorites, which are representative samples of various planetary bodies of the solar system. This will help us to understand the radial variation of elemental and isotopic composition in solar nebula.

(ii) The Earth is a differentiated body with well-defined crust, mantle and metallic core. Density of core is lower than pure Fe-Ni alloy and as such there are predictions for the presence of lighter elements in Earth's core. Presence of Si as the principal light element in Earth's core has been concluded from the heavier  $\delta^{30}$ Si in BSE compared to chondrites. Whether the heavier Si isotope composition of BSE is really due to equilibrium Si isotope fractionation during core formation or it has been inherited from solar nebula through precursor materials is a matter of debate. The primary objective of this research work is to decipher the role of equilibrium versus nebular fractionation for generating Si isotope offset between chondrite and BSE. Precise Si isotope measurement in different micro-phases of enstatite chondrites would help in estimating the extent of Si isotope fractionation that is feasible under reduced conditions. Since the Earth was formed under reduced conditions, a comparison of enstatite chondrite's phase specific Si isotopic data with BSE could put constrains on the physico-chemical processes associated with accretion and chemical differentiation event of the Earth.

(iii) Another objective of this study is to determine simultaneous Si and Mg isotope variations in different meteorites, mineral separates of enstatite chondrite and representative samples of BSE with the aim to ascertain whether isotopic variations in

terrestrial samples compared to chondrites are related to volatility, core partitioning or has been inherited from solar nebula through precursor accreting materials.

#### **1.8 Thesis overview**

In this research work, high precision Si and Mg isotope measurements in a number of terrestrial and extra-terrestrial rock samples have been used as an investigative tool to understand the distribution of Si and Mg isotopes in the solar nebula (Sikdar and Rai, 2016, 2017). Based on Si and Mg isotopic data in phase separates of reduced chondrites, an attempt has been made to constrain the accretion and differentiation sequence of Earth. Apart from the introduction chapter, the presentation of rest of this thesis is divided into five chapters and the content of each of the chapters is described here briefly.

- Chapter 2 provides the basic concepts of non-traditional isotopes and its application in understanding accretion and differentiation of planetary bodies. The high temperature geochemistry of silicon and magnesium isotope systematics is described along with its analyses technique using MC-ICPMS. Si and Mg isotopic variations in different terrestrial and extra-terrestrial rock samples have been discussed.
- Chapter 3 describes mineral characterization of meteorite samples using EPMA and sampling of the pre-characterized phases by micro milling. A thorough description of the new silicate digestion technique to process micron size samples and the development of a new chromatographic protocol for simultaneous purification of silicon and magnesium from a single aliquot of rock sample is provided in this chapter (Sikdar and Rai, 2017). The chromatographic purification procedure is based on a combination of two-step cation exchange chromatography using AG 50W-X8 (200–400 mesh) resin. Various parameters for high precision analyses of Si and Mg isotopes using MC-ICPMS are discussed.

- Chapter 4 discusses results and implications from high precision Si and Mg isotopic composition among different groups of meteorites: carbonaceous chondrites, ordinary chondrites, enstatite chondrites and HED meteorites (Howardite, Eucrite, Diogenite clan), Sikdar and Rai, (2016). Determining Si and Mg isotopic composition in a broad range of extra terrestrial samples helped in assessing Si and Mg isotopic homogeneity in solar system.
- In Chapter 5, we have discussed the results from Si and Mg isotopic measurements carried out in micro phases (metal, matrix and silicate fractions) of primitive enstatite chondrite (EH3). The possible astrophysical setting for the origin of preserved Si isotopic signatures within unequilibrated enstatite chondrite and its association with bulk Earth composition is discussed.
- In Chapter 6, importance of our Si and Mg isotopic data in the context of present understanding of Earth's building blocks, its accretionary scenario and the nature of light elements present in its core of Earth have been summarized. The future scopes of the research work are also provided.

## **CHAPTER 2**

#### **NON-TRADITIONAL STABLE ISOTOPES**

Isotopes of an element have different number of neutrons (n) and same number of protons (z) and electrons (e). Stable isotopes undergo neither a radioactive decay nor a radiogenic growth over time (Hoefs, 2008; de Groot, 2004). The only difference between isotopes of an element is its mass. Every isotope in a molecule has its own characteristic vibration energy and rate of movement depending on its mass. The lighter isotopes move and react faster than heavier isotopes during any physico-chemical process. This results in unequal distribution of two or more isotopes of an element between two different phases, which is referred as isotope fractionation (Faure, 1977). Such isotopic fractionation causes variations in stable isotopic abundance depending on the existence or magnitude of key processes involved with elemental cycling. Therefore, measurement of isotopic abundances in specific systems act as an important tracer for varied types of bio-, geo- and cosmo- chemical processes.

Although stable isotopic composition of 'traditional' elements such as carbon, hydrogen, oxygen, nitrogen and sulfur are being used in the scientific community since a long time, but only in the last decade, the advent of Multi Collector Inductively Coupled Plasma mass spectrometry (MC-ICPMS) has enabled routine isotopic measurements of 'non-traditional' elements: Si, Ca, Li, Mg, Fe, Cu, Zn, Mo etc (Rehkämper, 2002; Luck *et al.*, 2005; Georg *et al.*, 2007; Seitz *et al.*, 2007; Burkhardt *et al.*, 2011; Heng *et al.*, 2013; Valdes *et al.*, 2014; Teng *et al.*, 2015a,b; Dauphas *et al.*, 2014; Savage *et al.*, 2015; Teng, 2017). Since high precision Si and Mg isotopic analyses in a varied type of extra-terrestrial samples is the major aim of this research

work, an introduction to the high temperature geochemistry of stable silicon and magnesium isotopes as a non-traditional stable isotope system is provided in this chapter.

#### 2.1 Theory of stable isotope geochemistry

The field of stable isotope geochemistry deals with determing the variations in the relative abundances of heavy or light isotopes with respect to a standard (Hoefs, 2008; Groot, 2004). Apart from relative mass difference, the degree of isotopic fractionation between two phases also depends on parameters such as reaction temperature, reaction rate, bonding environment and oxidation state (Hoefs, 2008; Schauble *et al.*, 2009; Steven *et al.*, 2016). There are two primary types of isotope fractionation in nature: (i) equilibrium, and (ii) kinetic isotope fractionation (Urey, 1947; Bigeleisen and Mayer, 1947; Young *et al.*, 2002).

#### 2.1.1 Equilibrium fractionation

During equilibrium fractionation, the reactants and products are in contact with each other continuously and maintain equilibrium in bi-directional reaction, *e.g.*, condensation of liquid from gas. Equilibrium fractionation is a quantum-mechanical phenomenon that arises due to the reduction in the zero-point energy when a heavier isotope is substituted for a lighter one (Urey, 1947; Bigeleisen and Mayor, 1947; Schauble, 2004; Abraham, 2010). The zero-point energies differ for variable atomic masses and are lower for heavier isotopes than lighter ones. For this reason, higher energy is required to dissociate the heavy molecules whereas the light isotopes are easily dissociated by the application of even a very low energy. Due to higher momentum, the lighter isotopes. O'Neil, 1986 and Schauble, 2004 provided the following qualitative rules for equilibrium fractionation:

- (i) There is a decrease in equilibrium isotopic fractionation with increase in temperature, roughly in proportion to  $1/T^2$
- (ii) The isotopic fractionation is more extensive in elements with relatively large mass difference between rare and abundant isotope
- (iii) The magnitude of fractionation depends on the stiffness of bond. The heavy isotope of an element prefers to get incorporated in substances with the highest bond-strength (Schauble, 2004).

#### 2.1.2 Kinetic fractionation

Kinetic fractionation occurs in reactions that are fast, unidirectional and incomplete such as diffusion and evaporation (Hoefs, 2008). Occurrence of kinetic isotope fractionation is frequent in low-temperature bio-chemical processes such as photosynthesis, bacterial reduction etc. The differential translational motion of different molecules in a phase leads to kinetic fractionation as the light molecules with higher average velocity compared to heavier molecules react faster and get enriched in reaction product.

Due to the dependence of kinetic fractionations on many variables (such as temperature, reaction rates and presence of exchange catalysts), it is difficult to describe kinetic fractionation with a list of applicable rules. Isotopic variations associated with kinetic fractionation processes can be easily resolved using analytical techniques due to its larger magnitude of fractionation than equilibrium reactions (Young *et al.*, 2002). Fractionation of oxygen isotopes between liquid water and vapor is one of the classic examples of kinetic effect. The lightest molecule ( ${}^{1}H_{2}{}^{16}O$ ) evaporates preferentially at a higher rate due to its higher velocity compared to the heaviest water molecule ( $D_{2}{}^{18}O$ ), thereby enriching water vapor in isotopically lighter molecules relative to liquid (Luz *et al.*, 2009).

#### 2.2 Non-Traditional stable isotopes

The basic principles of isotope fractionation were long established by Bigeleisen, Mayer, and Urey during the middle 20th century (Urey, 1947; Bigeleisen and Mayer, 1947). Isotope geochemists have since applying these principles and rules to isotope systems such as H, C, N, O, and S. But the era of non-traditional isotopic systematics (stable isotopes of elements other than the more traditional H, C, N, O, and S) have emerged recently with the advances in high precision data acquisition techniques (Albarède *et al.*, 2004a; Teng *et al.*, 2017). The capability to measure very minute fractionations of the non-traditional stable isotopes (e.g., Li, Si, Mg, Ca, Fe, Ni, Zr, Cu, Mo, Ru and Zn) has emerged as a new tool in geochemistry and cosmochemistry to trace a number of geo- and cosmochemical processes (Albarède *et al.*, 2004a; Young *et al.*, 2015; Teng *et al.*, 2017).

The higher temperature associated with igneous processes and small relative mass difference between the stable isotopes of Mg, Si and Fe leads to very small degree of isotope fractionation (Bourdon *et al.*, 2010). It was traditionally thought that Si, Mg, Fe, Cr and other such isotopes are bonded too strongly or are too heavy to fractionate at a resolvable level, which could be detected using analytical techniques. With the development of MC-ICPMS, high precision isotopic measurements (<100 ppm per atomic mass unit) of "non-traditional" stable isotopes have become routine in the past decade. This allows the determination of extremely small variations in the relative abundance of isotopes in natural samples (Albarède *et al.*, 2004b).

Due to temperature dependency of equilibrium isotope fractionations, most nontraditional isotopes finds application in the field of thermometry, *i.e.*, calculation of temperature from the distribution of isotopes between phases. Stable isotopic distribution of various elements among different reservoirs is also used in the identification of paragenesis (Young *et al.*, 2009; Pogge von Strandmann *et al.*, 2011; Young *et al.*, 2015). On a planetary scale, determination of isotope abundances is used to infer the composition of unseen reservoirs, the most prominent example being the inference of light Si, Cr isotopes to be present in the core of Earth (Georg *et al.*, 2007; Shahar *et al.*, 2009; Ziegler *et al.*, 2010; Fitoussi and Bourdon, 2012). The stable isotope composition of planetary objects depend both on the initial composition of primordial constituents and also on characteristic processes that might have induced isotope fractionation during accretion and differentiation. Evaluating and comparing the stable isotopic ratios of various elements among chondrites and terrestrial samples helps in elucidating the building blocks of planets and various processes of planet formation, accretion and differentiation (Bourdon *et al.*, 2010; Fitoussi and Bourdon, 2012; Dauphas *et al.*, 2015).

#### 2.3 High temperature geochemistry of stable silicon isotopes

Silicon (Si, Z=14, atomic weight = 28.08553) is the second most abundant element (after oxygen) in the Earth's crust (Suess and Urey, 1956). Si has three stable isotopes:  $^{28}$ Si,  $^{29}$ Si and  $^{30}$ Si with relative abundances of 92.23 %, 4.67 % and 3.10 % respectively (Faure and Mensing, 2004). The atomic masses of  $^{28}$ Si,  $^{29}$ Si and  $^{30}$ Si are 27.97693, 28.97649 and 29.97377 respectively. The Si stable isotope composition of a sample is reported using "delta notation", defined as the deviation of a sample's isotopic ratio from that of a standard isotopic ratio (Eqn. 2.1). The delta value is widely used in isotope geochemistry because it is relatively easier to determine the difference between samples and standards rather than to determine the absolute value of isotopic ratios. Because the fractionation is usually small, the unit of the delta value is reported in per mil (‰), which is one part per thousand. The isotopic composition of Si is mostly represented by  $\delta^{30}$ Si values, which is approximately twice the magnitude of  $\delta^{29}$ Si values, assuming mass dependent fractionation.

$$\delta^{30} \text{Si} (\%) = \left[ \frac{\left(\frac{30_{\text{Si}}}{28_{\text{Si}}}\right)_{\text{sample}}}{\left(\frac{30_{\text{Si}}}{28_{\text{Si}}}\right)_{\text{NBS-28}}} - 1 \right] \times 1000 \quad ---- (2.1)$$

Silica and reference material SRM 8546, distributed by the National Institute of Standards and Technology (NIST) and commonly known as NBS-28, is used as the primary reference material for reporting Si isotopic data because it is isotopically homogeneous and also used as standard for oxygen isotope measurements (Carignan *et* 

*al.*, 2004). A positive delta value (>0) indicates relative enrichment of heavy isotopes compared to the reference standard (heavier isotopic composition corresponds to higher  ${}^{30}\text{Si}/{}^{28}\text{Si}$  in sample), while a negative delta value (<0) means that the sample is depleted in heavy isotope compared to the standard (lighter isotopic composition corresponds to lower  ${}^{30}\text{Si}/{}^{28}\text{Si}$ ).

Although the relative mass difference between Si isotopes is large (~7% between  $^{30}$ Si and  $^{28}$ Si), the degree of Si isotopic fractionation in high temperature conditions prevalent in igneous realm is limited because of similar bonding environment of Si in almost all silicates, wherein Si always occurs in tetrahedral coordination with four oxygen atoms. Single oxidation state of Si (Si<sup>4+</sup>) does not allow formation of volatile compounds readily and hence Si isotopes do not get easily fractionated. Silicon isotopic variation is typically on the order of <0.5‰ at high temperature. Because of the limited Si isotopic fractionation recorded by igneous rocks and meteorites, it is often difficult to resolve Si isotopic fractionation between two phases.

#### **2.3.1 Mass dependent fractionation of Si isotopes**

In general, isotopic fractionation is a mass-dependent process and hence isotopic variations are commonly described by mass-dependent fractionations in a three-isotope plot of  $\delta^{30}$ Si vs.  $\delta^{29}$ Si, Fig. 2.1. Since Si has three stable isotopes, so the extent of fractionation of  ${}^{30}$ Si/ ${}^{28}$ Si ratio should be twice of  ${}^{29}$ Si/ ${}^{28}$ Si as a function of mass difference of the ratios. Thus all mass-dependent Si isotopic fractionations should fall on a straight line in the  $\delta^{30}$ Si- $\delta^{29}$ Si space. In case of terrestrial samples, no mass-independent isotope fractionations have been documented till now because none of the three Si stable isotopes has a radiogenic component and Si does not take part in any photochemical or spin-forbidden reactions (Thiemens, 2006; Bergquist and Blum, 2007). The presence of non-mass dependent isotope effect is certified by any deviation from mass dependent fractionation line (Clayton *et al.*, 1993). For example, mass-independent Si isotopic values have been documented from silicon carbide (SiC)

grains in carbonaceous chondrites ( $\delta^{29}$ Si = -20.0 to +124.2‰, Stone *et al.* 1991), which have been attributed to presolar nucleosynthetic anomaly (Zinner *et al.*, 1989).

Mass fractionation laws governing equilibrium and kinetic processes differ because kinetic fractionation is primarily associated with difference in effective masses, whereas equilibrium exchange arises due to quantum phenomenon (Young *et al.*, 2002). Mass dependent process are described in terms of fractionation factors given by:

$$\alpha_{29/28} = (\alpha_{30/28})^{\beta}$$

The exponent  $\beta$  differs for kinetic and equilibrium fractionation based on atomic masses of each of the isotopes. For equilibrium and kinetic fractionation among silicon isotopes, these exponents are calculated as follows:

For equilibrium fractionation,

$$\beta_{eq} = \frac{\left(\frac{1}{m_{28}} - \frac{1}{m_{29}}\right)}{\left(\frac{1}{m_{28}} - \frac{1}{m_{30}}\right)}$$

For kinetic fractionation,

$$egin{aligned} eta_{kin} &= rac{\ln\left(rac{m_{28}}{m_{29}}
ight)}{\ln\left(rac{m_{28}}{m_{30}}
ight)} \end{aligned}$$

where 'm' refers to masses of Si isotopes,  $m_{28} = mass$  of <sup>28</sup>Si,  $m_{29} = mass$  of <sup>29</sup>Si and  $m_{30} = mass$  of <sup>30</sup>Si. The different slopes for equilibrium and kinetic fractionation has been calculated as:  $\beta_{eq} = 0.5178$  and  $\beta_{kin} = 0.5092$ . On a three-isotope plot of  $\delta^{30}$ Si vs.  $\delta^{29}$ Si, mass dependent isotopic data falls on a straight line with slope of  $\beta_{eq}$  or  $\beta_{kin}$ , depending on how the isotopes are fractionated (Young *et al.*, 2002).

At low degrees of fractionation, these slopes are extremely similar and current level of precision is not sufficient enough to distinguish between equilibrium and kinetic fractionation over limited ranges in isotopic composition (Young *et al.*, 2002).

Therefore, the mass dependent fractionation relationship is used more as an indicator of data quality since presence of any unresolved interferences in Si isotope can artificially alter the isotope ratios away from the expected mass-dependent fractionation line (Sikdar and Rai, 2017). Through out this research work, all Si isotopic data are checked for mass dependence trend before it is utilized further to measure the Si isotopic composition of unknown samples.



**Figure 2.1:** Plot of  $\delta^{29}$ Si versus  $\delta^{30}$ Si. Error bars represent  $\pm 2\sigma$ . The slopes for mass dependent equilibrium fractionation (0.5178) and kinetic fractionation (0.5092) are extremely close and mostly cannot be distinguished. Image credit: Armytage *et al.* (2011)

#### 2.3.2 Historical analysis of Si isotopes

The first mass spectrometric investigations of stable silicon isotopes started as early as in 1950s (Reynold and Verhoogen, 1953; Allenby, 1954), who used Gas Source Mass Spectrometry (GS-MS) with an analytical precision of  ${}^{30}\text{Si} = \pm 0.4\%$ . New analysis methods such as Isotope Ratio Mass Spectrometry (IRMS) increased precision upto ~0.2‰ in the subsequent years (Douthitt, 1982; Molini-Velsko *et al.*, 1986; De La Rocha *et al.*, 1997, 2002; Ding *et al.*, 1996). In case of IRMS measurement, the sample

preparation method makes the use of hazardous bromine pentoxide (BrF<sub>5</sub>) to convert the samples into gaseous SiF<sub>4</sub> and hence only a few laboratories equipped with such device were able to carry out Si isotopic analyses. The research in the field of Si isotopes saw much development after the extensive study of terrestrial rock samples by Douthitt, 1982 and Ding *et al.*, 1996. But theses data were standardized with respect to Caltech Rose Quartz Standard (RQS), whose isotopic composition was poorly constrained against NBS-28. Hence a direct comparison of  $\delta^{30}$ Si values analyzed with respect to two different standards (NBS-28 and RQS) was questioned until Georg *et al.*, 2007 reported that both standards have approximately similar isotopic compositions. Alternatively, secondary ion mass spectrometry (SIMS) was being used for in-situ Si isotopic analysis without complex sample preparation technique. However, SIMS measurements were limited by precision of 0.75‰ (Zinner *et al.*, 1987; Robert and Chaussidon, 2006) and hence SIMS was not considered for routine Si isotopic measurements except for presolar grains where the observed isotopic variation exhibits very large range.

With the advent of MC-ICPMS, the research in the field of Si isotopes have gained momentum as it is now possible to carry out high precision Si isotopic analyses with precision reaching upto sub-per mil level (Teng *et al.*, 2017 and references therein). This enables the measurement of small but systematic isotopic variations recorded in samples from high temperature realm. The capability of MC-ICPMS to replicate measurements in very less time has led to an increase in precision. Furthermore the sample preparation technique for carrying out Si isotope analyses in MC-ICPMS does not require the use of hazardous HF gases. De La Rocha, (2002) has made the initial studies demonstrating the application of MC-ICP-MS to carry out Si isotopic analysis in wet plasma conditions with 2SD = 0.18%. This was followed by an increase in precision (2SD = 0.08%) because of improvement in silicate digestion and mass spectrometric technique (Cardinal *et al.*, 2003; Engström *et al.*, 2006; Georg *et al.*, 2006; Van den Boorn et al., 2006, 2009; Dauphas *et al.*, 2015; Sikdar and Rai, 2017).

# 2.3.3 Si isotopic variations in terrestrial and extra terrestrial rock samples

Since the continental and oceanic crusts are primarily composed of silicate minerals (Faure and Mensing, 2004), isotopes of silicon are widely used as a tracer in a number of processes of geological interest such as silicate weathering, water-rock interactions, global biogeochemical cycles, magma differentiation and core formation (Douthitt *et al.*, 1982; De La Rocha *et al.* 1997, 1998, 2000a; Ding *et al.* 1996; Singh *et al.*, 2015, Ziegler *et al.* 2005, 2010; Georg *et al.* 2007; Armytage *et al.* 2011; Fitoussi *et al.*, 2009, 2012; Savage *et al.*, 2014, Dauphas *et al.*, 2014a, 2015; Patrick *et al.*, 2016). Silicon is also a main constituent in extraterrestrial rocks (Faure and Mensing, 2004) and a number of studies have been carried out to investigate the silicon isotopic composition in meteorites. The mass-independent Si isotopic fractionation show a much larger range in extra-terrestrial meteorite samples compared to terrestrial rock samples due to presence of "isotopic anomalies" having magnitude of tens to hundreds of permil as reported in calcium-aluminium-rich inclusions (CAIs) and presolar circumstellar SiC (silicon carbide) grains (Ding *et al.*, 1996; Shahar and Young, 2007).

The similarity in  $\delta^{30}$ Si among mantle derived rocks and bulk meteorites suggests that negligible Si isotopic fractionation occurs during partial melting (Douthitt, 1982; Ding *et al.*, 1996; Georg *et al.*, 2007). The variation in Si isotopic composition among chondrites and achondrites is very limited indicating that the solar system was wellmixed and isotopically homogenous in terms of Si isotopes (Ramananda and Chakrabarti, 2010a). Although Molini-Velsko *et al.* (1986) presented a large compilation of Si isotopic composition in meteorites but it the work of Georg *et al.* (2007), which has initiated the current interest in Si isotopic composition of extraterrestrial material. The detection of resolvable isotopic offset between Bulk Silicate Earth (BSE) and meteorites (Fig. 2.2) has galvanized a great deal of further research for constraining the amount of Si in Earth's core and estimating the building blocks of Earth (Fitoussi *et al.*, 2009; Shahar *et al.*, 2009, Ziegler *et al.*, 2010, Armytage *et al.*, 2011; Fitoussi and Bourdon, 2012, Savage and Moynier, 2013; Zambardi *et al.*, 2013,



Dauphas *et al.*, 2015). An in depth discussion of the Si isotopic results from these studies is provided in chapter no. 4 and 5.

**Figure 2.2:** Si isotopic compositions of various planetary reservoirs. Angrites have  $\delta^{30}$ Si values a little heavier than BSE and moon. Carbonaceous chondrite, ordinary chondrite, HEDs, enstatite chondrites are lighter compared to BSE. Image courtesy Dauphas *et al.* (2015)

#### 2.4 Magnesium stable isotope systematics

Magnesium, one of the major elements in the solar system, is a lithophile and moderately refractory element with a condensation temperature of ~1400 K (Lewis, 1997; Lodders, 2003). It has three stable isotopes: <sup>24</sup>Mg, <sup>25</sup>Mg, and <sup>26</sup>Mg with natural abundances of 78.99%, 10.00%, and 11.01% respectively (Rosman and Taylor, 1998; Huang *et al.*, 2015). Mg isotopes are known to be an excellent tracer to study various geological and cosmological processes (Teng *et al.*, 2007). Apart from stable isotopes, radiogenic <sup>26</sup>Mg isotope, produced by  $\beta^+$  decay of <sup>26</sup>Al isotope (t<sub>1/2</sub> = 0.72 Ma) can cause non-mass-dependent anomalies in objects formed in the early solar system (Lee

*et al.*, 1976, 1977; Jacobsen *et al.*, 2008). The abundances of <sup>26</sup>Mg isotopes in meteorites form the basis of an important and the most widely used short-lived chronometer for dating various events such as solid formation, planetesimal accretion, differentiation in the young solar system, planetary volcanism (Lee *et al.*, 1976, 1977; Russell *et al.*, 1996; Srinivasan *et al.*, 1999, 2007, Schiller *et al.*, 2010) and constraining the timing of grain condensation in early solar nebula (Russell *et al.*, 1996; Bizzarro *et al.*, 2004; Larsen *et al.*, 2016).

Due to larger extent of fractionation, the detection of "anomalous" Mg isotopic effects is easier than investigations of mass-dependent fractionation. Therefore, many past studies of Mg isotope ratios have focused on detection of non-mass dependent fractionation (Wasserburg, 1977; Clayton and Mayeda, 1977; Young and Galy, 2004). With the advent of MC-ICPMS and TIMS, high precision Mg isotope data acquisition with precision about 0.05‰ amu<sup>-1</sup> (2SD) or better has allowed mass-dependent Mg isotope fractionations to be used as tracers in natural systems. Stable Mg isotopes are now widely used to study differentiation of magma by fractional crystallization (Teng *et al.*, 2007; Liu *et al.*, 2010; Larsen *et al.*, 2016); the origin of planets, moon, chondrites and chondrules (Wiechert and Halliday, 2007; Bourdon *et al.*, 2010; Teng *et al.*, 2010a; Sedaghatpour *et al.*, 2013; Teng *et al.*, 2015a; Olsen *et al.*, 2016; Schiller *et al.*, 2010, 2017), crustal weathering and Mg geochemical cycling (Galy *et al.*, 2002; Tipper *et al.*, 2006 b, c; Huang *et al.*, 2009, 2015).

To report the variation in Mg isotopic composition among natural samples, international standard reference material DSM-3 (manufactured by Dead Sea Mg Ltd., Israel) is used as a zero delta reference material following Galy *et al.* (2003). Mg isotope data are reported as  $\delta^{25}$ Mg and  $\delta^{26}$ Mg (‰) relative to the DSM-3 following Eqn. 2.2, where x=25 or 26.

#### 2.4.1 Magnesium isotopic distribution in the solar system

High precision Mg isotope composition by Schiller et al. (2010) suggests absence of any measurable Mg isotope nucleosynthetic variations between different planetary bodies of solar system. Bourdon et al. (2010) measured Mg isotopic compositions of peridotites, ocean-island and mid-ocean ridge basalts, and several chondritic meteorites. With the uncertainty of  $\pm 0.1$  ‰ (2SD), they reported negligible variation for the Mg isotope ratios of these samples, reflecting similar homogeneous reservoir for the bulk silicate Earth and chondrites with  $\delta^{26}$ Mg of -0.23‰ (Bourdon *et al.*, 2010). Based on the more comprehensive database (mid-ocean ridge basalts covering global major ridge segments, ocean island basalts, peridotite xenoliths and diverse chondrite groups); Teng *et al.* (2010) estimated the average  $\delta^{26}$ Mg value of Earth's mantle to be  $-0.25 \pm 0.07$  ‰ (2SD), which is identical to that of chondrites ( $\delta^{26}Mg = -0.28 \pm 0.06$ ‰, 2SD). Several other studies of Mg isotope analyses in terrestrial mantle rocks, lunar rocks, chondrites and achondrites indicate homogeneous distribution of Mg isotopes in solar system and a chondritic Mg isotopic composition for the Earth (Norman et al., 2006; Teng et al., 2007; Yang et al., 2009; Huang et al, 2009a; Bourdon et al., 2010; Chakrabarti and Jacobsen, 2010a; Schiller et al., 2010; Teng et al., 2010a; Pogge von Strandmann et al., 2011; Sedaghatpour et al., 2013, 2016).

Although high-precision Mg isotope data of meteorites largely indicates limited stable Mg isotopic variations in solar system but there have been debates about the chondritic Mg isotopic composition of the Earth and the possibility of any significant Mg isotope fractionation at mantle temperature (Young and Galy, 2004; Pearson *et al.*, 2006; Wiechert and Halliday, 2007; Yang *et al.*, 2009; Young *et al.*, 2009; Xio *et al.*, 2013). Pearson *et al.*, 2006 reported a large Mg isotope fractionation (>2 ‰) within olivine crystals of mantle-derived peridotite xenoliths indicating the potential of Mg isotopes to get fractionated at high temperature during terrestrial magmatic evolution. Small Mg stable isotope fractionations are known to exist between co-existing terrestrial mantle olivine, orthopyroxene and clinopyroxene, with olivine being the isotopically lightest phase (Handler *et al.*, 2009; Young *et al.*, 2009; Pogge von Strandmann *et al.*, 2011; Xiao *et al.*, 2013). Mg isotopic analysis of chondrites and terrestrial rocks by Wiechert and Halliday, (2007) suggested a heavy Mg isotopic composition for the Earth (0.0‰)

compared to the chondrites (with  $\delta^{26}$ Mg ranging from -0.49 ‰ to -0.24 ‰ for 9 chondrites). This non-chondritic Mg isotopic composition of the Earth is interpreted as a result of the relative contribution of chondrules in the formation of the terrestrial planets and physical sorting of these objects in proto-planetary disk (Wiechert and Halliday, 2007). Using laser ablation MC-ICPMS and analyzing mantle olivines and carbonaceous chondrites, Young *et al.* (2009) also reported a heavy non-chondritic Mg isotopic composition for the Earth. Schiller *et al.* (2016) have carried out Mg isotopic investigations in a wide variety of HED meteorites (known to sample asteroid Vesta) and concluded that diogenites have stable Mg isotopes that are indistinguishable from those for Earth's mantle and chondrite meteorites. In contrast, eucrites (represent the crust of Vesta) are isotopically heavier than all these materials. Schiller *et al.* (2017) suggested that this isotope effect is not readily observed on Earth due to the production of lower magnesium contents during smaller degrees of melting and less extensive amounts of mafic mineral crystallization.

Thus it has remained uncertain whether bulk Earth and chondrites have similar Mg isotope composition. One reason might be that there occurs inconsistency in the reported Mg isotopic compositions of some widely studied USGS rock standards such as SCo-1, BCR-1 and BCR-2 that has been measured in different international laboratories. The lack of enough Mg isotope data for commonly available geological reference materials severely hinder direct inter-laboratory comparison of Mg isotopic composition to examine the accuracy of Mg isotopic measurement. More international reference materials are required to be measured for Mg isotopic composition in different international laboratories to establish an accurate isotopic value of these standards before concluding chondritic/non-chondritic nature of Earth.

Our high precision Si and Mg isotopic analyses of some widely available rock standards and in varied groups of meteorites provides constraints on the accurate Si and Mg isotopic composition of international rock standards and helps in understanding the extent of homogeneity of Si and Mg isotopes in solar nebula, the details of which are discussed in the subsequent chapters.

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### **CHAPTER 3**

### **EXPERIMENTAL TECHNIQUES**

One of the primary aims of this research work is to determine the micro-scale distribution of Si and Mg isotopic composition in various mineral phases of meteorites as precisely as possible to better understand the formation and differentiation event of terrestrial planets. To achieve this goal, mineralogical characterization of meteorites is one of the preliminary steps, which was carried out using CAMECA Electron Probe Micro Analyzer (EPMA). Since most of the mineral phases present in meteorites are not big enough to provide sufficient material for their respective isotopic analyses, so emphasis have been made to look for larger, least altered and impurity free phases. After mineral characterization, micro sampling of the target phases was carried out followed by chromatographic purification and high precision isotopic analyses of Si and Mg using MC-ICPMS. This chapter provides detailed information of various analytical techniques utilized for mineral characterization and the development of an entirely new procedural protocol for high precision Si and Mg isotopic analyses in very limited amount of sample. In the entire research work, a wide variety of ordinarycarbonaceous-enstatite chondrites, achondrites, HED meteorites and terrestrial rock samples were analyzed using the analytical techniques detailed in this chapter.

#### 3.1 Mineralogical characterization of meteorite samples

Most of the meteorite samples studied during the course of this research work were provided by Antarctic Search for Meteorites (ANSMET), NASA in the form of mounted sections and hence were analyzed directly using EPMA. The Indian meteorites and others obtained from National Institute of Polar Research, (NIPR), Japan was in the form of chips and hence required further processing a prior to mineral characterization. The work carried out to make mount sections of meteorites is described below.

#### **3.1.1 Sample preparation**

The chips of meteorites were first examined under a reflecting microscope to make sure it is representative of fresh meteorite sample and lacks fusion crust. Then the samples were mounted in epoxy by adhering the meteorite's maximum flat exposure area on a glass slide with a double-sided tape. Epoxy and epoxy hardener was mixed in the ratio of 7:1 to make a mount of the samples. Extreme care was taken to avoid the formation of any air bubbles. A stirrer and infrared light was used for 2-3 minutes to evaporate away any air bubbles that might have formed during the experimental procedure. It was then kept in the oven overnight at 70°C to harden. The hardened mount section with the sample intact within it was taken off from the double-sided tape carefully.

#### 3.1.2 Sample polishing

The sample was first polished on 400 $\mu$ m grit abrasive on LOGITECH CL40 compact 40 Lapping/polishing machine at 100-150 rpm by using water as lubricant. It was then polished on 45 $\mu$ m, 8 $\mu$ m, 6 $\mu$ m, 3 $\mu$  and 1 $\mu$ m abrasive clothes using diamond paste, diamond suspension and hifin fluid as lubricant. While changing from coarser to finer abrasive, the sample was always cleaned with alcohol. It was constantly examined after intervals of 15 minutes under an Axiolab-Zeiss optical microscope. The procedure of sample polishing was carried out in petrology laboratory of Physical Research Laboratory. When most of the grains present in the sample became distinguishingly visible, then the polished sample was analyzed using optical microscope and electron probe micro-analyzer (EPMA) to identify different minerals

present therein. After final polishing, samples were coated with an approximately 20 nm layer of carbon using a carbon evaporator to make it conductive.

#### **3.1.3 Electron Probe Micro Analyzer (EPMA)**

Polished mounted sections of meteorite samples were analyzed using Electron Micro-Probe Analyzer (CAMECA SX 100) in order to identify different minerals and determine their compositions. Electron Probe Micro Analyzer (EPMA) is an electron microscope used for *in situ* microanalysis and imaging of solid materials (Willich, 1992). It can perform high spatial resolution ( $\sim 1 \mu m$ ) imaging and has high analytical sensitivity and detection limit. Focused electron beam with a typical energy of 5-30 keV is bombarded on the sample and X-ray photons emitted by the various elemental species are collected. X-rays are produced by inelastic collisions of the incident electrons with electrons in the inner shells of atoms in the sample. When an inner-shell electron is ejected from its orbit, leaving a vacancy, a higher-shell electron falls into this vacancy and emit X-rays. Since the wavelengths of these quantized X-rays are characteristic of the emitting species, the mineralogy of sample can be easily identified from WDS spectra (Wavelength Dispersive Spectroscopy), (Reed, 1996; Pownceby, 2007). WDS spectrometers are based on the Bragg's law ( $n\lambda = 2dSin\theta$ ) and it uses various movable mono-crystals as detectors (Goldstein et al., 2003). The secondary and back-scattered electrons are used for imaging the sample's surface. A high vacuum of  $< 10^{-6}$  torr is maintained in the sample chamber.

While carrying out mineralogical characterization of meteorites, the first step was to capture Back Scattered Electron (BSE) images of different areas of the sample, which were then stitched to form a collage of the whole surface. After finding out the areas of interest from the collage, its quantitative analyses were carried out using wavelength dispersive spectrometer to get idea of their chemical composition. The acceleration voltage and sample current used were 15 kV and 15 nA respectively. The beam diameter was of 1  $\mu$ m in size. For quantitative analyses, the three wavelength

dispersive spectrometers were standardized and calibrated using natural standards of known composition as mentioned in Table 3.1.

**Table 3.1:** List of natural standards used for calibration of spectrometers in EPMA for

 the determination of mineral composition in meteorites.

Elements	Natural Standards
Na	Jadeite (NaAlSi <sub>2</sub> O <sub>6</sub> )
Si	Diopside (CaMgSi <sub>2</sub> O <sub>6</sub> )
Mg	Olivine (Mg <sub>2</sub> SiO <sub>4</sub> )
Al	Kyanite (Al <sub>2</sub> SiO <sub>5</sub> )
Р	Apatite (Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (F,Cl,OH))
K	Orthoclase (KAlSi <sub>3</sub> O <sub>8</sub> )
Ca	Wollastonite (CaSiO <sub>3</sub> )
Ni, Co	Ni, Co metal
Fe, S	Troilite (FeS <sub>2</sub> )

#### 3.1.4 Mineralogy of chondrites determined by EPMA

Similar to results documented by Rubin, (2009), the individual minerals observed and mapped in various enstatite meteorites from this study are:

- Enstatite (MgSiO<sub>3</sub>)
- Hypersthene ((Mg,Fe)<sub>2</sub>Si<sub>2</sub>O<sub>6</sub>)
- Oldhamite (CaS)
- Troilite (FeS)
- Daubreelite (FeCr<sub>2</sub>S<sub>4</sub>)

- Niningerite [(Mg, Fe,Mn)S]
- Schreibersite (Fe, Ni)
- Kamacite (Si, Fe–Ni alloy)
- Perryite (Ni,Fe)<sub>5</sub>(Si,P)<sub>2</sub>

The photo-micrographs of various components (metals, silicates, chondrules, sulphides and clasts) found in primitive enstatite chondrite and ordinary chondrite are provided in Fig. 3.1 and Fig. 3.2.



**Figure 3.1:** Back-scatter electron images of PCA 91461 (EH3) showing 1(a) highly reflecting metal (Kamacite) surrounded by dark silicates. 1(b) Perryite, Troilite, Daubreelite, Enstatite and Glass can be identified from their decreasing order of reflectivity.



**Figure 3.2:** A composite back scattered electron image of QUE 97008 (H3.0 chondrite) 2a) Aggregates of chondrules, clasts, metals and sulphides set in opaque, fine-grained inter-chondrule matrix. 2e) A 1mm chondrule composed entirely of olivine crystals surrounded by a rim of sulphides.

The following minerals were identified after WDS analysis in QUE 97008 (H 3.0 chondrite): Enstatite (Mg<sub>2</sub>Si<sub>2</sub>O<sub>6</sub>), Forsterite ((Mg,Fe)<sub>2</sub>SiO<sub>4</sub>), Augite ((Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)<sub>2</sub>O<sub>6</sub>), Omphacite ((Ca,Na)(Mg,Fe,Al)Si<sub>2</sub>O<sub>6</sub>), Hornblende ((Ca,Na)<sub>3</sub>(Mg,Fe,Al)<sub>5</sub>(Si,Al)<sub>8</sub>O<sub>22</sub>(OH,F)<sub>2</sub>), Jadeite (Na(Al,Fe)Si<sub>2</sub>O<sub>6</sub>), Bytownite

((Ca,Na)(Si,Al)<sub>4</sub>O<sub>8</sub>), Kamacite (alpha-(Fe,Ni)), Troilite (FeS) and Taenite (gamma-(Fe,Ni)), Tetrataenite (FeNi).

#### **3.1.5 Micro-sampling of meteorite phases**

After mineralogical characterization of the target phases (kamacite-perryite (metals) and olivine-enstatite-feldspar (silicates)), the location of these phases was identified using Zeiss petrological microscope attached to NewWave Micro mill. Micro milling of the target phases were carried out using tungsten drill bit having a cross section of 100µm. MQ was added on the target location to avoid any dissemination of mineral dusts while drilling (illustrated in Fig. 3.3). Based on size of the target phase; point or line scan mode of drilling was used whereas raster scan mode of drilling was used to drill the representative of bulk meteorite sample. Cleaning of the drill bits were carried out by ultra-sonicating it with ethyl alcohol and MQ-water after each and every drilling session. Following micro milling, the samples were processed for Si and Mg isotopic measurements.



**Figure 3.3:** Micromilling of the target phases using NewWave micromill machine. Ultra pure water was added on the target drill location to avoid scattering of mineral dust while drilling.
### 3.2 Analytical techniques

Mixture of hydrofluoric acid (HF) with other mineral acids is traditionally used to digest rock samples but usage of HF leads to loss of Si in the form of volatile SiF<sub>4</sub> and thus introduces artificial isotopic fractionation (Georg *et al.*, 2006; Pringle *et al.*, 2016). Also the high ionization potential of fluorine suppresses the ionisation efficiency of the plasma and reduces the sensitivity of mass spectrometer. So, HF was avoided for digesting silicates in this study and silicates were digested using a new digestion technique that uses NaOH as flux.

#### 3.2.1 A new alkali digestion technique using NaOH

Most of the rock digestion methods adapted till date for Si isotopic analyses is followed by Georg et al., (2006), where alkali fusion of sample powder is performed in a silver crucible using NaOH flux. In all such procedures, the crucible is heated to 730°C for 10-12 minutes and the resulting fusion cake is transferred into Teflon vials filled with MQ (slightly acidified with HNO<sub>3</sub>), where the metastable cake gets dissolved. We initially started silicate digestion following the same procedure but found that most of the crucibles made of 99.99% purity Ag could not withstand the temperature reached in high temperature (blue) flame of bunsen burner and the crucibles started becoming ductile. Similar problem was faced while carrying out rock digestion in high purity Ag crucibles in furnace at >700°C. Although silver crucibles made of 99.5% purity Ag was found to withstand such a high temperature but digesting silicates in these crucibles contributed a very high Si blank level (> 50ng). To get rid of such problems and to digest extremely small amount of micro milled sample, we have developed a new silicate digestion procedure that has been used thorough out this research work. The description of the procedure is summarized in subsequent paragraphs.

The new alkali fusion procedure for digesting silicates developed in this study uses sodium hydroxide monohydrate (NaOH) flakes (Suprapure from Merck) as flux. Instead of using silver crucible, silicates were digested in precleaned Teflon (Savillex<sup>TM</sup>) vials. This procedure has been found to be very effective in handling small amount of samples obtained after micromilling of precious meteorites and also contribute to minimal blank level compared to that of silver crucible. Since the whole digestion procedure takes place in Teflon (Savillex<sup>TM</sup>) vial, so it is otmost necessary to clean the vials very rigorously. The Teflon vessels were cleaned in 8M HNO<sub>3</sub> (1 day at 100°C), 6N dilute HCl (2 days at 100°C), 10ml concentrated HF (analytical grade) followed by concentrated HNO<sub>3</sub> (1 day at 100°C) and finally with MQ water (1 day at 80°C). The vessels were rinsed with MQ water in between the different acid cleaning steps. The whole cleaning step was repeated using double distilled acids and rinsed with MQ water. Variable amounts of powdered whole rock sample of ~0.5-2 mg were weighed into each Teflon vial. For the fusion,  $\sim 2 \text{ mg}$  of finely powdered sample was mixed with ~80 mg of NaOH and 50  $\mu$ l of 18M $\Omega$  Milli-Q in Teflon (Savillex<sup>TM</sup>) vial. The sealed vial was ultrasonicated for 5 minutes followed by heating at ~250 °C in a hot plate for 18 hours. After slight cooling, 5 ml Milli-Q was added into the fusion cake and was subsequently dissolved in 500µl-1ml of double distilled concentrated HCl:HNO<sub>3</sub>. The relative proportions of sample and NaOH were maintained throughout the fusion process as suggested by Fitoussi et al. (2009). During the entire digestion procedure, extreme care was taken to inhibit the formation of any crystals since adsorption of Si on Fe hydroxides is reported to cause a shift in silicon isotope fractionation (Delstanche et al., 2009). Prior to loading the sample in column, the digested rock solutions were left undisturbed to equilibrate for at least 18 hours. This digestion technique enables to process samples more rapidly and efficiently compared to the traditional way of fusing silicates using silver crucible and it also ensures no loss of Si during the entire digestion step (Sikdar and Rai, 2017).

Fusion blanks were checked using 100 mg of solid NaOH in empty Savillex vial. The fused products were diluted with 5 ml MQ and subsequently dissolved in 500  $\mu$ l of double distilled HCl:HNO<sub>3</sub>. The concentration of Si in these blank solutions was found to be negligible (<10ng) compared to the amount of Si processed through the purification protocol (8µg). Hence the entire procedure was found to be very effective for processing small amounts of precious meteorite samples.

### 3.2.2 Ion-exchange chromatography

High precision stable isotopic analyses by MC-ICPMS require pure solution of analyte element (in this case Si and Mg), since interference from other elements can result in inaccurate isotopic analysis (Albarede *et al.*, 2004b). In order to purify Si and Mg from matrix elements, column chromatography was carried out using AG50W-X8 (200-400 mesh) cation exchange resin throughout this work.

Ion exchange materials are insoluble substances containing loosely held ions which are able to be exchanged with other ions in solutions that come in contact with them (Williams and Frasca, 2001; Patel *et al.*, 2007). These exchanges take place in the form of cation or anion complexes without any physical alteration to the ion exchange material. During ion exchange chromatography, the stationary phase interacts with analyte ions of opposite charge and the counter ions on the resin are replaced by sample ions having the same charge. The sample (solute) is initially dissolved in solution (mobile phase) and made to flow through a resin (stationary phase). The resin has different affinities for different ions of the solute and therefore the passage of these ions through the system gets delayed due to adsorption of some ions onto the resin. This delay causes different elements of the solute to separate out and emerge at different times from the resin. Upon careful consideration of the ionic behavior of various elements in different acids, it is possible to elute specific elements from the ion exchange resin by using different combination of acids having appropriate strength (Heftmann, 1966; Small, 1990).

The 'strength' with which different species of the sample compete with one other for the ionic sites, or equivalently, how long the species will spend in the stationary phase (resin) relative to the mobile phase, is quantified by the parameter called distribution coefficient,  $K_d$ ,  $K_d = C_s/C_M$ 

where,  $C_S$  and  $C_M$  represent the concentration of the solute in stationary phase (S) and mobile phase (M) respectively. The element with higher K<sub>d</sub> value spends more time in the resin (stationary phase) and hence takes longer time to elute. For a clean separation between two elements, a large difference in their respective K<sub>d</sub> values is required.

The cation-exchange resins retain positively charged cations because the stationary phase is a negatively charged ion and neutrally charged ions are passed out. The resin cross linkage determines the bead pore size. A lower cross-linked resin (X4) has a more open structure permeable to higher molecular weight substances compared to a highly cross-linked resin (X12). The flow rate in a chromatographic column increases with increasing particle size. Particle size is given either in mesh size or micron size. The resin with larger mesh size number has a smaller particle size. Fine mesh material (200-400) is used for high-resolution analytical separations.

# **3.2.3** Simultaneous chromatographic purification of Si and Mg from a single aliquot of rock sample

Si and Mg are one of the most abundant elements in the entire solar system and are found to be coexisting in a number of naturally occurring minerals such as forsterite  $(Mg_2SiO_4)$  and enstatite  $(MgSiO_3)$ . They are characterized by a moderately refractory nature ( $T_{c(Mg2SiO4)} = 1430^{\circ}C$ ) and have similar condensation temperature (50%) Condensation temperature of Si and Mg are 1311 and 1340 K respectively at 10<sup>-4</sup> atm), Lattimer et al. (1978); Schiller et al. (2010). These minerals are not only abundant in our solar system but also observed in other protoplanetary disks and circumstellar environments. Since such silicates undergo significant processing in planetary disk; so simultaneous study of stable isotopic composition of Si and Mg in primitive meteorites can provide better insight into the processes of planetary disk evolution and planet formation. Although a number of studies concerning high temperature Si and Mg isotope fractionation have already been carried out individually in different laboratories but till now a combined study of these two-isotope systematics is lacking in literature. In this thesis work, we have developed a chemical protocol for simultaneous and quantitative extraction of purified Si and Mg from a single aliquot of natural sample using cation exchange resin (BioRad AG 50W-X8, 200-400 mesh) in  $H^+$  form.

Si purification was achieved using 1.8 ml BioRad cation exchange resin AG 50W-X8 (200–400 mesh) in  $H^+$  form following a protol modified after Georg *et al.* (2006). The resin was precleaned by rinsing it several times with HCl, HNO<sub>3</sub> and MQ water. Resin

storage was always done in mild HCl to prevent bacterial growth. Briefly, samples containing  $\sim 5\mu g$  of Mg and  $\sim 8\mu g$  of Si were loaded on the resin for chemical purification. Prior to loading of sample on the resin, it was ensured that the eluting water had neutral pH. The prevailing Si species after fusion and at low pH, exists in non-ionic or anionic forms (Si(OH)<sub>4</sub> or H<sub>3</sub>SiO<sup>-</sup><sub>4</sub>) and Si becomes exchangeable with cation resin (Georg *et al.*, 2006). Hence Si is not retained by the cation exchange resin and is eluted using 12 ml of Milli-Q water (pH neutral, 18.2 MΩ). After purification, the samples were evaporated and acidified with 0.05N HCl for MC-ICPMS measurement. After separation of Si, all the ambient cationic species are effectively retained by the cation exchange resin. A novel procedure has been established for the quantitive purification of Mg from these cations which is detailed in the subsequent paragraph.

In order to extract Mg despite of the Na-overload from NaOH fusion procedure, 70-80 ml of 0.3 M HNO<sub>3</sub> was used to remove all Na. Mg along with other major cations were eluted using 16 ml of 3M HNO<sub>3</sub>. The Mg cut from this above-mentioned step was semi dried and re-dissolved in 0.5mL of 2M HNO<sub>3</sub>. A second step for Mg clean up was carried out using 2 mL of Bio-Rad AG 50W-X8 (200-400 mesh) resin in H<sup>+</sup> form. Following An *et al.* (2014); 8 ml 2N HNO<sub>3</sub> + 0.5N HF was used in the first stage to shift Ti, K, Ca, Al, Rb, V, Na and Fe peaks away from the Mg peak. Pure Mg was collected using 14 ml 1M HNO<sub>3</sub> that represented nearly 100% yield. To check the efficiency of separation, we collected solutions before and after the Mg cut and measured Mg content, which was found to be negligible. After the final step, Mg solution was partially evaporated and fluxed for 12 hours at  $110^{\circ}$ C in 3% HNO<sub>3</sub> for MC-ICPMS measurement. The whole chemical purification procedure is outlined in Table 3.2.

Eluent	Vol (ml)	Comments
Step 1: Si purification <sup>a</sup>		
3N HCl, 6N HCl, 7N HNO <sub>3</sub>	30	Preconditioning (three times)
Mili-Q	18	Conditioning until pH becomes neutral
Load sample in 2 pH acidic medium	0.5	Purified Si is eluted out and other cations
Mili-Q (Si elution)	12	are retained in resin
Mili-Q	1	After-cut collection
Step 2: Na clean-up <sup>a</sup>		
0.3N HNO3	70	Elute Na
Step 3: Cation elution <sup>a</sup>		
3N HNO <sub>3</sub>	16	Mg + other cations are eluted out
Step 4: HFSE clean-up <sup>b</sup>		
2NHNO <sub>3</sub>	25	Conditioning
2NHNO <sub>3</sub> +0.5N HF	10	Pre conditioning
Sample loading in 2NHNO <sub>3</sub>	0.5	
2NHNO <sub>3</sub> +0.5N HF	8	Elute Al, Ti, Fe, Na, Li, K, Ca, Rb, V
Step 5: Mg elution <sup>b</sup>		
1N HNO <sub>3</sub>	14	Collect Mg
1N HNO3	1	After-cut collection to check for any Mg loss

<sup>*a*</sup>1.8 ml Biorad AG50W-X8 200-400 mesh resin. <sup>*b*</sup>2ml Biorad AG50W-X8 200-400 mesh resin. New columns and fresh pre-cleaned resins were used in all steps. Precleaning was rigorously done using diluted HNO<sub>3</sub> - HCl and MQ before loading onto column.

All chemical procedures were carried out in a class 10000 metal free clean laboratory equipped with class 100 laminar flow exhaust hood and clean benches. High-efficiency

particulate air (HEPA) filters are used to provide the necessary clean room conditions and laminar flow hoods operating at positive pressure are kept in constant operation to minimize sample contamination. Ultrapure acids were prepared through double distillation of GR grade reagent using Savillex DST 1000. Acid dilution was performed with 18.2 M $\Omega$  Milli-Q water (from Millipore Element System) throughout all chemical procedure.

#### **3.2.4 Measurement of Si concentration using ICP-AES**

The working of ICP-atomic emission spectroscopy is based on the excitation of outer electron of a ground-state atom to produce wavelength-specific photons of light. Inductively coupled plasma excites the atoms and ions, which inturn emit electromagnetic radiation at wavelengths characteristic of the electron configuration of a particular element. The intensity of such atomic emission is proportional to the concentration of the elements present in the sample (Fassel and Kniseley, 1974; Fassel, 1978; Ebdon, 1982; Thompson, 1983). In case of Si concentration measurement, the blank level was measured in MQ and a blank of alkaline fused solution. Instrument was calibrated using pure Si and multi-element solutions (0.1, 0.5, 1, 5 and 10 ppm) from Merck.

Two sets of Si concentration measurements were carried out by inductively coupled plasma atomic emission spectrometry (ICP-AES, Jobin-Yvon, Ultima) to determine the yield and purity of Si: First, after the fusion step and second after the chromatographic Si purification procedure. Yield of Silicon after the alkali fusion stage was found to be  $99.5\pm 2.4\%$  (1 SD) and yield of Si after the 1<sup>st</sup> column procedure was found to be  $\sim 99.1 \pm 2.1\%$  (1SD).

# 3.2.5 Calibration of Mg elution profile using Quadrupole ICPMS

Because isotopes of lighter elements can be dramatically fractionated during ion exchange chromatography, the yield of the concerned element through the purification procedure must be close to 100% (An *et al.*, 2014). In order to avoid analytically induced isotope fractionation due to matrix effect, the final Si and Mg fraction eluted after column chromatography was checked for purity on Thermo X- series ICP-MS. Presence of any interfering cations and trace metals (Na, Al, K, Ca, Ti, Fe, Mn, Cr, Ti, and Ni) in the purified solution was found to be negligible. An adequate recovery of Mg (> 99 wt%) in processed sample solutions was obtained. Determination of elemental concentration with synthetic multi-elemental solutions, (ii) Accuracy check using BHVO-2, and (iii) Sample analyses, each separated by rinse with 0.3N HNO<sub>3</sub> for 50 seconds.

The Si and Mg elution curves were carefully calibrated using different samples such as Si ICP-AES standard solution, Merck Mg standard solution, Merck multi-element solution (23 elements solution doped with silicon), BHVO-2 and BCR-2. All were found to have similar elution peaks, which indicates that difference in matrices is not causing any significant elution curve drifting. The elution curve for calibrating the protocol of simultaneous purification of Si and Mg from a single aliquot of rock sample is demonstrated in Fig. 3.4. It was critically noticed that overloading the cation exchange column with sample and a slight variation in the strength of acid causes significant drift in the elution position of Mg cut.



**Figure 3.4:** Elution curve showing simultaneous purification of Si and Mg using different reagents. a. First column step for purification of Si using MQ followed by extraction of all major cations using 3N HNO<sub>3</sub>. The break in elution volume from 12 to 80 ml represents extraction of Na using 0.3N HNO<sub>3</sub>. b. Second column step for purification of Mg using 14 ml 1N HNO<sub>3</sub>. Cation exchange resin BioRad AG 50W-X8, 200–400 mesh in H<sup>+</sup> form has been used throughout the study.

### 3.3 Multi-Collector Inductively Coupled Plasma Mass Spectrometer

Despite of high abundance, natural isotopic fractionation of Si and Mg is very limited in terrestrial realm. Gas-source mass spectrometry (GS-MS) and Thermal Ionization Mass Spectrometers (TIMS) were insufficiently precise (up to  $\pm 0.6\%$  for  $\delta^{30}$ Si and ~1‰ for  $\delta^{26}$ Mg) (Douthitt, 1982; Young and Galy, 2004) to resolve such a small isotopic fractionation among natural samples. The increase in analytical precision and sensitivity with the advent of multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS) and establishment of novel digestion techniques have allowed the routine measurement of non-traditional isotopes by resolving very limited isotopic fractionations (sub permil level precision) among different geological reservoirs. The Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) consists of a sample-introduction system, an ICP ion source, an interface region, the mass analyzer and the detection unit. A detailed description of the principals and operation of MC-ICPMS can be found in Thompson, (1983); Halliday *et al.* (1995); Taylor, (2001); Rehkämper *et al.* (2001); Albarede *et al.* (2004b); Simon and Beauchemin, (2005); Thomas, (2013), Olesik, (2014) and a brief working principal of MC-ICPMS is given below.

#### The sample-introduction system:

The main function of introduction system is to convert the sample liquid into aerosol with small and homogeneous size distribution. This is done to ensure that complete atomization and ionization of the sample occurs in the plasma discharge. A nebulizer disintegrates the liquid into aerosol by applying mechanical forces to the gas flow. The aerosols are directed into the spray chamber, which separates the larger droplets from finer droplets.

The larger droplets are drained out whereas the finer aerosol eventually enters into the plasma via sample injector of the plasma torch. As it travels through the different heating zones of the plasma torch, the liquid aerosol undergoes atomization followed by ionization (production of positively charged ions).

#### The ICP ion source:

In MC-ICP-MS, argon plasma operating at high temperatures of ~10,000 K is used as an ionization source. The high ionizing efficiency of argon leads to the ionization of most of the elements in the periodic table having ionization potential lesser than that of argon (15.76 eV). The demountable plasma torch consists of three concentric quartz tubes: the outer, middle and the inner tube for sample injector. Argon gas, which is used to feed the plasma, passes between the outer and middle tube with a flow rate of ~ 12-17 l/min. Another flow of Ar (~1 l/min) gas called the auxiliary gas, flows between the middle and the sample injector and controls the position of the plasma within the torch. The sample aerosol is carried from the sample introduction system into the plasma by nebulizer gas, flowing at ~1 L/min. The torch is mounted horizontally with the end inside a RF coil. In this copper based induction coil, a RF signal generator delivers a 1200 W, high frequency (MHz) radio field and thus induces an intense electromagnetic field. A high voltage ignition spark is applied to the argon gas, which causes some electrons to be stripped off from argon atoms. These electrons are then passed through a strong magnetic field, where mutual collisions between electrons with other ground state argon atoms strips off more electrons causing ionization of Ar. This collision-induced ionization of the argon gas initiates a cascade reaction and finally forms inductively coupled plasma discharge.

#### The interface region:

The interface region transports the ions efficiently from the atmospheric pressure of plasma (760 Torr) to the high vacuum region of mass analyzer (10<sup>-6</sup> Torr) through a series of vacuum chambers held at successively lower pressures. The interface consists of two metallic cones, usually made of nickel - the sampler and skimmer cone. After the generation of ions, they first pass through the sampler cone having an orifice diameter of 0.8–1.2 mm. From sampler cone, the ions are directed towards a sharper cone called the skimmer cone, which has a much smaller orifice (0.4–0.8 mm i.d.). A vacuum of  $\sim 2$  Torr is maintained in the region between two cones with a high-speed booster pump. Due to the drop in pressure, a supersonic jet expansion of the plasma is created into the interface region that causes only  $\sim 1\%$  of the ions to arrive at the mass analyzer. A variable high voltage (10 kV) is applied to accelerate the positive ions in the neutral plasma towards the analyzer. A series of electrostatic lenses and apertures are placed in the path of the positive ion beam to steer, focus and reshape the ion beam to optimize maximal transmission before they enter the mass analyzer. A differential pumping system, comprising mechanical and turbo molecular pumps are used to reduce the pressure gradually from atmospheric pressure to analyzer pressure (>  $5 \times 10^{-1}$ <sup>9</sup> mbar).

#### The mass analyzer:

Ions of the same element emerge from the plasma with a range of kinetic energies due to their different excited states produced in high-energy environment. These ions acquire further kinetic energy as they are accelerated towards the magnetic sector, with potentials up to 10 kV. This results in a broad distribution of kinetic energy, due to which the ions might follow different trajectories despite of having same mass to

charge ratios. To avoid this, all ion beams arriving at the mass analyzer are filtered to narrow range of kinetic energy by electrostatic analyzer (ESA).

The ions are separated based on mass within the magnetic field by a fast scanning laminated magnet, where the adjacent isotopes are deflected by Lorentz force. Since the ions with lower masses are deflected more than the heavier ions, so ions get separated according to their mass to charge (m/e) ratio. Thermo Neptune MC-ICPMS, where all the isotopic measurement for this research work were performed, is a double focusing magnetic sector mass spectrometer where ions are first sorted by their velocity distribution (with an ESA) and then by their momentum distribution (with magnetic sector).

#### The detection unit:

The separated ion beams emerging from the magnetic sector are passed through a set of zoom lens to focus the beams onto the detector array. Thermo Neptune MC-ICPMS at PRL consists of nine Faraday cups, one axial secondary electron multiplier and a stack of five ion counters that record the number of ions emerging from the mass analyzer by converting the ions into electrical pulses. The intensity of ion beams generated by ICP-sources provides a direct measure of the analyte concentration. Because of simultaneous collection of ions by different detectors, the effect of plasma fluctuation on isotope ratios gets cancelled and therefore MC-ICPMS provides very precise isotopic ratio measurements.

#### 3.4 Mass spectrometric analyses of silicon isotopes

Silicon isotopic composition of seven international standard reference rock powders obtained from the United States Geological Survey (USGS) were analyzed in this study for accuracy check of our mass spectrometric measurements: BHVO-2 (Basalt, Hawaii), SCO-1 (Cody Shale, Wyoming), SDO-1 (Devonian Ohio Shale, Kentucky), BCR-2 (Columbia River Basalt), GSP-2 (Granodiorite, Colorado), DTS-2b (Dunite, Twin Sisters, Washington), AGV-2 (Andesite, Oregon). In addition Diatomite was used for accuracy check in Si isotopic analyses respectively. SiO<sub>2</sub> content of these rock

standards ranges from 66.6 wt% (GSP-2) to 39.4 wt% (DTS-2b). The international silica standard NBS-28 was used as the 'zero-point' reference material for Si isotopic measurement (Georg *et al.*, 2006).

The advent of MC-ICPMS has allowed routine measurement of many non-traditional stable isotope systems like Si, Mg, Cr, Fe, Zn etc. The excellent accuracy and higher precision achieved in MC-ICPMS can resolve very small isotopic differences that take place in high temperature systems. However, the accuracy and precision of MC-ICPMS are severely hindered by occurrence of interferences from plasma derived isobaric molecular species. To get rid of these interferences all isotope analyses was carried out using Apex-Q, from Elemental Scientific Inc., U.S.A attached with Nafion micro porous membrane. The dry plasma condition achieved through the above mentioned setup reduces the isobaric effects of interfering molecular species by minimizing introduction of H<sub>2</sub>O, CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> into the plasma. The liquid sample was aspirated via a 100µl/min PFA MicroFlow nebulizer into a heated cyclonic spray chamber. The instrumental operating conditions are briefed in Table 3.3.

Prior to each sets of measurements, baseline calibration (in defocussed mode) and gain calibration were routinely run to calibrate the detectors. The instrument was stabilized for 2–3 hours before initiation of sample analysis. Intensities of all the three isotopes of Si were measured simultaneously in static mode with Faraday collectors attached with  $10^{11} \Omega$  amplifiers. Mass 28 was collected by Faraday cup L3, mass 29 by the axial cup and mass 30 by H3 cup. We have noticed frequent occurrence of mass offset while carrying out peak centering on different analytical session. This is likely to be dependent on the nature of most prominent interference, which were quite variable in different sessions. So, peak centering was performed on <sup>29</sup>Si only at the beginning of an analytical session. Mass scanning was routinely done to determine the exact mass position on the interference free plateau where analyses were to be carried out. Typical sensitivity of <sup>28</sup>Si on a solution with concentration of 1 ppm Si was ~5 V with a background signal of lower than 180 mV when a Ni sampler cone and Skimmer X-cone was used. No detectable change in Si background signal was noticed while using either sapphire or quatrz injectors with semi-demountable glass torch.

**Table 3.3:** Instrumental operating parameters for high precision Si and Mg isotopeanalyses using MC-ICPMS (Sikdar and Rai, 2017).

Instrument parameters	Running conditions
RF Power	1200 W
Extraction voltage	-2000V
Acceleration voltage	10 kV
Plasma mode	Dry plasma
Introducing system	ESI Apex-Q attached with Nafion Spiro
Cooling Ar gas flow rate	15-16 l.min <sup>-1</sup>
Auxiliary Ar gas flow rate	0.9 1 min <sup>-1</sup>
Sample gas flow rate	0.8-0.9 l min <sup>-1</sup> for Si and 0.7-0.8 l min <sup>-1</sup> for Mg
Nebulizer type	100 μl min <sup>-1</sup> PFA micro-concentric nebulizer (ESI)
Running concentration	Si=1 µg/ml, Mg=250ng/ml
Sensitivity	$^{28}$ Si = ~4-5 V/ppm (HR)
	<sup>24</sup> Mg=~10 V/250 ppb (HR)
Backgrounds on diluted HCl/HNO <sub>3</sub> blank solution	$^{28}\text{Si} = \sim 180 \text{ mV}, ^{24}\text{Mg} = \sim 50 \text{mV}$
Washout time	3 minutes for Si, 80 seconds for Mg
Solution uptake time	80 seconds
Cup configuration	L3( <sup>28</sup> Si), Ax( <sup>29</sup> Si), H3( <sup>30</sup> Si)
	H3( <sup>24</sup> Mg), Ax( <sup>25</sup> Mg), H2( <sup>26</sup> Mg), H4( <sup>27</sup> Al)
Analyzer vacuum	$6-8 \times 10^{-9}$ mbar
ESA vacuum	$1-4 \times 10^{-7}$ mbar
Cones	Ni X-skimmer cone, Ni sampler cone for Si
	Ni H-skimmer cone, Jet sampler cone for Mg

#### 3.4.1 Sample Introduction system

For high precision stable isotope analyses, the performance of two introduction systems was evaluated in this study, namely the ESI Apex-Q attached with Nafion micro porous membrane spiro and the Aridus II desolvating nebulizer (dry plasma). While operating Aridus II, significant reduction in signal intensity was seen over a period of 3 hours, which severely affected the accuracy and precision of our measurement. To overcome this problem, frequent adjustments of sweep gas settings (Ar and N<sub>2</sub>) were required. Therefore, we stopped using Aridus II for our analyses and carried out isotopic measurements with Apex-Q attached to Nafion, which provides dry plasma and has good washout features. The Apex system was found to be quite stable during an entire analytical session (Fig. 3.5) and adjustment of tuning parameter was not required for  $\sim$ 20 hours of continuous measurement.

The sensitivity of the instrument while introducing samples through Aridus II was typically 30V/ppm for Si and 20V/100ppb for Mg. Compared to Aridus II sample introduction system, the sensitivity with Apex Q was found to be quite low which is its major disadvantage. While using Apex desolvation unit, a combination of Ni sampler cone and skimmer X-cone provided sensitivity of 4-5 V/ppm for <sup>28</sup>Si in HR mode.



**Figure 3.5:** Temporal evolution of <sup>30</sup>Si/<sup>28</sup>Si ratios during an analytical session of 20 hours while using Apex Q introduction system. Field circles represent the Si isotope ratios of standard.

### **3.4.2 Determination of shoulder peak plateau in pseudo highresolution (HR) mode for Si isotopic analyses**

The high ionization efficiency of the ICP source has the potential to ionize almost every element introduced in the plasma, which eventually leads to the formation of molecular interferences. To get rid of interference on Si isotopes, the instrument was operated at pseudo high-resolution mode with mass resolving power of ~8000 (m/ $\Delta$ m as defined by the peak edge width from 5–95% full peak height, Schiller *et al.*, 2016). This eliminated potential molecular interferences from <sup>14</sup>N<sub>2</sub> and <sup>12</sup>C<sup>16</sup>O for m/z = 28; <sup>14</sup>N<sub>2</sub><sup>1</sup>H, <sup>12</sup>C<sup>1</sup>H<sup>16</sup>O, <sup>14</sup>N<sup>15</sup>N and <sup>12</sup>C<sup>17</sup>O for m/z = 29; <sup>14</sup>N<sup>16</sup>O and <sup>12</sup>C<sup>18</sup>O for m/z=30. Interference from <sup>14</sup>N<sup>16</sup>O at mass 29.99799 amu is the most prominent, which significantly overlies the <sup>30</sup>Si peak at mass 29.97377 amu, Fig. 3.6 (Cardinal *et. al.*, 2003; Shahar *et al.*, 2007).

Since  ${}^{14}N_2$  and  ${}^{14}N^{16}O$  are slightly heavier than  ${}^{28}Si$  and  ${}^{30}Si$ , so performing the isotopic measurement on the left side of the Si peak shoulder allows only the analyte beam to enter into faraday cup and thus strips off any interfering beam (Abraham *et al.*, 2008). Achieving an interference free flat peak shoulder and the determination of exact mass position where isotopic analyses is to be carried out in high-resolution mode is extremely crucial for precise Si isotope analyses.



Figure 3.6: A typical mass spectrum of Si isotopes along with their most dominant interfering molecules.

Prior to each analytical session, we measured <sup>29</sup>Si/<sup>28</sup>Si and <sup>30</sup>Si/<sup>28</sup>Si ratios across different mass positions on the low-mass side of the Si peak to determine the exact mass position where possibility of detecting interferences was negligible. Based on this test, an ideal mass position was set up where measurements were carried out in an analytical session. The data are plotted in Fig. 3.7. It was noticed that  $\delta^{30}$ Si and  $\delta^{29}$ Si become erroneous and fluctuation in signal intensity causes uncertainty to increase as mass position approaches interfering peaks. Acquisition of Si isotope data was typically done at 0.005-0.007 amu from the initiation of Si peak, which is located at the left hand side of the center of Si shoulder peak plateau (Sikdar and Rai, 2017).



**Figure 3.7:** a) A typical profile of shoulder mass of Si peak. The hatched region demonstrates the mass range where the most accurate and precise Si isotopic value was achieved. b)  $\delta^{29}$ Si at different shoulder mass relative to the composition at mass 28.925 amu (center of hatched region). c)  $\delta^{30}$ Si at different shoulder mass relative to the composition at mass 28.925 amu. Most of the measurements were carried out at 28.925 amu.

# **3.4.3 Instrumental mass bias correction by standard-sample bracketing protocol**

Mass bias is described as mass fractionation that occurs within the mass spectrometer, which severely affects the precision and accuracy of isotope ratio measurements (Albarède et al., 2004b). It commonly originates in the plasma interface and the transfer optics and is associated with higher transmission of heavier isotopes into the mass spectrometer compared to the lighter ones. An advantage of MC-ICPMS for stable isotope measurement over TIMS is the occurrence of constant long term instrument mass bias and this can be adequately corrected by standard sample bracketing method (Wombacher et al., 2009). In the standard sample bracketing protocol, the isotope ratios of an unknown sample is estimated by alternating standard and sample measurements (Abraham et al., 2010). The instrumental mass bias for unknown sample are obtained by linearly interpolating the mass biases from bracketing standards and blank solutions. This protocol assumes similar mass bias among sample, blank and the bracketing standards (Chakrabarti and Jacobsen, 2010b). On peak zero blanks, which bracket both sample and standard measurement, are subtracted before mass bias estimation and delta calculation are performed. Working of this protocol depends critically on intensity and matrix matching between sample and standard. Best way for matrix matching between sample and standard is to purify the solution so that both of them do not contain any elements other than the analyte of interest. Attempt has been made to match the intensity of samples and standards within five percent. Another parameter, which is critical for accurate analysis are medium of solutions e.g., 3%HNO<sub>3</sub> or 0.05N HCl. It has been observed that slight mismatch in concentration of these run solutions can cause significant offsets in results. Therefore, all the samples, bracketing standards and blanks were diluted or prepared from the same batch of ultrapure acid in this study.

The Si isotope data are reported using  $\delta$  notation wherein  $\delta^{30}$ Si is defined as the deviation of the Si isotope ratio ( ${}^{30}$ Si/ ${}^{28}$ Si) in the sample relative to NBS-28 standard in parts per thousand. For accurate and precise silicon isotopic analyses, Si concentration of the samples and their bracketting standards should be matched to within 10% to

avoid potential mass bias effects (Georg *et al.*, 2006). Same batch of 0.05N HCl was used for on peak zero blank measurements and also for diluting samples and standards. The bracketing standard for Si (NBS-28) was dissolved and chemically processed in similar way as that of the samples. Sample uptake time was set to 80s while wash time (in diluted HCl) between consecutive sample and standard measurements was 3 min. It was ensured that Si background on the mass-spectrometer was reduced to ~180 mV prior to each sets of measurement (Sikdar and Rai, 2017).

### 3.4.4 Accuracy and precision of Si isotope ratio

The Si-isotope standard, NBS-28 (Standard Reference Material from IAEA) has been used as both bracketing as well as reference standards. A large number of zeros (where sample is same as standard) have been measured at the beginning of each analytical session.  $\delta^{30}$ Si value of NBS-28 measured with respect to itself should be zero within uncertainty, as per definition. The average of 155 measurements carried out during this study are  $\delta^{30}$ Si<sub>NBS-28</sub> =0.0063±0.09‰ (2 SD) (Fig. 3.8).



No. of Analyses

**Figure 3.8:** Plot showing excellent reproducibility of Si isotope data over the course of sample analysis. Solid horizontal line represents the average of  $\delta^{30}$ Si value. NBS-28  $\delta^{30}$ Si = 0.0063 ± 0.09 ‰ (2 SD); BHVO-2  $\delta^{30}$ Si = -0.28 ± 0.08 ‰ (2 SD).

The accuracy of silicon isotope analyses was checked by repeated measurements of Diatomite (Fig. 3.9), which is a well-characterized secondary reference material for Si. The average of 71 measurements of diatomite provided  $\delta^{30}$ Si = 1.23 ± 0.09‰ and  $\delta^{29}$ Si = 0.62 ±0.07‰ (2 SD), which are consistent with the reported values of  $\delta^{30}$ Si = 1.23 ± 0.15‰ and  $\delta^{29}$ Si = 0.63 ± 0.10‰ (Fitoussi *et al.*, 2009; Zambardi *et al.*, 2010; Armytage *et al.*, 2011). The long-term external reproducibility was checked by repeated measurements of BHVO-2 (Fig. 3.8), which yielded standard deviation of 0.08‰ and 0.06‰ on  $\delta^{30}$ Si and  $\delta^{29}$ Si respectively for 79 measurements spanned over a period of 14 months. A typical analysis consisted of one block of 50-60 cycles of data acquisition with an integration time of 8.389 seconds.



**Figure 3.9:** Silicon isotopic composition of Diatomite analyzed over a period of 11 months. Each data point represents independent measurements carried out in different analytical sessions and in varied instrumental settings. The horizontal line represents the mean  $\delta^{30}$ Si value ( $\delta^{30}$ Si = 1.23 ± 0.09‰).

# **3.4.5 Inter-laboratory comparison for isotope data of terrestrial rock standards**

We assessed the accuracy and precision of our chemical purification procedure and mass spectrometric measurements by conducting repeat Si and Mg isotopic analyses of various rock standards. The replicates include independent digestion carried out for the same rock powder, repeat chemical purification procedure of the respective sample, and isotopic measurement of the purified solutions on different analytical sessions and in different instrumental settings. The isotopic values of these rock samples are in good agreement with the published isotopic values (Table 3.4), which demonstrates the achievement of high level of precision and reproducibility by our chemical and mass spectrometric technique. The isotopic values from our study and from the literature are plotted together in Fig. 3.10 for inter laboratory comparison.



**Figure 3.10:**  $\delta^{30}$ Si analyses of silicate rock standards measured in this work are plotted along with literature values. The triangles pointing upwards represent data from this work and all other colored symbols represent various literature data. Errors of data obtained from this study and literature reflect 2SD of the mean.

The plot of  $\delta^{29}$ Si versus  $\delta^{30}$ Si for all samples shows mass dependent fractionations (Fig. 3.11). This further verifies that all potential interferences on the three isotopes of Si and Mg were well resolved using high-resolution slits.



Figure 3.11:  $\delta^{29}$ Si versus  $\delta^{30}$ Si plot of silicon showing mass dependent fractionation of all isotopes.

**Table 3.4:** Si isotopic composition of reference materials determined in this study and its corresponding values as obtained from published data. Number (N) refers to repeat analysis of the same rock sample.

	<b>δ</b> <sup>29</sup> Si (‰)	2 SD	<b>δ</b> <sup>30</sup> Si (‰)	2 SD	N
NBS-28 (ZERO)					
This study	0.002	0.08	0.006	0.09	155
Diatomite					
This study	0.62	0.07	1.23	0.09	71
Savage et al., 2011	0.64	0.08	1.23	0.10	177
Armytage et al., 2011	0.63	0.10	1.23	0.15	100
Fitoussi et al., 2009	0.64	0.01	1.24	0.02	89
	1		1		

BHVO-2					
DII VO-2					
This study	-0.15	0.06	-0.28	0.08	79
Dauphas et al., 2015	-0.13	0.04	-0.26	0.05	9
Armytage et al., 2011	-0.15	0.08	-0.28	0.14	223
Zambardi et al., 2010	-0.11	0.03	-0.21	0.05	42
BCR-2					
This study	-0.13	0.06	-0.21	0.10	15
Zambardi et al., 2013	-0.11	0.03	-0.19	0.03	6
GSP-2					
This study	-0.14	0.06	-0.23	0.07	14
Savage et al., 2012	-0.10	0.07	-0.20	0.11	44
SCo-1					
This study	-0.16	0.06	-0.27	0.09	38
Savage et al., 2011	-0.17	0.04	-0.28	0.03	11
SDO-1					
This study	-0.13	0.07	-0.23	0.09	16
Savage et al., 2011	-0.10	0.07	-0.24	0.04	11
DTS-2b					
This study	-0.14	0.05	-0.26	0.09	23
Zambardi et al., 2013	-0.10	0.04	-0.23	0.05	6
AGV-2					
This study	-0.10	0.05	-0.21	0.05	8
Savage <i>et al.</i> , 2011	-0.10	0.03	-0.21	0.07	11

### 3.5 Mass spectrometric analyses of magnesium isotopes

High precision Mg isotopic measurements were carried out in the same aliquot of USGS rock standards where Si isotopic analyses were performed following the

chemical purification protocol described above. The magnesium isotopic composition of seven international standard reference rock powders that were analyzed in this study are: BHVO-2, SCO-1, SDO-1, BCR-2, GSP-2, DTS-2b, AGV-2; all obtained from the United States Geological Survey (USGS). In addition, SRM-980 was used for accuracy check in Mg isotopic analyses. MgO content of these rock standards ranges from 49.4 wt% (DTS-2b) to 0.96 wt% (GSP-2).

In the case of Mg, the peak was always flat and no interference was visibly apparent indicating absence of significant interference for Mg isotopes. However, we found that conducting Mg isotopic measurements on center of the peak or at low resolution always gave erroneous values with relatively large uncertainty. Thus we have performed all Mg isotopic analysis in high-resolution mode and at left side of Mg mass spectrum to resolve potential molecular interferences (e.g.  $C_2^+$ ,  $C_2H^+$ ,  $C_2H_2$ ,  $CN^+$  and NaH<sup>+</sup>) on different Mg isotopes. The analysis mass position is shown in Fig. 3.12 of Mg isotope spectrum.



**Figure 3.12:** Mass scan during a typical Mg isotopic measurement session. Solid vertical line represents the mass position where analysis was carried out.

With a nebulizer uptake rate of 100  $\mu$ l/min and usage of jet sampler and H skimmer cones, a 250 ppb solution typically produced sensitivity of 10V for <sup>24</sup>Mg in highresolution mode. The background Mg signals for <sup>24</sup>Mg (<20 mV) were negligible relative to the sample signals (10V). Cross-contamination between samples was eliminated by washing the probe for 80 seconds between each measurement until the <sup>24</sup>Mg signal became less than 20 mV. The three isotopes of magnesium (<sup>24</sup>Mg, <sup>25</sup>Mg, <sup>26</sup>Mg) and <sup>27</sup>Al were measured simultaneously using four Faraday collectors (L3, axial, H4 and H6 cups respectively) connected to amplifiers with 10<sup>11</sup>  $\Omega$  feedback resistors. <sup>27</sup>Al was measured to verify the absence of Al in the Mg fraction.

To report the variation in Mg isotopic composition among USGS rock standards, international standard reference material DSM-3 (manufactured by Dead Sea Mg Ltd., Israel) has been used as a zero delta reference material. Mg isotope data are reported as  $\delta^{25}$ Mg and  $\delta^{26}$ Mg (‰) relative to the DSM-3 following the Eqn. 3.1, where x=25 or 26.

Instrumental mass bias was corrected by standard-sample bracketing wherein each sample was bracketed by two measurements of DSM-3 and two blank measurements (Galy *et al.*, 2003).

#### 3.5.1 Accuracy and precision of Mg isotope ratios

The in-run precision of  ${}^{25}\text{Mg}/{}^{24}\text{Mg}$  and  ${}^{26}\text{Mg}/{}^{24}\text{Mg}$  ratio of one block measurement of 50 cycles is typically lesser than 15 and 20 ppm (1 SE) respectively. The external precision of  $\delta^{25}\text{Mg}$  is  $\pm 0.04\%$  and  $\pm 0.08\%$  for  $\delta^{26}\text{Mg}$  in the case of BHVO-2 (n=44, Fig. 3.13).

The accuracy of the Mg isotope analyses was assessed using SRM-980, which is a highly pure Mg metal prepared and distributed by the National Institute of Standards and Technology (Gaithersburg, USA). The metal was dissolved in ~1M HNO<sub>3</sub> at room

temperature. After complete dissolution, the solution was diluted using 3% HNO<sub>3</sub> to make final stock solution of 50 ppm Mg. The average of 47 measurements of SRM-980 provided  $\delta^{26}Mg = -3.96 \pm 0.08\%$  and  $\delta^{25}Mg = -2.01 \pm 0.07\%$ , 2 SD.



**Figure 3.13:** Plot showing the reproducibility of Mg isotopic measurements over the course of analysis. Solid line represents the average of all measurements. Zero measurement using DSM-3 provide  $\delta^{26}Mg = 0.03 \pm 0.06 \%$  (2 SD, n=80); the average of BHVO-2 measurement is  $\delta^{26}Mg = -0.256 \pm 0.08 \%$  (2 SD, n=44).

The Mg isotope composition of all silicate reference samples analyzed in this study was found to range from  $\delta^{26}Mg = -0.12$  to -0.87%. All Mg isotopic data are provided in Table 3.5 and plotted in Fig. 3.14 for inter-laboratory comparison. For most of the samples, Mg isotopic values are consistent with the previously reported values (Young and Galy, 2004; Tipper *et al.*, 2008; Teng *et al.*, 2007; Wiechert and Halliday, 2007). However, there occurs inconsistency in the published Mg isotopic compositions of some widely studied rock standards such as SCo-1 and BCR-2 that has been measured in different international laboratories. The lack of enough Mg isotope data for commonly available geological reference materials hinders direct inter-laboratory comparison of Mg isotopic composition to examine accuracy of measurement. More measurements of international reference materials are required for Mg isotopic composition in different international laboratories to establish an accurate isotopic value of these rock standards.



**Figure 3.14:**  $\delta^{26}$ Mg analyses of silicate rock standards for inter-laboratory comparison. The triangles represent the data from this work and colored circles represent various literature data. Errors of data from the literature and this study reflect  $2\sigma$  of the mean.



**Figure 3.15:** Magnesium three-isotope plot of  $\delta^{25}$ Mg versus  $\delta^{26}$ Mg showing data from all samples analyzed in this study. Error bars are 2SE of mean

The two standard deviation precision for measurements of the rock standards carried out in this study varies from 0.05‰ to 0.11‰ with an average of ~0.08‰, representing excellent long-term external precision for Mg. Mass dependent fractionation trend is seen in 3-isotope plot of  $\delta^{25}$ Mg versus  $\delta^{26}$ Mg (Fig. 3.15).

**Table 3.5:** Mg isotopic composition of reference materials determined in this study and its corresponding literature values. Number (n) refers to repeat analysis of the same sample

	$\delta^{25}$ Mg (‰)	2 SD	$\delta^{26}$ Mg (‰)	2 SD	n
DSM-3 (ZERO)					
This study	0.002	0.08	0.03	0.06	80
Bourdon et al., 2010	0.003	0.033	0.001	0.047	90
Galy et al., 2003	0.01	0.07	0.02	0.12	31
BHVO-2					
This study	-0.14	0.04	-0.26	0.08	44
An <i>et al.</i> , 2014	-0.10	0.03	-0.22	0.035	14
Huang et al., 2009	-0.14	0.06	-0.30	0.08	4
BCR-2					
This study	-0.10	0.07	-0.21	0.10	14
An et al., 2014	-0.08	0.02	-0.16	0.01	35
Teng et al., 2007	-0.16	0.09	-0.30	0.08	28
Bizzarro et al., 2011	-0.09	0.17	-0.17	0.35	7
Huang <i>et al.</i> , 2009	-0.15	0.07	-0.30	0.11	18
SCo-1					
This study	-0.42	0.04	-0.87	0.09	4
Teng et al., 2016	-0.47	0.05	-0.89	0.077	3
Li <i>et al.</i> , 2010	-0.50	0.06	-0.94	0.08	

GSP-2					
This study	-0.05	0.03	-0.12	0.05	15
An <i>et al.</i> , 2014	0.03	0.01	0.04	0.02	15
Huang et al., 2009	-0.03	0.13	-0.07	0.2	16
SRM- 980					
This study	-2.01	0.07	-3.96	0.08	47
Galy et al., 2003	-1.74	0.07	-3.40	0.13	10
Bolou-Bi et al., 2009	-2.04	0.05	-3.98	0.05	20
DTS-2b					
This study	-0.13	0.04	-0.27	0.10	29
An et al., 2014 (DTS-1)	-0.15	0.003	-0.28	0.04	10
Teng et al., 2014	-0.17	0.04	-0.32	0.06	10
Huang et al., 2009	-0.13	0.02	-0.30	0.16	10
AGV-2					
This study	-0.11	0.07	-0.24	0.09	8
Huang <i>et al.</i> , 2009	-0.16	0.05	-0.32	0.08	16
	1				

The excellent long-term reproducibility of 0.09‰ (2 SD) for  $\delta^{30}$ Si and 0.08‰ (2 SD) for  $\delta^{26}$ Mg allows us to resolve limited isotopic fractionation that occurs at high temperature processes (Sikdar and Rai, 2017). This multi proxy approach can provide important information for a variety of fundamental cosmo- and geo- chemical processes. It will be noteworthy to investigate combined high precision Mg and Si isotope data in extra-terrestrial samples to identify the process that led to Mg/Si variation among various planetary bodies and any isotopic fractionation that might have occurred during early stages of nebular evolution and planetary accretion.

Several meteorite samples and their phase separates have been analyzed using the new alkali digestion technique and chromatographic purification protocol of Si and Mg as detailed in this chapter, the results of which are discussed in subsequent chapters.

# **CHAPTER 4**

## SILICON AND MAGNESIUM ISOTOPES IN BULK METEORITES

As summarized in earlier chapters, it is evident that Si isotopes have become a very popular tool to trace various processes of geological interests such as silicate weathering, water-rock interactions, global biogeochemical cycles, estimation of bulk Earth composition, magma differentiation and core formation (Douthitt et al., 1982; De La Rocha et al., 1997, 1998, 2000a, 2003, 2005, 2006; Ding et al., 1996; Singh et al., 2015, Ziegler et al., 2005a, 2005b, 2010; Georg et al., 2007; Armytage et al., 2011; Fitoussi et al., 2009; Fitoussi and Bourson, 2012; Savage et al., 2010, 2011, 2012, 2014; Savage and Moynier, 2013; Dauphas et al., 2015). Mg isotopes have also been used to address similar types of issues such as differentiation of magma by fractional crystallization (Teng et al., 2007; Liu et al., 2010); the origin of planets, moon, chondrites, chondrules (Wiechert and Halliday, 2007; Bourdon et al., 2010; Teng et al., 2010) and understanding Mg geochemical cycling (Galy et al., 2002; Tipper et al., 2006, b, c; Huang et al., 2009). In addition to stable isotopic application of Mg isotopes, the <sup>26</sup>Al-<sup>26</sup>Mg systematics is widely used to constrain the timing of grain condensation and asteroidal magmatism in early solar nebula (Russell et al., 1996; Bizzarro et al., 2004, 2005; Jacobsen et al., 2008; Schiller et al., 2010; Krot et *al.*, 2012).

Si and Mg are two most abundant elements in the entire solar system and are found to be coexisting in a number of naturally occurring minerals such as forsterite (Mg<sub>2</sub>SiO<sub>4</sub>,

Olivine) and enstatite (MgSiO<sub>3</sub>, pyroxene). Si and Mg have nearly similar condensation temperatures (50% condensation temperature of Si and Mg are 1311 and 1340 K respectively at 10<sup>-4</sup> atmospheric pressures (atm), Lodders, 2003). Since Si and Mg are major elements that co-exist together in most of the minerals, investigation of Si and Mg isotopic composition in a variety of terrestrial and extra-terrestrial samples could be of fundamental importance in constraining the physico-chemical conditions that prevailed either during geochemical (melting and differentiation) or cosmochemical processings (condensation and evaporation). For example, evaporation is known to make any residual phases enriched in heavy isotopes of both Si and Mg, as evinced from the heavy Si and Mg isotopic composition of CAIs (Clayton et al., 1988; Davis et al., 1990; Grossman et al., 2000; Sugiura et al., 2004). Since the extent of Mg isotope fractionation is larger than Si during evaporation, a simultaneous study of Si and Mg isotope pattern in meteorites could be potential indicators of varied degrees of evaporation that the planetary bodies underwent. Moreover, mass dependent variations of Si and Mg isotopes in meteorites also have the potential to unravel the nature of materials from which planetesimals accreted.

To better understand the earliest stages of planet formation, we have carried out Si and Mg isotopic analyses in a wide variety of bulk meteorite samples following our newly developed chromatographic procedure; the results and implications of which are discussed in this chapter. Since the samples investigated here belong to varied groups of meteorites that are known to originate at different heliocentric distances, they will shed light on the distribution of Si and Mg isotopes in the solar system. A comparative study of our isotopic results along with the recent data from different laboratories has also been documented in this chapter.

#### 4.1 Mg/Si ratio variation in the solar system material

Being the least altered objects of the solar system, chondrites should ideally preserve Mg/Si ratio of ~1 as expected from their similar condensation temperature. However, a large variation in Mg/Si ratio among different groups of meteorites, planetary bodies (Moon and Mars) and bulk silicate Earth (BSE) has been documented, which remains

one of the longstanding debates in cosmo-chemistry (Ringwood, 1989, Palme and O'Neil, 2003; Fitoussi *et al.*, 2009, Dauphas *et al.*, 2015). The atomic Mg/Si ratio is the highest for terrestrial mantle (BSE= ~1.25, Wänke, 1981; Allègre *et al.*, 1995) and decreases in the order from carbonaceous chondrites (Mg/Si = ~1) to ordinary chondrites (Mg/Si = ~0.95). Enstatite chondrite shows the lowest Mg/Si ratio (EH = 0.73; EL = 0.88) of all planetary materials analyzed so far (Dauphas *et al.*, 2015 and references therein).

Looking at the complex evolutionary history of Earth, it is very likely that the superchondritic Mg/Si ratio of BSE (Fitoussi *et al.*, 2009; Dauphas *et al.*, 2014b) is a reflection of various events that might have operated at different stages of Earth's accretion. As a result, a number of hypotheses have been provided for explaining the superchondritic Mg/Si of bulk silicate Earth (BSE). For example, some of the popular hypothesis suggested to explain higher Mg/Si of BSE includes its origin during:

- (i) chondrule formation in the early solar nebula (Hewins and Herzberg, 1996),
- (ii) during high-energy impacts followed by erosive loss of Si (Boujibar et al., 2015),
- (iii) the preferential evaporation of SiO over MgO from magma ocean (Fegley and Schaefer, 2005) due to the relatively higher volatility of Si compared to Mg (Ringwood, 1979)
- (iv) Mg/Si of Earth's mantle is heterogeneous (Anderson, 1988).

The most promising explanation for higher Mg/Si ratio of terrestrial mantle compared to chondrites is that the missing Si resides in Earth's core, which is also supported by core's density deficit compared to Fe-Ni alloy (Ringwood, 1959; Birch, 1940, 1964).

Comparing the stable isotopic compositions of certain elements in terrestrial rock samples and primitive meteorites help in getting better insights into various planetary processes that might have operated during various stages of planet formation and subsequent evolution. The fact that BSE has heavier Si isotopic composition than any of the chondrite groups has prompted a series of studies suggesting the presence of light Si isotopes in the Earth's core (Georg *et al.*, 2007). The most common argument given for Si isotopic offset between BSE and chondrites is that if Earth accreted from

chondritic material, then equilibrium Si isotopic fractionation between silicate mantle and metallic core during differentiation has enriched the silicate reservoir of Earth in heavier isotopes of Si (Georg *et al.*, 2007; Fitoussi *et al.*, 2009; Shahar *et al.*, 2011; Armytage *et al.*, 2011; Zambardi *et al.*, 2013).

Although Si isotopes have been used extensively to understand the cause of superchondritic Mg/Si ratio of terrestrial mantle but Mg isotopes have been sparsely used to investigate the cause of it. Since some of the mechanisms proposed to fractionate Si isotopes are expected to generate Mg isotopic fractionation, a proper knowledge of isotopic fractionation pattern of both the elements can be used to test the different hypothesis proposed for the origin of Mg/Si variation among planetary bodies. To constrain the processes responsible for the variation of Mg/Si ratio and Si isotopic composition among planetary materials, we have carried out simultaneous analyses of Si and Mg isotopic composition in the same aliquot of terrestrial rock and meteorite samples (Sikdar and Rai, 2016).

#### 4.2 Samples and analytical techniques

Si isotopic analyses were carried out in five carbonaceous chondrites (three CV3, two CM2), ten ordinary chondrites (three H, six L, one LL), six enstatite meteorites (four EH3, one EL6, one aubrite) and eight HED meteorites (three Howardites, two Eucrites, three Diogenites). Whereas, Mg isotopic analyses were performed for one carbonaceous chondrite, two ordinary chondrites, two enstatite chondrites and four HED meteorites in the same aliquot of meteorite sample where Si isotopic analyses have been carried out.

Despite the high abundance, natural isotopic fractionation of Si and Mg are limited in terrestrial realm due to the four-fold coordination of Si. The limited isotopic differences expected at high temperature systems can only be resolved by the higher precision data acquisition achieved using MC-ICPMS. However, in the case of Si isotopic analyses there are some potential pitfalls, which hinders the accuracy and

precision in MC-ICPMS measurements and hence needs to be critically monitored to avoid erroneous isotopic measurements.

- (i) The first one is the occurrence of interferences from isobaric molecular species derived from reactions in the argon plasma (Abraham *et al.*, 2010). To eliminate these interferences, the Neptune MC-ICP-MS was run in pseudo high-resolution mode for both Si and Mg isotopic analyses.
- (ii) The second is the occurrence of large instrumental mass bias in plasma source mass spectrometry due to high fractionation potential of lighter elements (Millet *et al.*, 2012). Instrumental mass bias corrections were performed using standard-sample-standard bracketing technique with intensity of ion beam matching between sample and standard to <5% as per Zeigler *et al.* (2010).
- (iii) Isotopes of lighter elements get significantly fractionated during ion exchange reactions (Chang *et al.*, 2003; An *et al.*, 2014). Therefore, accurate measurement of Si and Mg isotope ratios on natural samples requires close to 100% recovery of the concerned element.

To get rid of interferences and avoid erroneous isotopic measurements, all isotopic analyses were carried out in pseudo high-resolution mode of Thermo Scientific Neptune Plus MC-ICPMS. The pseudo high-resolution mode eliminated potential molecular interferences from <sup>14</sup>N<sub>2</sub> and <sup>12</sup>C<sup>16</sup>O for m/z = 28; <sup>14</sup>N<sub>2</sub><sup>1</sup>H, <sup>12</sup>C<sup>1</sup>H<sup>16</sup>O, <sup>14</sup>N<sup>15</sup>N and <sup>12</sup>C<sup>17</sup>O for m/z = 29; <sup>12</sup>C<sup>18</sup>O and <sup>14</sup>N<sup>16</sup>O for m/z=30 (Fig, 4.1). Simultaneous collection of all three isotopes of Si by faraday cups L3, C and H3 for mass 28, 29 and 30 reduces the effect of plasma fluctuations in isotope ratio measurement. Mass bais corrections were performed using sample-standard bracketting technique with NBS-28 as the bracketting standard and 0.01N HCl as the blank solution.

The accuracy of silicon isotope analyses was assessed by repeated measurements of diatomite, which provided  $\delta^{30}$ Si = 1.23±0.09‰ and  $\delta^{29}$ Si = 0.62±0.07‰ (n=71), consistent with the measurements from literature (Fitoussi *et al.*, 2009; Armytage *et al.*, 2011; Zambardi *et al.*, 2010). The accuracy of Mg isotopes was checked using BHVO-2, which provided  $\delta^{26}$ Mg = -0.26±0.08‰ (2 SD), in agreement with the published values (Teng *et al.*, 2007; Bourdon *et al.*, 2010) (Refer to chapter 3 for more detail).



**Figure 4.1:** a) Peak center performed on mass <sup>29</sup>Si showing the lower intensity of <sup>30</sup>Si compared to <sup>14</sup>N<sup>16</sup>O interference. b) The interference free mass region has been zoomed to show the analysis mass position.

#### 4.3 Results from Si and Mg isotopic analyses in meteorites

The silicon isotopic data of 28 meteorite samples analyzed in this study are given in Table 4.1 and plotted together in Fig. 4.2. To facilitate inter-laboratory comparison of our isotopic data, the Si isotopic composition of various chondrite and achondrite groups determined in different laboratories are also provided. It can be seen that most of our isotopic data from various meteorite groups agree well with their recently published values.
**Table 4.1:** Si isotopic composition of BSE (obtained from published data) and bulk meteorites (obtained from this study and published data). The number of analyses has been referred by 'n'.

	Error			Error		
	Rock type	δ <sup>29</sup> Si (‰)	2 SD	<b>δ</b> <sup>30</sup> Si(‰)	2 SD	n
BSE						
Armytage et al., 2011		-0.15	0.05	-0.29	0.08	35
Savage et al., 2010		-0.15	0.05	-0.29	0.06	
Fitoussi <i>et al.</i> , 2009	Peridotite/	-0.14	0.04	-0.28	0.06	8
Zambardi et al., 2013	OIB	-0.13	0.03	-0.27	0.06	20
Carbonaceous Chondrite						
Y-86751	CV3	-0.19	0.04	-0.39	0.08	2
Y-74662	CM2	-0.21	0.03	-0.46	0.05	3
EET 96 029	CM2	-0.18	0.04	-0.41	0.05	2
GRA 06 101	CV3	-0.20	0.07	-0.38	0.09	2
ALH 84 028	CV3	-0.21	0.03	-0.43	0.10	2
Average		-0.20	0.03	-0.41	0.06	5
Savage et al., 2013		-0.26	0.07	-0.47	0.08	5
Zambardi et al., 2013		-0.21	0.03	-0.43	0.04	3
Armytage et al., 2011		-0.26	0.05	-0.48	0.10	8
Ordinary Chondrite						
WSG 95300	Н 3.3	-0.26	0.04	-0.45	0.06	3
ALHA 77299	Н 3.7	-0.20	0.04	-0.38	0.06	2
KASAULI	H4	-0.19	0.03	-0.39	0.04	2
Y 980448	L3	-0.19	0.03	-0.45	0.07	3
Y 981274	L3	-0.20	0.02	-0.38	0.07	2
QUE 97008	L3.0	-0.21	0.07	-0.44	0.08	2
ALHA 77216	L 3.7-3.9	-0.19	0.04	-0.46	0.10	3

JODIA	L5	-0.22	0.03	-0.47	0.06	2
ALHA 83007	LL3.2	-0.17	0.04	-0.39	0.04	2
ITAWA	L 3-5	-0.21	0.06	-0.41	0.05	2
Average		-0.20	0.05	-0.42	0.07	10
Zambardi et al., 2013		-0.22	0.04	-0.47	0.02	6
Armytage et al., 2011		-0.24	0.03	-0.46	0.06	8
Enstatite meteorites						
PCA 914 61 (EH3)	EH3	-0.31	0.09	-0.64	0.12	8
LAR 06 252 (EH3)	EH3	-0.33	0.05	-0.67	0.07	2
MIL 07 028 (EH3)	EH3	-0.34	0.03	-0.69	0.05	1
Y-961 (EH3)	EH3	-0.35	0.08	-0.71	0.11	5
ALHA 81 021 (EL6)	EL6	-0.29	0.03	-0.59	0.04	2
LAR 04 316 (Aubrite)	AUBRITE	-0.26	0.05	-0.57	0.07	2
Average		-0.31	0.07	-0.64	0.11	6
Zambardi et al., 2013	EH	-0.31	0.04	-0.61	0.07	2
Fitoussi et al., 2012		-0.31	0.09	-0.59	0.10	3
Armytage et al., 2011		-0.32	0.07	-0.63	0.07	3
HEDs						
LOHAWAT	Howardite	-0.19	0.03	-0.41	0.05	2
QUE 97001	Howardite	-0.21	0.05	-0.43	0.05	2
EET 87503	Howardite	-0.24	0.04	-0.47	0.08	2
EET 89542	Eucrite	-0.18	0.06	-0.40	0.09	3
ALHA 76005	Eucrite	-0.19	0.07	-0.43	0.12	2
SHALKA	Diogenite	-0.23	0.07	-0.41	0.10	2
SHALKA LAP 03569	Diogenite Diogenite	-0.23 -0.21	0.07 0.04	-0.41 -0.45	0.10 0.07	2 2
SHALKA LAP 03569 MIL 07 001	Diogenite Diogenite Diogenite	-0.23 -0.21 -0.17	0.07 0.04 0.07	-0.41 -0.45 -0.39	0.10 0.07 0.09	2 2 3
SHALKA LAP 03569 MIL 07 001 <b>Average</b>	Diogenite Diogenite Diogenite	-0.23 -0.21 -0.17 <b>-0.20</b>	0.07 0.04 0.07 <b>0.05</b>	-0.41 -0.45 -0.39 <b>-0.42</b>	0.10 0.07 0.09 <b>0.05</b>	2 2 3 <b>8</b>
SHALKA LAP 03569 MIL 07 001 <b>Average</b> Fitoussi <i>et al.</i> , 2009	Diogenite Diogenite Diogenite Eucrite	-0.23 -0.21 -0.17 <b>-0.20</b> -0.19	0.07 0.04 0.07 <b>0.05</b> 0.06	-0.41 -0.45 -0.39 <b>-0.42</b> -0.41	0.10 0.07 0.09 <b>0.05</b> 0.11	2 2 3 <b>8</b> 2

Zambardi et al., 2013	How, Euc	-0.19	0.04	-0.41	0.06	7
Armytage et al., 2011	HED	-0.23	0.05	-0.45	0.10	7

In agreement with most of the previous studies, it has been found that the extraterrestrial samples *i.e.*, the meteorites are considerably lighter ( $\delta^{30}$ Si = -0.47±0.20‰) than any of the terrestrial rock standards ( $\delta^{30}$ Si = -0.24±0.05‰) analyzed in this study. Considering the average  $\delta^{30}$ Si value of BSE (Bulk Silicate Earth) to be -0.29±0.08‰, 2SD (Savage *et al.*, 2010), our isotopic data clearly reveals the presence of at least 0.15‰ differences in  $\delta^{30}$ Si value between meteorites and terrestrial samples. The  $\delta^{30}$ Si for meteorites and terrestrial samples obtained in this study ranges from -0.71‰ to -0.38‰ and from -0.28‰ to -0.21‰ respectively, which is in excellent agreement with most of the previous studies (Georg *et al.*, 2007; Fitoussi *et al.*, 2009; Savage *et al.*, 2010; Zambardi *et al.*, 2013).

### 4.3.1 Si isotopic variability among planetary materials

#### **CARBONACEOUS CHONDRITES**

The carbonaceous chondrites are reported to display a relatively wide range of  $\delta^{30}$ Si values depending upon the proportions of CAIs present in the sample, which are known to carry heavier Si isotopes (Clayton *et al.*, 1988; Shahar and Young, 2007; Armytage *et al.*, 2011). To avoid heterogeneity at the sampling level, we made sure that the representative fraction of carbonaceous chondrites considered for Si isotopic analyses do not have visibly large CAIs. The  $\delta^{30}$ Si value of carbonaceous chondrites (two CM2 and three CV3 chondrites) analyzed here was found to cover only a small range and fall along the fractionation trend. The lowest observed value of  $\delta^{30}$ Si value of – 0.38±0.05‰ (2 SD) for CV3 chondrite. The average  $\delta^{30}$ Si value of five carbonaceous chondrites analyzed in this study is –0.41±0.06‰ (2 SD), which is identical within instrumental uncertainties to the previously reported values: –0.38 ± 0.02‰, 2SE

(Chakrabarti and Jacobsen, 2010);  $-0.36 \pm 0.02\%$ , 2SE (Fitoussi *et al.*, 2009) and  $-0.43 \pm 0.04\%$ , 2SE (Zambardi *et al.*, 2013).

#### **ORDINARY CHONDRITES**

The ordinary chondrites analyzed in this study possess an average  $\delta^{30}$ Si value of – 0.42±0.07‰, which is similar to reported value of –0.41±0.02‰, 2SE (Chakrabarti and Jacobsen, 2010b) and –0.46±0.06‰, 2SD (Armytage *et al.*, 2011, 2012) for ordinary chondrites. We measured Si isotopic composition of ten ordinary chondrites with wide range of metamorphic grade ranging from 3 to 5. The similarity in  $\delta^{30}$ Si value among different varieties of ordinary chondrites suggests that parent body alteration did not cause any variations in Si isotopic composition that could be detected with the present level of instrumental uncertainties. We have not found any significant variation in  $\delta^{30}$ Si among different groups of ordinary chondrite as  $\delta^{30}$ Si values of H, L and LL chondrites are indistinguishable within uncertainty, which is in accordance with Armytage *et al.* (2011). This indicates Si isotopic composition is not dependent on metal content of meteorites.

Although Fitoussi *et al.* (2009) argued that  $\delta^{30}$ Si in ordinary chondrites are lighter compared to carbonaceous chondrites by 0.06‰, but we have not detected any such difference in  $\delta^{30}$ Si value between carbonaceous and ordinary chondrites, which is consistent with reported  $\delta^{30}$ Si values by Georg *et al.* (2007a); Armytage *et al.* (2011) and Zambardi *et al.* (2013). The most likely reason for a slightly heavier Si isotopic composition in carbonaceous chondrite as determined by Fitoussi *et al.* (2009) could be the sampling of heavy Si isotope bearing CAIs in carbonaceous chondrites. Certainly, more analyses are required to be done to resolve this issue.

### **ENSTATITE CHONDRITES**

The enstatite chondrites are known as the lightest planetary material in terms of Si isotopes.  $\delta^{30}$ Si of the enstatite chondrites analyzed by Georg *et al.* (2007a); Fitoussi *et al.* (2009); Armytage *et al.* (2011); Zambardi *et al.* (2013); Savage and Moynier, (2013) have shown that enstatite chondrites are much lighter ( $\delta^{30}$ Si = -0.63±0.07‰,

2SD, Armytage *et al.*, 2011) compared to any other meteorites in terms of Si isotope composition. Although we have analyzed only six bulk enstatite meteorite samples but there is a clear indication that these meteorites possess lighter Si isotopic composition  $(\delta^{30}\text{Si} = -0.64 \pm 0.11\%, 2\text{SD})$  compared to other meteorites, Table 4.1.

A noteworthy point, which is clearly visible in Figure 4.2, is that EH chondrites (enstatite chondrite with high metal content) are lighter (mean value of  $\delta^{30}Si = -0.68 \pm 0.06\%$ ) than EL chondrites and aubrites (Enstatite meteorites with low Fe content),  $\delta^{30}Si = -0.58 \pm 0.03\%$ . These isotopic results are in good agreement with the results by Savage and Moynier, (2013), who has previously reported that EH chondrites have lighter Si isotope composition ( $\delta^{30}Si = -0.77 \pm 0.08\%$ ) than EL chondrites ( $\delta^{30}Si = -0.60 \pm 0.09\%$ ) and aubrites ( $\delta^{30}Si = -0.61 \pm 0.11\%$ ).

### ACHONDRITES

We have analyzed a suite of HED clan of meteorites: three howardites, two eucrites and three diogenites. Within analytical uncertainty, they are indistinguishable from each other and also from carbonaceous and ordinary chondrites in terms of silicon isotopes. The mean  $\delta^{30}$ Si value of howardite, eucrite and diogenite are  $\delta^{30}$ Si= –  $0.44\pm0.06\%$ ,  $\delta^{30}$ Si= – $0.41\pm0.04\%$  and – $0.42\pm0.06\%$  respectively. Our results are consistent with Georg *et al.* (2007a), suggesting that the Si isotopic composition of differentiated meteorites ( $\delta^{30}$ Si= – $0.42\pm0.05\%$ ) is similar to carbonaceous and ordinary chondrites ( $\delta^{30}$ Si= – $0.42\pm0.07\%$ ).



**Figure 4.2:** Plot showing the range of Si isotopic compositions among different groups of meteorites measured in this work. The  $\delta^{30}$ Si of angrites is from Dauphas *et al.* (2015). The range of  $\delta^{30}$ Si established for BSE in literature is shaded for comparing the offset in  $\delta^{30}$ Si between meteorites and terrestrial samples (refer to text for reference).



**Figure 4.3:** Three isotope plot of Si showing mass dependent fractionation of all meteorite samples analyzed in this study.

No nucleosynthetic isotopic anomaly is evident as all Si isotope data from bulk rock samples fall along mass dependent fractionation trend in a three-isotope plot of  $\delta^{29}$ Si vs.  $\delta^{30}$ Si, Fig. 4.3. The mass dependent trend further suggests the removal of all potential interferences on the three isotopes of Si using highresolution slits.

The robustness of our Si isotopic measurements is evident in Fig. 4.4, in which Si isotopic data from our studies (represented by pink upside triangle) are plotted together with the previously published data for a varied group of meteorites that has been analyzed so far in different laboratories.



**Figure 4.4:** Inter-laboratory comparison of Si isotopic data of various meteorite groups from different laboratories. Our silicon isotopic data (represented by pink colored triangle) for most of the meteorite samples fall within the isotopic range established by different laboratories. Literature data of EH, EL chondrites and aubrites are from Savage and Moynier, (2013); Armytage *et al.* (2011). Data for ureilites and SNCs are from Armytage *et al.* (2011), Zambardi *et al.* (2013). Data for carbonaceous, ordinary chondrites and HED meteorites are from Armytage *et al.* (2013). Literature data for isotopic composition of lunar rocks have been taken from Armytage *et al.* (2012); Zambardi *et al.* (2013); Poitrasson and Zambardi, (2015). Data for angrites are from Dauphas *et al.*, (2015). Si isotopic composition of terrestrial rock samples representing bulk silicate Earth (BSE) are from Savage *et al.* (2009); Fitoussi *et al.* (2009); Zambardi *et al.* (2009); Zambardi *et al.* (2009); Zambardi *et al.* (2009); Si isotopic composition of terrestrial rock samples representing bulk silicate Earth (BSE) are from Savage *et al.* (2009); Fitoussi *et al.* (2009); Zambardi *et al.* (2013); Poitrasson and Zambardi, (2015).

#### ANGRITES

Angrites are highly volatile element depleted basaltic achondrites. Due to lower ratio of volatile-to-refractory elements in angrites compared to any other meteorite groups (Davis, 2006), angrites are known to be well suited for evaluating the extent to which planetary bodies might have undergone silicon isotope fractionation during nebular and disk processing (Dauphas *et al.*, 2015). In terms of silicon isotopic composition, angrites are a special case due to its comparable silicon isotopic value with BSE (Pringle *et al.*, 2014; Dauphas *et al.*, 2015). Although we have not carried out isotopic analyses of angrites due to its unavailability in our meteorite collection, but any interpretation on the origin and evolution of planetary bodies must consider angrites.

The heavy Si isotope composition of angrites compared to lunar and terrestrial rock samples have questioned the long standing belief that heavy Si isotopic composition of terrestrial rock samples is due to equilibrium Si isotopic fractionation during high temperature silicate-metal differentiation event associated with core formation. The isotopic composition of angrites rule out the incorporation of Si in the core of Earth as an explanation for heavy Si isotope signature of terrestrial mantle. This is because unlike Earth, core formation in the angrite parent-body occurred under oxidizing conditions at relatively low pressure and temperature (Dauphas et al., 2015). Being formed in an oxidizing environment, the incorporation of significant amount of silicon in angrites's core is extremely unlikely. Therefore, nebular fractionation associated with condensation of forsterite seems to be the only plausible explanation for heavier Si isotopic composition of angrites, which is evident from the correlated variations between the  $\delta^{30}Si$  and Mg/Si ratio following a slope of  ${\sim}1$  in chondrites, Fig. 4.5 (Dauphas et al., 2015). It has been suggested that equilibrium isotopic fractionation between gaseous SiO (Mg/Si=0;  $\delta^{30}$ Si= -1.59‰) and solid forsterite (Mg/Si=2;  $\delta^{30}$ Si= 0.71‰) at  $\sim$ 1370 K in the solar nebula could have produced the observed Si isotope variations among planetary bodies (Dauphas et al., 2015). An alternate explanation for heavy isotopic composition of angrites is the impact-induced Si volatilization on angrite parent body (Pringle et al., 2014).



**Figure 4.5:** Co-related variation of  $\delta^{30}$ Si versus Mg/Si ratio in planetary objects. Image courtesy: Dauphas *et al.* (2015).

Although till date, fractionation of silicon isotopes during silicate-metal equilibration was the most promising theory to explain Si isotope offset between chondrite and the Earth, but the recent isotopic data from angrites have clearly questioned the association of heavier  $\delta^{30}$ Si of terrestrial rocks with equilibrium Si isotopic fractionation during high temperature core formation event. The extent of kinetic fractionation experienced by any planetary bodies needs to be revisited to get a proper understanding of the role played by nebular processing in fractionating silicon isotopes. We will shed light to this issue in our next chapter.

## 4.3.2 Mg isotopic composition of solar nebula

There are two schools of thoughts regarding distribution of Mg isotopes in the solar system. Wiechert and Halliday, (2007) detected distinct differences in Mg isotope ratios between upper mantle peridotites and bulk chondrites and suggested its

association with preferential sorting of chondrules characterized by high  $\delta^{26}$ Mg values during Earth's accretion. The later studies, however, could not reproduce any such Mg isotopic differences between terrestrial basalts and chondrites (Teng *et al.*, 2007; Handler *et al.*, 2009; Chakrabarti and Jacobsen, 2010a; Schiller *et al.*, 2010b; Teng *et al.*, 2010a; Pogge von Strandmann *et al.*, 2011; Sedaghatpour *et al.*, 2013; Sedaghatpour and Teng, 2016).

Despite limited database, our Mg isotope data from nine meteorite samples belonging to broad classes of chondrites and achondrites indicate that homogeneous Mg isotopic composition prevails among Earth and chondrites (Table 4.2, Fig. 4.6). The  $\delta^{26}$ Mg value in meteorites range from  $-0.23\pm0.09\%$  to  $-0.33\pm0.08\%$ , with an average of  $\delta^{26}$ Mg=  $-0.27\pm0.07\%$ . The  $\delta^{26}$ Mg averages of the various meteorite groups analyzed in this study are as follows:  $-0.28\pm0.09\%$  for one carbonaceous chondrite,  $-0.23\pm0.02\%$  for two ordinary chondrite,  $-0.27\pm0.06\%$  for two enstatite chondrite and  $-0.29\pm0.08\%$  for 4 HED meteorites. Thus our results reveal that no systematic difference in  $\delta^{26}$ Mg value exists between different types of meteorites. Moreover, the Mg isotopic composition of all chondrites ( $\delta^{26}$ Mg=  $-0.27\pm0.07\%$ ) is similar to  $\delta^{26}$ Mg value that has been established for Earth's mantle (Teng *et al.*, 2007, 2010a; Bourdon *et al.*, 2010; Pogge von Strandmann *et al.*, 2011; Xiao *et al.*, 2013). Thus, the Mg isotope results indicate that BSE is chondritic and solar system is homogeneous in terms of Mg isotopes.



**Figure 4.6:** Plot of  $\delta^{26}$ Mg vs Mg/Si for different classes of meteorites suggesting homogeneous stable Mg isotope composition among enstatite chondrite (EC), carbonaceous chondrite (CC), ordinary chondrite (OC), HED meteorites and terrestrial mantle (BSE).

**Table 4.2:** Mg isotopic composition of terrestrial rock samples and meteorites analyzed in this study along with their average Mg isotope value obtained from published data. 'n' refers to the number of samples analyzed in this study.

			Error		Error	
		δ <sup>25</sup> Mg (‰)	2 SD	δ <sup>26</sup> Mg (‰)	2 SD	n
Upper mantle (BSE)						
Handler et al., 2009	Peridotite	-0.14	0.07	-0.27	0.14	
Teng <i>et al.</i> , 2010	Peridotite	-0.13	0.03	-0.25	0.04	
Carbonaceous Chondrite						
EET 96029	CM2	-0.12	0.06	-0.28	0.09	3
Teng et al., 2010		-0.16	0.03	-0.28	0.06	

Schiller et al., 2010		-0.14	0.1	-0.27	0.2	
Ordinary Chondrite						
QUE 97008	L3.0	-0.11	0.06	-0.23	0.09	2
Y 980448	L3.0	-0.14	0.08	-0.24	0.1	2
Average		-0.12	0.04	-0.23	0.02	
Teng et al., 2010		-0.15	0.05	-0.28	0.06	
Schiller et al., 2010		-0.15	0.08	-0.29	0.19	
Enstatite Chondrite						
PCA 91461	EH3	-0.12	0.08	-0.29	0.12	3
ALHA 81022	EL6	-0.15	0.06	-0.25	0.08	2
Average		-0.14	0.03	-0.27	0.06	
Teng et al., 2010		-0.15	0.02	-0.28	0.05	
Schiller et al., 2010		-0.12	0.04	-0.23	0.09	
HED meteorites						
LOHAWAT	Howadite	-0.16	0.06	-0.30	0.07	2
QUE 97001	Howardite	-0.17	0.05	-0.33	0.08	2
LAP 03569	Diogenite	-0.14	0.04	-0.31	0.07	3
EET 87503	Eucrite	-0.10	0.05	-0.24	0.09	2
Average		-0.14	0.06	-0.29	0.08	

## **4.4 Discussions**

The terrestrial rock standards display very limited range in silicon isotope values  $(\delta^{30}\text{Si}=-0.31 \text{ to } -0.21\%)$  that are indistinguishable from BSE value (Fig. 4.2).  $\delta^{30}\text{Si}$  values of ordinary/carbonaceous chondrites and HED meteorites are significantly lighter than BSE and fall in a restricted range ( $\delta^{30}\text{Si}=-0.38\pm0.06\%$  to  $-0.47\pm0.09\%$ ). The enstatite meteorites (three EH3, one EL6 and one Aubrite) are considerable lighter ( $\delta^{30}\text{Si}=-0.65\pm0.11\%$ ) than BSE, which is in agreement with the literature values. Although there occurs variation in  $\delta^{30}\text{Si}$  among different groups of meteorites and BSE

but no such variation in Mg isotopic composition has been observed in several meteorite samples that has been analyzed in this study.

# 4.4.1 Role of impact evaporation in the generation of Si isotope fractionation

The processes responsible for the enrichment of Mg relative to Si in bulk silicate Earth (BSE) and its heavy Si isotopic composition compared to chondrites has been debated between two leading processes: evaporation *versus* partitioning into metallic core. Since large-scale evaporation should ideally cause Mg isotopes to fractionate more than Si isotopes, a simultaneous study of Si and Mg isotopes in single aliquot of meteorite and terrestrial rock samples could help in better constraining the role played by evaporation in causing Si isotope offset between chondrites and BSE.

To understand the extent to which evaporation following giant impact could have produced Si isotopic fractionation, we have carried out Mg isotopic analyses in the same aliquot of meteorite sample in which Si isotopic analyses have been performed. Although Si isotopic variations has been noted for varied groups of meteorites, but the Mg isotopes look homogeneously distributed, with  $\delta^{26}$ Mg ranging from  $-0.23\pm0.09$ % to  $-0.33\pm0.08\%$  (Fig. 4.6). The Si isotopic variation among planetary bodies and lack of detectable Mg isotopic offset between BSE and diverse groups of meteorites indicate that any aftermath planetary processes that have shaped our Earth, such as impact erosion or the preferential loss of SiO over Mg from magma ocean were not significant enough to fractionate Si isotopes. Strikingly similar Si isotopic composition of BSE and bulk silicate moon (Armytage et al., 2012) also suggests evaporation or loss of vapor have played negligible role in causing Si isotopic discrepancy. Therefore, Mg and Si isotopic signature in meteorites and terrestrial samples must have been either inherited from the nebular gas during accretion of planetary bodies or it could be generated during removal of Si into the core and were not affected by any large-scale secondary planet shaping processes.

# 4.4.2 Si isotope fractionation due to core formation in oxidized nebula

HEDs represent a clan of differentiated meteorites consisting of Howardites, Eucrites and Diogenites. They are representative of their parent asteroid 4-Vesta (Consolmagno and Drake, 1977), which is a well-known differentiated asteroid having a prominent crust, mantle and core. Eucrites are known to be representative of Vesta's upper crust, whereas Diogenites and Howardites probably originated from deeper levels of Vesta (Mittlefehldt, 1994). The Si isotopic compositions of HEDs are found to be uniform with no resolvable difference in  $\delta^{30}$ Si between Howardite (-0.44±0.06‰), Eucrites (-0.41±0.04‰) and Diogenites (-0.42±0.06‰), which is in agreement with the previously reported data by Fitoussi *et al.* (2009); Armytage *et al.* (2011) and Chakrabarti and Jacobsen, (2010b). The terrestrial samples (mean  $\delta^{30}$ Si = -0.24±0.06‰) display a much heavier silicon isotope composition compared to HED meteorites and chondrites ( $\delta^{30}$ Si=-0.47±0.26‰).

As far as the Earth is concerned, the heavier  $\delta^{30}$ Si of terrestrial mantle compared to chondrites is suggested to be due to equilibrium Si isotope partitioning between Earth's metallic core and silicate mantle during core-mantle segregation event (Georg et al., 2007; Fitoussi et al., 2009; Shahar et al., 2009, 2010; Armytage et al., 2011). However, if the heavy Si isotopic signature of BSE had been exclusively due to equilibrium Si isotope fractionation during core formation then we should expect to observe similar heavy Si isotopic composition in Eucrites too, which is known to represent the crust of the differentiated 4-Vesta. Despite the presence of a metallic core, the lack of Si isotopic fractionation among HED meteorites question the role of core-forming events in generating Si isotopic fractionation among all differentiated planetary bodies and this issue requires re-evaluation. Moreover, similarity of silicon isotopic composition of other differentiated planetary objects, e.g., martian meteorites (SNCs) and ureilites with those of carbonaceous and ordinary chondrites also challenge the scenario of equilibrium silicon isotope fractionation due to core formation as a likely cause for generating  $\delta^{30}$ Si offset between silicate fraction of the planet and the bulk planetary body (chondrite). Therefore, the Earth must have

undergone unique evolutionary history that has shifted its Si isotopic composition to heavier side compared to any other meteorites. We believe that the environmental conditions in which Earth formation occurred was a deciding factor that controlled Si isotopic distribution in terrestrial samples relative to meteorites. This topic will be addressed in greater detail in our next chapter.

# 4.4.3. Types of planetary materials based on Mg/Si ratio and Si isotope composition

From the trend observed in  $\delta^{30}$ Si and Mg/Si variation among planetary materials, it is clear that there are three broad types of planetary bodies available in our collection based on Si isotopic differences:

(i) Enstatite meteorites, characterized by the lightest  $\delta^{30}$ Si value ( $\leq -0.64 \pm 0.11\%$ ) among all extra-terrestrial samples.

(ii) Carbonaceous-Ordinary chondrites, HEDs, SNCs, and Ureilites characterized by  $\delta^{30}$ Si value ( $\delta^{30}$ Si ranging from -0.41 to -0.48‰).

(iii) Terrestrial samples, lunar meteorites and angrites, characterized by a heavier composition ( $\delta^{30}$ Si  $\geq -0.29\pm 0.08\%$ ).

The distinct Si isotopic signature of enstatite chondrites compared to any other rock samples indicate enstatite chondrites are sampling a different Si isotope reservoir compared to other meteorite parent bodies. The enstatite chondrites are known to have formed in reduced inner parts of the proto planetary accretion disk. Unlike Mg, that remains strictly lithophilic in both oxidizing and reducing condition, Si has very unique cosmochemistry of behaving siderophilic under reducing condition and hence gets incorporated into metallic phases. This behavior is quite evident in enstatite chondrites, which is characterized by significant incorporation of Si in its metallic phases (Ringwood, 1961; Zieglar *et al.*, 2010; Savage *et al.*, 2013).

The fact that Mg isotopic distribution is not playing any role in the origin of Mg/Si ratio variation is evident from chondritic  $\delta^{26}$ Mg (-0.27±0.06‰) of two enstatite chondrites (1 EH3 and 1 EL6) analyzed in this study. In agreement with Savage and Moynier, 2013, we have noticed distinct isotopic compositions in EH and EL chondrites, with EH ( $\delta^{30}$ Si= -0.67±0.06‰) being lighter than EL chondrite and aubrite ( $\delta^{30}$ Si= -0.58±0.03‰). Savage and Moynier, 2013 have also reported that the silicon isotopic composition of the non-magnetic components of EH and EL are similar to  $\delta^{30}$ Si of bulk carbonaceous/ordinary chondrite ( $\delta^{30}$ Si= ~ -0.47‰). These observations are best explained by the presence of isotopically light Si isotope in the metallic phases, with EH containing more metal enriched in lighter isotopic analyses in metal fractions of aubrite (differentiated counterpart of enstatite chondrite) by Ziegler *et al.* (2010) has clearly shown that there is an enrichment of light Si isotopes of up to  $\delta^{30}$ Si= -6.62±0.28‰ in metallic fractions of enstatite chondrite.

Therefore, it is very evident that partitioning of light Si isotopes in enstatite chondritic metals has dragged the  $\delta^{30}$ Si value of enstatite chondrite towards overall lighter isotope composition compared to any other meteorites. Incorporation of Si in both metallic and silicate phases makes enstatite chondrite enriched in Si, thereby driving the Mg/Si ratio of enstatite chondrite to lower values compared to other meteorites. Although Zieglar *et al.* (2010) reported Si isotopic composition of metals from reduced meteorites, but he analyzed aubrite samples that are known to have undergone large-scale differentiation event. Since primitive enstatite chondrite preserves the pristine chemical and isotopic signature of reduced planetary bodies, a precise determination of the isotopic composition in reduced planetary systems. In this work, we have precisely determined the extent of Si isotopic heterogeneity within various phases of enstatite chondrites, the results and implications of which are detailed in our next chapter.

# **CHAPTER 5**

# SILICON ISOTOPE RESULTS FROM MICRO-PHASES OF EH3 CHONDRITE: IMPLICATIONS TO ACCRETION AND DIFFERENTIATION OF EARTH

In the previous chapter, we have discussed the extent of Si and Mg isotope homogeneity in solar nebula based on Si and Mg isotope analyses in bulk meteorite samples that are representative of diverse varieties of planetary bodies in solar system. In this chapter, we will discuss the results of high precision Si and Mg isotope analyses carried out in different micro-phases of un-equilibrated enstatite chondrites. Based on our isotope data, we propose a new Earth forming model that can explain the Si isotope differences between different planetary bodies of solar system *i.e.*, BSE (terrestrial samples), enstatite chondrite, ordinary-carbonaceous chondrites, HEDs and angrite.

Enstatite chondrites show striking isotopic similarity with terrestrial rock samples for a large number of stable isotopic systematics such as O, N, Mo, Ru, Ni, Cr, Ti, Fe, Os, Sr, Ca and Nd with the exception of silicon. Since Si is a major element of the solar system that participate in almost every cosmochemical processes, the isotopes of Si are robust tracers of planetary accretion, evolution and differentiation. The relatively large Si isotope offset between BSE and enstatite chondrites compared to other meteorites led Fitoussi and Bourdon, (2012) to conclude that enstatite chondrites did not

contribute a major fraction of material during Earth's accretion. However, Savage and Moynier, (2013) have shown that the non-magnetic/silicate phases of enstatite chondrites have heavier  $\delta^{30}$ Si than its bulk composition, suggesting the possibility of light Si isotopic enrichment in its metallic phases and therefore the likelihood of heterogeneous distribution of Si isotopes within different phases of enstatite chondrite. To get an estimate of the extent of Si isotopic heterogeneity within enstatite chondrites, more Si isotopic analyses within its various micro-phases should be carried out before deeming off these group of meteorites as a possible precursor of Earth.

Savage and Moynier, (2013) used hand magnets to separate magnetic and nonmagnetic phases from enstatite chondrite. In such procedures, it is difficult to sample purest end members of metal and silicate since these phases are finely disseminated within each other in enstatite chondrites. In order to accurately estimate the Si isotopic composition of metal and silicate fractions of enstatite chondrite, we have chosen a different approach and carried out high precision Si isotopic analyses in various micromilled phases (metals, silicates and matrices) of primitive EH3 chondrite. To understand the role of any impact related evaporation and vaporization to fractionate Si isotope, we have carried out Mg isotopic analyses in the same aliquot of micro-phases (silicates and matrices) of enstatite chondrite where Si isotope analyses were performed.

Throughout the experiments, the newly developed silicate digestion and chromatographic purification technique for Si and Mg by Sikdar and Rai, (2017) has been used to process very small amount of micro milled samples. The results and implications from these sets of experiments are discussed in this chapter.

### 5.1 Si isotope fractionation during core formation

The core (constituting  $\sim$ 32% of Earth's total mass and 16% of its volume) is the most inaccessible part of the Earth. Direct sampling of material from the core is impossible due to the prevalence of ultrahigh pressure and temperature conditions exceeding 136 GPa and >4,000 K inside the core of Earth. Hence, the composition of core is mostly

estimated by indirect means through geophysical or geochemical investigations in conjunction with their analogy to iron meteorites. Based on seismic studies, it has been well established that core of Earth is made up predominantly of iron and nickel alloy along with ~10% light elements (Birch, 1952; Anderson and Isaak, 2002). Although Si has been suggested to be the principal low-density diluent since long time (MacDonald and Knopoff, 1958; Ringwood, 1959; Birch, 1964; Allegre et al., 1995; Georg et al., 2007) but carbon, hydrogen, sulfur and oxygen are also speculated to be present in Earth's core (Poirier, 1994; Allegre et al., 1995; Sherman, 1995; Kilburn and Wood, 1997; Gessmann et al., 2001; Li et al., 2001a,b; Rubie et al., 2003, 2007; Asahara et al., 2007; Badro et al., 2007, 2014; Cote et al., 2008; Corgne et al., 2009; Antonangeli et al., 2010; Ricolleau et al., 2011; Zhang et al., 2016). Thus, there have been conflicting debates on the nature of light elements in the core of Earth. Since the scenario of Earth's differentiation and subsequent evolution is linked with concentration and nature of light elements in the core, a proper knowledge of the light elements in Earth's core has very important implications (Chakrabarti and Jacobsen, 2010b; Morard et al., 2013).

A basic premise in estimating the composition of Earth and its core is to make an assumption that chondrites are the starting material of all planetary bodies and hence are the best representative of bulk Earth. Using this concept, it has been suggested that the superchondritic Mg/Si ratio of the silicate reservoir of Earth (Bulk Silicate Earth, BSE) reflects the presence of missing Si in the core of Earth. Geophysical investigations and high temperature-pressure experimental constraints suggest that a maximum of 2.5% sulfur and 4-5wt% silicon can be incorporated in the core of Earth (Ricolleau *et al.*, 2011; Morard *et al.*, 2013 and references therein).

Si is the third most abundant element of Earth after oxygen and iron (Baskaran, 2012). The distribution of stable isotopic forms of silicon in BSE and meteorites provides better insights into the processes of planet formation, accretion and its subsequent differentiation. Si isotopes are recently being used as a fingerprint to estimate the Si content in Earth's core and as a tracer of generic link between meteorites and the Earth. A major clue for the presence of Si in Earth's core comes from the fact that BSE is heavier than chondrites in terms of silicon isotopes (Georg *et al.*, 2007). It is

suggested that the preferential partitioning of lighter isotopes of Si in core of Earth has enriched the terrestrial mantle samples in heavier isotopes of Si relative to starting material 'chondrites' (Georg *et al.*, 2007; Fitoussi *et al.*, 2009; Fitoussi and Bourdon, 2012; Shahar *et al.*, 2009, 2011; Ziegler *et al.*, 2010; Armytage *et al.*, 2011; Zambardi *et al.*, 2013). Based on Si isotopic offset between BSE and ordinary/carbonaceous chondrites ( $\Delta^{30}$ Si<sub>BSE-OC/CC</sub> =  $\delta^{30}$ Si<sub>BSE</sub>-  $\delta^{30}$ Si<sub>OC/CC</sub> =0.15‰), an estimation of ~6-12 wt% Si in the Earth's core has been proposed by a number of authors in the recent past (Georg *et al.*, 2007, Zieglar *et al.*, 2010; Armytage *et al.*, 2011; Zambardi *et al.*, 2013).

The validity of such core forming models to estimate the Si content in Earth's core lie on the assumption that observed offset in Si isotopic composition between BSE and chondrites result solely from equilibrium Si isotopic fractionation during silicate-metal segregation event (Georg et al., 2007, Chakrabarti and Jacobsen, 2010b; Zieglar et al., 2010; Shahar et al., 2009, 2011; Armytage et al., 2011; Fitoussi and Bourdon, 2012; Zambardi *et al.*, 2013, Kempl *et al.*, 2016). However, the  $\delta^{30}$ Si signatures of Mars and Vesta (well known differentiated planetary bodies) do not show any shift with respect to chondrites (Zambardi et al., 2013). This suggests that the hypothesis of Si isotope fractionation during core formation does not hold true for all planetary materials. The recent metal-silicate partition experiments suggest that equilibrium metal-silicate Si isotope fractionation is lower (0.5) at 3000K (Hin et al., 2014) than previously reported values of 0.8 by Shahar et al. (2009; 2011). Moreover, the association of core formation for generating heavier  $\delta^{30}$ Si in planetary bodies has been questioned after the  $\delta^{30}$ Si value of angrites was found to be heavier than BSE (Pringle *et al.*, 2014; Dauphas et al., 2015). Since Si easily alloys with Fe under low oxygen fugacity, the incorporation of Si in core of a planet requires the prevalence of reduced environment during its formation. Unlike Earth, angrite parent-bodies originated in oxidizing conditions where partitioning of silicon in metallic phases is very unlikely. Therefore, there is another school of thought who believes that that the variability in Si isotopic composition among terrestrial objects and different varieties of chondrites could be strongly associated with nebular fractionation rather than core formation (Dauphas et al., 2015).

Most of the chemical, isotopic, and petrological features found in primitive chondrite are a result of several complex processes that occurred in the cloud of gas and dust, referred as solar nebula. Primitive meteorites have accreted from nebular condensates and the condensing phases are likely to have undergone various degrees of kinetic fractionation whereas only equilibrium fractionation (if any) is possible in the high temperature-pressure and closed system environment prevalent in the interior of a planetary body. High temperature melting and recrystallization occurring inside the Earth's core should homogenize isotopic abundances rather than creating heterogeneities. Also, the equilibrium stable isotope fractionations decrease dramatically with increase in temperature. Therefore, it is extremely important to understand the role played by kinetic effects to create any isotope fractionation between chondrites and BSE before anchoring the difference to equilibrium isotope fractionation in core-mantle boundary.

The idea of equilibrium Si isotope fractionation between metal and silicate during core formation to explain isotope offset of BSE and chondrites faces another major hurdle as the estimated amount of Si in Earth's core varies with the choice of the representative proxy for bulk Earth composition. There occurs variation in the Si isotopic composition among different groups of chondrites that ranges from  $\delta^{30}Si$  = - $0.63 \pm 0.07\%$  for enstatite chondrite to  $-0.47\pm 0.01\%$  and  $-0.43\pm 05\%$  for ordinary and carbonaceous chondrites respectively (Armytage et al., 2011; Zambardi et al., 2013). Accordingly, the Si isotopic offset between BSE and ordinary/carbonaceous (OC/CC) chondrites ( $\Delta^{30}$ Si<sub>BSE-OC/CC</sub> = ~0.15‰) provides an estimation of 3-12wt% Si in the Earth's core, which is acceptable according to geophysical models of core composition (Georg et al., 2007, Zieglar et al., 2010; Zambardi et al., 2013, Armytage et al., 2011; Badro et al., 2007). But in the case of enstatite chondrite Earth model, the relatively larger offset in  $\delta^{30}$ Si between enstatite chondrite and BSE demands the presence of >26 wt% Si in Earth's core (Georg et al., 2007, Zambardi et al., 2013, Armytage et al., 2011; Fitoussi and Bourdon, 2012), which far exceeds the amount of light elements required to explain core's density deficit (Badro et al., 2007). The lower Mg/Si and Al/Si ratio in enstatite chondrite compared to BSE (Larimer and Anders, 1970; Baedecker and Wasson, 1975) also requires the presence of an unrealistically high amount of Si in Earth's core to balance the Mg and Si budget of bulk Earth and chondrite. Due to the significant Si isotopic offset between BSE and enstatite chondrite  $(\Delta^{30}\text{Si}_{\text{BSE-E-chond}} = \sim 0.34\%)$ ; it has been suggested that a maximum 15% of Earth's precursor material could be derived from enstatite chondritic like precursor planetary bodies (Fitoussi and Bourdon, 2012).

Thus, in order to identify the processes that have led to heavy Si isotope composition of BSE and better constrain the amount of Si in Earth's core, the precise determination of bulk Earth composition is extremely crucial. Although a number of Earth forming models have been proposed requiring the accretion of variable chondritic sources to form the Earth such as carbonaceous/ordinary/enstatite chondrites or a random mixture of different types of chondrites and achondrites but till date there are no strict constrains on the exact nature of building blocks of Earth that can be efficiently taken as a proxy for bulk Earth composition (Allegre et al., 1995, 2001; Palme and O'Neill, 2003; Trinquier et al., 2007; Carlson et al., 2007; Leya et al., 2008; Simon and DcPaolo, 2010; Javoy et al., 2010; Schonbachler et al., 2010, Fitoussi and Bourdon, 2012). Since the relative abundances of elements in CI chondrites matches perfectly well with Solar photosphere, so it is generally assumed that evolution of all the planetary bodies were started with CI composition. But isotope investigations have revealed the existence of significant differences between the Earth and CI (carbonaceous) chondrites. Among all the chondrites, enstatite chondrites are the closest match to the BSE with respect to isotopic composition for most of the elements. Isotope anomalies of chondrites with respect to BSE generally increase from enstatite to ordinary to carbonaceous chondrites (Fisher-Godde and Kleine, 2017).

### 5.2 Enstatite chondrite: A unique meteorite group

Enstatite chondrites are a highly reduced group of meteorites known to have formed in a nebula with higher C/O (>1) than solar value (C/O~0.6) (Mason, 1966; Keil, 1989, Latimer and Bartholomay, 1979; Kong *et al.*, 1997). The highly reduced nature of the enstatite chondrites suggests that these planetary bodies were originated in the innermost region of the solar nebula (Kallemeyn and Wasson, 1986; Kong *et al.*,

1997). Enstatite chondrites comprise two groups based on iron content: high-Fe (EH) and low-Fe (EL) chondrite (Sears et al., 1982; Shukolyukov et al., 2004). They are predominantly composed of FeO-poor enstatite (MgSiO<sub>3</sub>, typically with Fe contents of less than 1wt%); Si-bearing Fe-Ni metal; free silica; diverse sulfide minerals e.g., troilite (FeS), oldhamite (CaS), niningrite (MgS), daubréelite (FeCr<sub>2</sub>S<sub>4</sub>), alabandite (MnS); nitrides (osbornite, TiN), sinoite  $(Si_2N_2O)$ ) and a suite of rare minerals, which are not typically stable and observed in terrestrial rocks (Keil, 1968; Savage and Moynier, 2013; Defouilloy et al., 2016). The metals occur in irregular blobs within enstatite chondrite and are known to incorporate significant amounts of Si (up to 5wt% in EH3 chondrites; Weisberg et al., 1995; Hutson et al., 2000). Kamacite (Fe-Ni alloy), perryite ((Ni,Fe)<sub>8</sub>(Si,P)<sub>3</sub>) and schreibersite ((Fe,Ni)<sub>3</sub>P) are the common metallic phases found in enstatite chondrite, which are known to contain on average 2.6, 11.8, and 0.1 wt% Si respectively. Extremely high refractory lithophile element (RLE) fractionation has lowered the Mg/Si ratio in enstatite chondrite (0.65-0.75) compared to BSE (1.05, Jagoutz *et al.*, 1979) and any other meteorites (Mg/Si =  $\sim$ 1), (Ahrens *et* al., 1968, Larimer and Anders, 1970; Baedecker and Wasson, 1975).

The unique mineralogy of enstatite chondrite, its different oxidation state (Mason, 1966; Keil, 1989), dissimilar elemental concentrations (Ca, Al, Fe, Zn) from BSE and enstatite chondrite's lower Mg/Si and Al/Si ratio compared to superchondritic Mg/Si of BSE suggest least involvement of enstatite chondritic material in the accretion of Earth. However, with metals comprising 21 wt% of the bulk EH3 meteorite, enstatite chondrites are the only group of meteorites whose siderophilic and lithophilic elemental ratios are similar to the Earth (Mayeda and Clayton, 1980; Herndon, 1996; Newton *et al.*, 2000). The most striking feature of enstatite chondrite is its similarity to BSE in stable isotopic composition for most of the elements analyzed so far such as O (Clayton and Mayeda, 1984, Newton *et al.*, 2000), N (Javoy *et al.*, 1986), Mo (Dauphas *et al.*, 2002a), Ru (Dauphas *et al.*, 2004, Godde and Kleine, 2017), Ni (Regelous *et al.*, 2010), Ti (Trinquier *et al.*, 2009, Zhang *et al.*, 2012), Fe (Wang *et al.*, 2014), Os (Meisel *et al.*, 1996), Sr (Moynier *et al.*, 2012), Ca (Valdes *et al.*, 2014) and Nd (Gannoun *et al.*, 2011). In most of these cases, ordinary and carbonaceous

chondrites fall far apart from stable isotopic range occupied by terrestrial rock samples.

Isotopic abundances are more robust tracers of any geochemical processes than elemental abundances. For example, in any geochemical processes like partial melting or magma crystallization, different minerals that are crystallized at different intervals of time might have very different elemental proportions relative to parent material leading to elemental fractionation (Mg/Si, Al/Si) but these processes do not induce any Si isotopic fractionation (Savage *et al.*, 2010). Unlike elements, isotopes are less prone to fractionate by any complex processes due to the similarity in chemistry of all the isotopes of an element. Whatever minor fractionations are observed, they arise due to differences in physical properties of isotopes based on mass. Therefore, isotopic characteristics of a planetary body are less likely to be over-ridden by any minor physico-chemical processes that usually alter the chemical composition of a planetary body. Thus, isotopic compositions provide more strict constraints and are appropriate tracers for the identification of the parent body of a meteorite rather than chemical composition.

Among all isotopic systematics, oxygen isotopic composition is the most important tracer to classify meteorite groups based on their origin. In oxygen three-isotope realm, meteorites from similar parent body clusters around specific region. Only enstatite chondrites and its differentiated counterpart - the aubrites - fall on the terrestrial fractionation line defined by the Earth-Moon system (Clayton *et al.*, 1984). All other meteorites fall on very different regions of the three-isotope space of oxygen isotopes, distinct from the terrestrial fractionation line. Due to isotopic similarities between enstatite chondrite and BSE, it is suggested that enstatite chondrites are the major building blocks of Earth (Javoy, 1995; Javoy *et al.*, 2010).

Since Si is also one of the most abundant elements in the solar system similar to oxygen, the relatively larger offset in Si isotope composition between chondrites and BSE led Fitoussi and Bourdon, (2012) to preclude enstatite chondrites as a significant source of Earth's precursor material. However, Savage and Moynier, (2013) have shown that the non-magnetic phases of enstatite chondrites have heavier Si isotope

composition than bulk enstatite chondrites, suggesting the possibility of light Si isotopic enrichment in the metallic phases of enstatite chondrite and therefore the likelihood of heterogeneous distribution of Si isotopes within different phases of enstatite chondrite. Therefore, it is important to reinvestigate the reasons for Si isotopic offsets between enstatite chondrites and the Earth considering the fact that enstatite chondrite itself is quite heterogeneous with respect to silicon isotopes.

Calculating silicon content of Earth's core based on Si isotopic offset between bulk enstatite chondrite and BSE, without estimating the extent of isotopic heterogeneity within various micro-phases of enstatite chondrite could lead to erroneous conclusions. Thus establishing a link towards the compositional setting of the Earth's core via Si isotope offset between chondrite and BSE requires an understanding of the extent of kinetic Si isotope fractionation that might have occurred during nebular accretion stage of meteorite parent body. To revisit the entire scenario of Earth and core formation from Si isotopic point of view, we have performed high precision Si isotopes analyses in various pre-characterized phases (metals, silicate, matrices) sampled after micromilling from very primitive enstatite chondrite (EH3 chondrites). Simultaneous analyses of Mg isotope composition in the same aliquot of silicate and matrix fractions of EH3 chondrite has been used as an additional tool to constrain the origin of Si isotopic heterogeneity to impact *vs* core partitioning processes.

### 5.3 Materials and methods

To estimate Si isotope heterogeneity within enstatite chondrite, a comprehensive analyses of Si isotopic composition was carried out in different groups of enstatite chondrites: PCA 914 61 (EH3), LAR 06 252 (EH3), MIL 07 028 (EH3), Y-961 (EH3), ALHA 81 021 (EL6), LAR 04 316 (Aubrite) and within different micro-phases of four EH3 chondrites (PCA 914 61, LAR 06 252, MIL 07 028, Y-961).

### 5.3.1 Mineralogical characterization of EH3 chondrite

A detailed mineralogical characterization of polished mounted sections of enstatite chondrites were carried out using Electron Probe Micro Analyzer (CAMECA SX 100) to identify different minerals and their compositions. The EH3 chondrites are distinguished by the presence of highly reduced and unequilibrated mineral assemblages, relatively smaller chondrules and abundant Si rich metal. The presence of abundant chondrules with sharp boundaries and unequilibrated mineral assemblages in EH3 chondrites suggest that they have undergone least alteration since its formation. In order to identify different phases present in EH3 chondrites, the back-scattered electron images of the various phases were taken and their quantitative chemical analyses were carried out using Wavelength Dispersive Spectrometer (WDS). As the name suggests, enstatite is the most dominant mineral in the EH3 chondrite and the composition of enstatite was found to be fairly uniform in chondrules and matrix with ~60% SiO<sub>2</sub> and ~40% MgO respectively (Fig. 5.1). Metals and sulfides are evenly distributed in the meteorite and presence of disseminated metals within enstatite chondrite is prominent in a submicron scale (Fig. 5.2). A list of common minerals found in enstatite chondrites after WDS analyses include: Silicates: (Enstatite (MgSiO<sub>3</sub>), Albite (NaAlSi<sub>3</sub>O<sub>8</sub>), Hypersthene ((Mg,Fe)<sub>2</sub>Si<sub>2</sub>O<sub>6</sub>)); Sulfides: (Oldhamite (CaS), Troilite (FeS), Daubreelite (FeCr<sub>2</sub>S<sub>4</sub>), Niningerite [(Mg, Fe, Mn)S]); Metals: (Schreibersite ((Fe, Ni)<sub>3</sub> P), Kamacite (Fe-Ni alloy with Si), Perryite (Ni,Fe)<sub>5</sub>(Si,P)<sub>2</sub>. Presence of these minerals in enstatite chondrite have been earlier reported by Rubin, (2009); Lehner et al., (2014).



**Figure 5.1:** BSE images of chondrules in PCA 91461 (EH3 chondrite). The chondrules are mostly of enstatitic (MgSiO<sub>3</sub>) composition.



**Figure 5.2:** BSE images of the most dominant silicate: Enstatite (MgSiO<sub>3</sub>) in PCA 91461 and LAR 06 252 (EH3 chondrites). The boundaries of silicate phases are sharp and highlighted in black. The preserved sharp boundaries of the silicate grains indicate little metamorphic alteration of its parent body.

Enstatite chondrites are the only meteorites with an appreciable content of Si in its metallic phase because of its formation in reduced conditions. The two metallic phases in enstatite chondrite: kamacite and perryite were found to incorporate an average of 2.3 wt% and 12.9 wt% Si respectively (Fig. 5.3). Due to the distribution of Si among silicate (Enstatite, MgSiO<sub>3</sub>, with FeO <1 wt %) and metallic phases (Kamacite-Perryite) of enstatite chondrite, enstatite and kamacite were our potential targets for further Si isotopic investigation. We could not analyze  $\delta^{30}$ Si of perryite due to size

constrain. The BSE images of the metals and matrices of EH3 chondrite are provided in Fig. 5.4 and Fig. 5.5 respectively.



**Figure 5.3**: Distribution of Si between the two metallic phases (Kamacite and Perryite) of EH3 chondrite



**Figure 5.4:** BSE image of EH3 chondrite showing highly reflecting metallic phases: Perryite and Kamacite. The sulfides (troilite-daubreelite), silicates (enstatite) and glass can be identified from their decreasing order of reflectivity.



**Figure 5.5:** BSE image of matrices in EH3 chondrite showing highly reflecting metallic phases surrounded by dark silicates (enstatite). Presence of disseminated sulphides and metals within silicates is evident in micron scale.

After mineralogical characterization of the target metal and silicate phases through EPMA, the locations of these phases were identified using Zeiss petrological

microscope attached to New-Wave Micromill. Then the target phases were micro milled using tungsten drill bit having a cross section of 100µm. Prior to drilling, 20-50µl of ultrapure water (MQ) was added on the target location to avoid scattering of the powdered phases while drilling. Following micro milling, the sample slurry was carefully transferred into pre-weighed and cleaned 15 ml PFA (Savillex<sup>TM</sup>) vial using micro pipette. After each micromilling session, the mounted sample was cleaned with ethyl alchohol and ultrapure water (MQ) to avoid cross contamination among different phases. The vials were kept on hotplate at 80°C to evaporate water and then weighed again on a micro balance to estimate the amount of samples present in each vial. To avoid contamination and sample loss, the micro-milled samples were digested in the same vial using alkali digestion technique and then processed further for isotopic measurements. Presence of disseminated metals throughout enstatite chondrite is prominent in a submicron scale and therefore only a few pure silicate phases could be sampled without contamination from surrounding metal bearing matrices.

### 5.3.2 Sample preparation and analytical methods

Si isotopic analyses were carried out for 6 bulk enstatite meteorites (four EH3, one EL6, one aubrite) and phase separates of four EH3 chondrites (PCA 914 61, LAR 06 252, MIL 07 028, Y 961). For digestion, approximately 0.05-0.2 mg of samples were fused with ~40× mg of NaOH flakes and 50  $\mu$ l of 18M $\Omega$  Milli-Q in Teflon Savillex<sup>TM</sup> vial at ~250°C for 18 hours. For chromatographic separation of Si, samples containing ~1-2 $\mu$ g of Si were loaded on the resin and Si was eluted using 15 ml of Milli-Q water (pH neutral, 18.2 M $\Omega$ ). All isotopic analyses in this study was carried out using a Thermo Scientific Neptune Plus MC-ICPMS in dry plasma mode using APEX-Q attached with Nefion desolvation. For high precision Si isotopic analyses, MC-ICPMS was operated in pseudo high-resolution mode and correction of instrumental mass bias was done using standard sample bracketing technique with NBS-28 as bracketing standard and 0.01N HCl as blank solution. Typical sensitivity of <sup>28</sup>Si in solution of meteorite phase separates was ~2-3V with a background signal of <30 mV. The detailed experimental procedure is described in Chapter 3.

### 5.4 Si isotopic results from mineral phases of EH3 chondrite

Under the oxidizing conditions prevalent in Earth's surface, Si is never found in its atomic state but always occurs in bonding with oxygen as silicate ion  $(SiO_4^{2-})$ , Abraham *et al.*, (2010). Only in reducing environments, silicon starts behaving siderophilic and gets incorporated into metallic phases. Enstatite chondrites, being formed in extremely reducing environment, are the only primitive meteorites with appreciable amount of Si content (on the order of 5%) in its respective metallic phase (Ringwood, 1960, 1961; Humayun *et al.*, 2009). Theoretical work suggests that due to very different bonding environment of Si in metallic and silicate phases, the isotopes of Si get fractionated in reduced environment (Schauble *et al.*, 2009). In general, the heavy isotopes get enriched in the phase with the 'stiffer' bonds whereas lighter isotopes get partitioned in phase having 'weaker' bonds. Since the Si–O bonds in silicates are stiffer compared to Si-Fe bonds, the heavier isotopes get preferentially incorporated into silicates and lighter isotopes get enriched in metals (Georg *et al.*, 2007).

Our comprehensive investigation of Si isotopic composition from phase separates of different EH3 chondrites has revealed variable  $\delta^{30}$ Si compositions among different micro-phases of EH3 chondrite, which clearly reflects the occurrence of Si isotope fractionation among metal and silicate phases in reduced environment. The  $\delta^{30}$ Si in matrices (finely disseminated mix phase) of enstatite chondrite was found to be identical to the bulk enstatite chondrite value, with  $\delta^{30}$ Si = -0.67±0.17‰. The metals were found to possess extremely enriched in lighter Si isotopes, extending upto  $\delta^{30}$ Si = -6.94±0.09‰ (Fig. 5.6). This should not be considered as the end member of metallic phases since metals were too small to micro-mill without avoiding contamination from the surrounding silicates. The presence of highly negative  $\delta^{30}$ Si value in metallic phases of enstatite chondrite has been already established from theoretical, (Georg *et al.*, 2007, Javoy *et al.*, 2012), experimental (Shahar *et al.*, 2009, 2011) and empirical ( $\delta^{30}$ Si ~ -6.00‰, Ziegler *et al.*, 2010) studies, which have well proven the fact that light Si isotopes get partitioned into metal under reducing conditions (Savage and Moynier, 2013).

Because enstatite is the primary mineral of enstatite chondrites, so it is the key component to understand the conditions and processes that prevailed during the formation of these meteorites (Hsu et al., 1998). Experimental studies by Savage and Moynier, (2013) & Fitoussi and Bourdon, (2012) have revealed that  $\delta^{30}$ Si value of the non-magnetic components of EH and EL chondrite is heavier than bulk meteorite sample. The heaviest Si isotope composition in an enstatite separate of EH3 chondrite was determined to be  $\delta^{30}$ Si = -0.38 ± 0.03‰ by Fitoussi and Bourdon, (2012) with an average  $\delta^{30}$ Si = -0.49 ± 0.07‰. Savage and Moynier, (2013) determined average  $\delta^{30}$ Si value of enstatite mineral separate from enstatite chondrites to be  $-0.51 \pm 0.13\%$ , which is considerably heavier than Si isotopic composition of bulk EH3 chondrite  $(\delta^{30}\text{Si}=-0.77\pm0.08)$ . In such studies, 1–5 g of meteorite samples were first ground to a fine powder using an agate/boron carbide mortar and then the metal-free fractions were separated using hand magnet or by hand-picking of enstatite grains under a microscope. The samples were digested in silver crucible and processed for further Si isotopic analyses. But as seen in BSE images of enstatite chondrite, the presence of disseminated metals within bulk enstatite chondrite is prominent in sub-micron scale. Therefore, it seems impossible to separate pure silicate fraction from metals using hand magnet. Apart from in situ analyses, micro milling of the pure phases followed by the isotopic analysis of distinct phases is a better option to effectively measure the isotopic composition of silicate and metals within enstatite chondrite.

Therefore, to better quantify the Si isotopic composition of silicate phases of EH3 meteorite, we have carefully micro milled a few silicate grains with little contamination from any metal and then processed further for Si isotopic analyses. Surprisingly, we have found a much heavier isotopic signature of  $\delta^{30}$ Si =  $-0.33\pm0.11\%$ , n=15 in these silicate phases, which is similar to the Si isotopic composition of BSE ( $\delta^{30}$ Si =  $-0.29\pm0.08\%$ , Savage *et al.*, 2010) within analytical uncertainties (Fig. 5.6). The heavy  $\delta^{30}$ Si of silicates in enstatite chondrite is in agreement with ab initio calculations predicting heavier isotopic enrichment in silicates condensing from SiO and SiS nebula gas (Javoy *et al.*, 2012).

It is however, crucially noticed that presence of even an extremely small fraction of metal in these silicate phases was enough to shift the isotopic ratio of silicates to a significantly lighter side. As a result, a broad range of Si isotopic compositions were determined based on the variation of silicate: metal ratio present in the sample.



**Figure 5.6:** Variation of Si isotopic composition among different micro phases of EH3 chondrites. The yellow band represents the range of Si isotope composition established for BSE in the literature.

From fig. 5.7, it can be seen that isotope data fall on a mass dependent fractionation line in a three-isotope plot of Si. This indicates the absence of any interferences or mass independent fractionation either related to chemical or nucleosynthetic origin among various phases of EH3 Chondrite. Si isotopic data from phase separates of EH3 chondrites are provided in Table 5.1.



Figure 5.7: Mass dependent Si isotopic fractionation among micro-phases of EH3 chondrite.

Table	<b>5.1</b> .	Si	isoto	pic co	mpo	osition	of	phase s	separates	from	EH3	meteorites

	δ <sup>29</sup> Si (‰)	2 SD	δ <sup>30</sup> Si (‰)	2 SD	Mg/Si	Fe/Si
Silicates						
PCA 91461 (EH3)	-0.14	0.03	-0.32	0.10	1.06	0.007
PCA 91461 (EH3)	-0.18	0.03	-0.38	0.11	0.99	0.009
PCA 91461 (EH3)	-0.15	0.04	-0.27	0.06	0.99	0.004
PCA 91461 (EH3)	-0.17	0.05	-0.39	0.05	0.99	0.009
PCA 91461 (EH3)	-0.22	0.09	-0.41	0.06	0.99	0.008
PCA 91461 (EH3)	-0.16	0.03	-0.30	0.07	1.02	0.006
PCA 91461 (EH3)	-0.18	0.09	-0.39	0.05	1.05	0.006
PCA 91461 (EH3)	-0.18	0.04	-0.35	0.06	1.04	0.005
PCA 91461 (EH3)	-0.16	0.07	-0.29	0.06	1.03	0.008
LAR 06252 (EH3)	-0.14	0.08	-0.28	0.07	-	-
LAR 06252 (EH3)	-0.23	0.07	-0.41	0.06	-	-
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LAR 06252 (EH3)	-0.20	0.09	-0.37	0.08	-	-
MIL 07028 (EH3)	-0.15	0.06	-0.31	0.09	-	-
MIL 07028 (EH3)	-0.16	0.05	-0.28	0.07	-	-
Y 961(EH3)	-0.14	0.05	-0.27	0.07	-	-
Average	-0.17	0.06	-0.33	0.11	1.01	0.006
Matrices						
PCA 91461 (EH3)	-0.36	0.05	-0.78	0.06	0.89	0.38
PCA 91461 (EH3)	-0.34	0.02	-0.65	0.05	0.84	0.63
PCA 91461 (EH3)	-0.34	0.02	-0.69	0.07	0.80	0.60
PCA 91461 (EH3)	-0.38	0.05	-0.74	0.07	0.76	0.28
PCA 91461 (EH3)	-0.41	0.03	-0.85	0.09	0.64	0.61
PCA 91461 (EH3)	-0.29	0.05	-0.66	0.05	-	-
PCA 91461(EH3)	-0.28	0.04	-0.58	0.06	-	-
Y 961(EH3)	-0.32	0.05	-0.68	0.09		
Y 961(EH3)	-0.27	0.04	-0.67	0.05		
LAR 06252 (EH3)	-0.25	0.04	-0.66	0.11		
MIL 07028 (EH3)	-0.27	0.04	-0.69	0.06		
MIL 07028 (EH3)	-0.29	0.02	-0.57	0.09		
Average	-0.35	0.18	-0.67	0.17		
Metals						
PCA 91461 (EH3)	-3.60	0.11	-6.71	0.19	0.002	34.36
PCA 91461 (EH3)	-2.54	0.10	-4.74	0.14	0.006	31.47
PCA 91461 (EH3)	-2.41	0.07	-4.49	0.14	0.001	31.62
PCA 91461(EH3)	-2.57	0.09	-4.69	0.10	0.005	31.93
PCA 91461 (EH3)	-2.13	0.09	-4.01	0.16	0.008	31.46
PCA 91461 (EH3)	-2.42	0.07	-4.40	0.10	0.008	31.18
PCA 91461 (EH3)	-2.53	0.13	-4.74	0.18	0.008	30.35

LAR 06252 (EH3)	-2.41	0.12	-4.49	0.15	0.002	33.41
LAR 06252 (EH3)	-2.57	0.09	-4.69	0.12		32.01
PCA 91461 (EH3)	-3.69	0.07	-6.94	0.09		33.39
PCA 91461 (EH3)	-3.03	0.06	-6.09	0.08		32.42
MIL 07028 (EH3)	-3.32	0.08	-6.73	0.10		33.69
MIL 07028 (EH3)	-3.52	0.08	-6.59	0.09		31.80
Average	-2.82	1.06	-5.33	2.17		
PARSA METAL	-2.06	0.07	-4.11	0.15		

## **5.5 Discussion**

## 5.5.1 The evolution of Si and Mg isotopes in reduced vs. oxidized nebula

As discussed in chapter 4, resolvable statistical variation in Si isotopic composition is not evident between ordinary ( $\delta^{30}$ Si = -0.42±0.07‰), carbonaceous ( $\delta^{30}$ Si = -0.41±0.06‰) and HED meteorites ( $\delta^{30}$ Si = -0.42±0.05‰) based on Si isotope analyses in bulk meteorite samples. In addition, Mg isotope composition also appears homogenous among these groups of meteorites (Mean  $\delta^{26}$ Mg= -0.27±0.07‰). Considering the insignificant differences in overall isotopic composition among these meteorites, it is reasonable to argue that initially the nebula had a homogenous Si and Mg isotopic reservoir (Illustrated as Stage I in Fig. 5.8) similar to that of carbonaceous chondrites. The origin of carbonaceous chondrites from relatively unfractionated homogenous material is further supported by the similarity in relative abundances of refractory lithophile elements between CI chondrites and solar photosphere (Lodders and Fegley 1998, Lodders 2003). The fact that carbonaceous chondrites have Mg/Si = ~1 also suggests that these meteorites have retained its Mg/Si ratio established by nucleosynthesis (McSween, 1979 and references therein). As the homogenous nebula started evolving, it was gradually partitioned into two different reservoirs of Si with varying C/O ratio. Si is the one of the elements that got influenced by change in oxygen fugacity, as illustrated in Stage II of Figure 5.8.

i) Reduced reservoir closer to Sun with C/O ratio greater than solar C/O ratio (>0.8). Due to unavailability of oxygen in reducing conditions, silicon formed alloy with metals and thus got incorporated into metallic phases. The partitioning of silicon among metal and silicate phases led Si isotopes to get fractionated in the inner region of solar system.

ii) Away from the Sun, the environment was oxygenated with solar C/O ratio (<0.6). In such conditions, Si cannot partition into metals and gaseous Si gets quantitatively condensed in silicate phases. As such, no Si isotope fractionation is expected to occur in oxygen-dominated nebula. The similar isotopic composition of relatively oxidized HEDs, ordinary-carbonaceous chondrite, SNCs and ureilites indicates that the parent bodies of these meteorites have avoided any Si isotope fractionation during metal-silicate segregation. Therefore these meteorites must be sampling an isotopically homogeneous reservoir that has preserved the pristine  $\delta^{30}$ Si signature of solar nebula.

Moreover, enstatite chondrites and its phase separates have been found to possess similar Mg isotopic composition as that of any other chondrites (ordinarycarbonaceous chondrite, HEDs, SNCs, Ureilites). The most probable cause for the different Si but similar Mg isotopic composition of enstatite chondrite compared to any other chondrites is that unlike silicon, magnesium isotopes remains strictly lithophilic in both reducing and oxidizing conditions. Therefore, Mg isotopes never got partitioned into metals and as such Mg was quantitatively condensed into silicates. Therefore Mg isotopes have remained homogeneously distributed among all planetary bodies.

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**Figure 5.8:** An illustration of Si and Mg isotopic evolution in different accretionary regions of the solar nebula. Stage 1 illustrates homogenous nebula with carbonaceous chondritic Mg and Si isotopic composition. Stage 2 represents the separation of nebula into a reduced and oxidized counterpart. Being formed under oxidizing environment; the HED meteorites, carbonaceous chondrites (CC) and ordinary chondrites (OC) escaped Si isotope fractionation during metal-silicate segregation and hence these planetary bodies preserve pristine  $\delta^{30}$ Si value of the solar nebula. Enstatite chondrite (EC) formed in reduced nebula where Si isotopes underwent metal-silicate partitioning and hence its isotope composition was altered relative to initial carbonaceous chondritic composition. Mg remained strictly lithophilic in both oxidizing and reducing environment and therefore isotopes of Mg did not undergo any fractionation.

#### 5.5.2 Silicon isotopic composition of enstatite chondrite

Since Si behaves strictly lithophilic in oxygen-dominated nebula, the planetary bodies that formed in such regions (ordinary-carbonaceous chondrites, HEDs, SNCs) avoided any Si isotope fractionation during metal-silicate segregation and hence they must be preserving pristine Si isotopic signature of solar nebula. Therefore, it is safe to presume that initially the composition of solar nebula was homogeneous and similar to carbonaceous chondritic composition ( $\delta^{30}$ Si =  $-0.41\pm0.06\%$ ) in terms of Si isotopic distribution. The difference in Si isotopic composition of enstatite chondrite compared to other meteorites reflects some very specific processes that occurred in the inner reaches of solar system where reduced conditions prevailed. Two likely causes to fractionate Si isotopes in inner reduced solar nebula compared to outer oxidized region are the incorporation of lighter Si isotopes in metal and the loss of gaseous silicate reservoir by solar wind. The effect of these two processes in fractionating Si isotopes are detailed below.

Let us assume that the incorporation of fraction 'f' of total nebular Si into metal (with preferential partitioning of lighter isotopes of Si with  $\delta^{30}$ Si= -6.9‰, lightest Si measured in metal) had enriched the residual silicate gas reservoir (SiO+SiS) in heavier  $\delta^{30}$ Si of -0.29‰ relative to initial carbonaceous chondritic composition ( $\delta^{30}$ Si = -0.41±0.06‰). If this is the case, then 'f' can be calculated using simple mass balance equation using the following relationship 5.1:

$$f \times \Delta_{\text{CC-Metal}} = (1-f) \times \Delta_{\text{CC-Earth}} ---(5.1)$$

where  $\Delta_{\text{CC-Metal}} = \delta^{30} \text{Si}_{\text{carbocaceous chondrite}} - \delta^{30} \text{Si}_{\text{metal of EC}}$ ,  $\Delta_{\text{CC-Earth}} = \delta^{30} \text{Si}_{\text{carbocaceous chondrite}} - \delta^{30} \text{Si}_{\text{BSE}}$  and 'f' refers to fraction of total nebular Si in metal.

The value of f' comes out to be 1.8±0.65%, which is within the range of Si concentrations that have been reported in metal fractions of enstatite chondrites (Weisberg *et al.*, 1995; Hutson *et al.*, 2000). To account for any higher difference in  $\delta^{30}$ Si value between carbonaceous/ordinary chondrite and BSE, more fractions of Si are required to be incorporated into the metal. In other words, the results clearly show that the removal of nearly ~1-3% of light Si isotopes in metals with ( $\delta^{30}$ Si~ -6.9‰) is

able to alter the residual SiO reservoir towards a heavier  $\delta^{30}$ Si composition that is observed in BSE and silicate phases of enstatite chondrites (up to -0.29‰).

Nevertheless, the distribution of Si isotopes could also be affected by the significant loss of silicate reservoir by violent solar wind in the proximal regions of Sun. By taking  $\delta^{30}$ Si<sub>nebula</sub>= $\delta^{30}$ Si<sub>CC</sub> and  $\delta^{30}$ Si<sub>lost</sub>= $\delta^{30}$ Si<sub>BSE</sub>, the following mass balance equation can be used to calculate the fraction *f* of Si that was either never accreted into enstatite chondrite parent body or eventually lost from it:

$$\delta^{30} Si_{CC} = f \times \delta^{30} Si_{BSE} + (1 - f) \times \times \delta^{30} Si_{EC} ---(5.2)$$

Taking Si isotopic compositions of CC (carbonaceous chondrite), EC (enstatite chondrite) and BSE, f comes out to be 0.65 or 65%. Therefore, relative to carbonaceous chondrite formation regions where condensation is assumed to be 100%, only 35% of gaseous SiO (and SiS) was able to condense into solids in inner enstatite chondrite forming region. This is inline with most of the enstatite chondrite formation models that invokes condensation of its respective minerals from a reduced nebular gas over a broad temperature range and a substantial loss of materials from enstatite chondrite forming region (Grossman *et al.*, 2008; Hutson and Ruzicka, 2000 and references therein). The lost gaseous silicate reservoir from the inner solar system could have either accreted onto any nearby planetary embryo or removed completely by violent solar or accreted into proto-Sun.

Mg is an element that remains closely associated with Si due to the similarity in their condensation temperature and therefore most of the silicates found on terrestrial and extra-terrestrial rock samples are made up of Mg, Si bonded together by O. If heavier  $\delta^{30}$ Si composition in BSE and silicate fractions of enstatite chondrite had been because of substantial loss of silicate reservoir in inner solar system, then we should expect to observe similar extent of fractionation in Mg isotopes too. But till date no such Mg isotope fractionation has been reported among planetary bodies. Therefore we can say that the incorporation of extremely light Si isotopes in metallic phases ( $\delta^{30}$ Si ~ <- 6.94±0.16‰) in reduced environment of Sun's proximal region was the most important parameter that fractionated Si isotopes across planetary materials rather than stripping away of gaseous reservoir by solar wind in inner regions of solar system.

# 5.5.3 Origin of Si isotope heterogeneity within enstatite (EH3) chondrite

The existence of a chemical gradient in the solar nebula is very likely, with enstatite chondrite like reduced materials forming in inner high temperature regions of the proto-planetary disk and carbonaceous chondrite like more oxidized material occurring preferably farther away from the Sun. The consistency in Si isotopic composition of bulk silicate Earth and silicate fraction of enstatite chondrites provides very strong evidence that enstatite chondritic like planetary bodies and the Earth were formed from similar reduced isotopic reservoir of inner protoplanetary disc. Therefore, the formation sequence of Earth can be constrained by understanding the dynamics of enstatite chondrite forming region.

The highly-reduced character of enstatite chondrite indicates its formation in nebular region with higher C/O ratio (>0.8) than the solar value (<0.6) (Larimer and Bartholomay, 1979; Tsuchiyama et al., 1995). The incorporation of significantly light Si isotope in the metallic phase ( $\delta^{30}$ Si = -6.94±0.09‰) of EH3 chondrite is possible only in nebular environment where fractionations are kinetically controlled as the highest equilibrium Si isotopic fractionation experimentally determined by Shahar et al. (2009, 2011) is ~2‰. Larimer and Bartholomay, (1979) suggested that in a reducing environment with high C/O ratio, the condensation temperature of all silicates and oxides gets markedly dropped by 400°C as compared to silicates and oxides that condenses in solar C/O ratio (Fig. 5.9). In such an extreme environment, the condensation temperature of only metallic Fe remains unaffected since its condensation temperature is independent of the availability of oxygen in the nebula and as such Fe behaves as an ultra refractory phase (~1400°C) among condensates of inner solar nebula. Thus, in reduced conditions, iron (along with other siderophilic elements) appears before silicates in the condensation sequence (Larimer and Batholomoy, 1979). Unlike carbonaceous-ordinary chondrite forming region, the significant temperature difference between the first appearance of metals and silicates in reduced conditions suggests a significant a time lag between formation of metals and silicates. Since Si alloys easily with Fe in reduced regions, therefore metals

incorporating extremely light isotopes of Si is likely to have condensed earlier than corresponding silicates. The fact that silicates formed or equilibrated later than the metals in enstatite chondritic region is also corroborated by Hf-W systematics, which suggests a time gap of 13.8±5.3 Ma between formation of magnetic and non-magnetic components of enstatite chondrite (Lee and Halliday, 2000).

Presence of both light and heavy Si isotopes in the same body of enstatite chondrite is intriguing. Assuming that the gas has remained in contact with the condensed solids, it is very likely that the condensation of extremely light Si enriched metals ( $\delta^{30}$ Si  $\leq$  - 6.94±0.09‰) had altered the residual silicate reservoir towards heavier  $\delta^{30}$ Si value (see previous section). As this silicate gas reservoir cooled further, the major Si and Mg bearing mineral *i.e.*, forsterite (Mg<sub>2</sub>SiO<sub>4</sub>, Mg/Si=2) started to condense from the residual silicate gaseous reservoir with  $\delta^{30}$ Si ~  $\geq$  -0.29. As the nebula temperature kept on decreasing, the remaining forsterite reacted back with SiO (or SiS) gas to form



**Figure 5.9:** The condensation temperature at which oxides and silicates first appear in a cooling cosmic gas decreases with the increase in C/O ratio from solar value (C/O = 0.6) to highly reduced gas (C/O =1). Fe remains unaffected as its condensation temperature does not depend on the amount of O available. Image and text credit: Larimer and Bartholomay, (1979).

enstatite at ~700°C (Grossman *et al.*, 2006). These silicates with its characteristic heavy  $\delta^{30}$ Si value finally accreted with early-condensed metals to form enstatite chondrite parent bodies.

Although condensation of forsterite (Mg<sub>2</sub>SiO<sub>4</sub>) itself might have fractionated Si isotopes (Dauphas *et al.*, 2015) because nearly half of the Si still remains in gaseous phase when forsterite condenses but any such isotope fractionation effect should also be reflected in Mg isotope, which has not been reported so far. Moreover, any isotope fractionation that could be generated by forsterite condensation should eventually get nullified during formation of enstatite (MgSiO<sub>3</sub>). This is because the formation of enstatite (MgSiO<sub>3</sub>, Mg/Si=1) via reaction between forsterite (Mg<sub>2</sub>SiO<sub>4</sub>) and SiO (and SiS) enriched gas marks the nearly quantitative consumption of Si from gaseous reservoir when condensation sequence at C/O ratio 0.83 is taken into consideration (Fig. 5.10). Therefore, the heavier  $\delta^{30}$ Si signature in silicates of enstatite chondrite is likely to be the representative isotope proxy of the residual silicate reservoir that was significantly left altered after the preferential incorporation of extremely light Si isotopes in metallic phases of inner region of solar nebula.



**Figure 5.10:** Distribution of Si between condensed solids and vapor as a function of temperature at  $P^{tot}=10^{-4}$  atm in a system with elevated C/O ratio of 0.83. Abbreviations: Sin-sinoite, Si<sub>2</sub>Ni<sub>2</sub>O; Ab-albite, NaAlSi<sub>3</sub>O<sub>8</sub>; Qtz-quartz, SiO<sub>2</sub>; Fs-ferrosilite- FeSiO<sub>3</sub>. When forsterite condenses, half of Si still remains in gaseous phase whereas half condenses to silicate (forsterite). Thus there is a chance that Si isotopes might get fractionated during forsterite condensation. But formation of enstatite quantitatively consumes all Si from gas and hence enstatite minerals must be sampling the  $\delta^{30}$ Si of the residual silicate gas reservoir that was left altered mainly after the incorporation of light Si isotopes in metals. Image credit: Grossman *et al.* (2008).

The consistency in isotopic composition between BSE and enstatite chondrite for a large number of elements including Si suggests that the Earth also might have gradually evolved through similar sequence as that of enstatite chondrite but on a more extensive scale. It is likely that in the initial stages of Earth's formation when environmental conditions were extremely reduced, planetesimals similar to enstatite chondrite accreted together to form proto-Earth. Due to substantial time lag in the condensation of metal and silicate, the early-condensed metals could not achieve a state of equilibrium with the later formed silicates. Therefore, upon partial melting of enstatite chondrite like embryos, the metals (containing ~2-5wt% Si) segregated to the

center thereby forming the core of proto Earth without much equilibration with the silicate counterpart during very early stages of planet formation.

In the subsequent stages after the massive core and a substantial layer of silicates was already formed, the nebula in nearby regions of Earth's accretion gradually started to become relatively more oxygenated compared to starting enstatite chondritic composition and therefore the chemical pathway of proto-Earth became different from highly reduced enstatite chondrite although their isotope character remained the same. With further drop in temperature as the time progressed, enstatites formed at the expense of already condensed forsterite by reaction of forsterite with isotopically altered silicate gas reservoir. The remaining forsterite and enstatite eventually accreted together to form Bulk Silicate Earth (BSE). The presence of forsterite along with widespread presence of enstatite in BSE suggest that unlike enstatite chondrite parent bodies which contains only enstatite as the dominating silicate phase, the reaction between already condensed forsterite and SiO gas to form enstatite could not go to completion in the planetesimals that accreted to form BSE. The dearth of such partially oxygenated materials in meteorite inventory suggests that these types of planetesimals were eventually exhausted during Earth accretion. This is in line with the hypothesis that was put forward by Drake and Righter, (2002) to constrain the building blocks of Earth. Considering the fact that overall nebular composition was conserved, sequestration of forsterite (Mg/Si = 2) rich component along with significant amount of enstatite into Proto-Earth must have enhanced the Mg/Si ratio of BSE to 1.26 compared to silicate fraction of enstatite chondrite (Mg/Si = 1). This explains the distinct chemical differences that prevail between enstatite chondrites and Earth's upper mantle.

Gravitational dominance of the Jupiter during this temporal regime might have started influencing the orbit of distant asteroid (as it is happening today). As a result, a suite of ordinary chondrites/un-sampled planetary bodies could have accreted in the final stages of Earth's accretion to account for Earth's present water content and oxidation state but they may not be enough to generate detectable isotopic shift of BSE from enstatite chondrite. Thus, both nebular processes and Si partitioning in metal actively participated in fractionating Si isotopes across planetary bodies. Nevertheless,

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understanding the exact mechanism that caused heavy Si isotope enrichment in BSE, silicate phases of enstatite chondrite and angrite requires more theoretical and experimental affirmation. Since silicon isotopes are a promising tracer of physico-chemical conditions prevailing at the time of core and silicate Earth formation, we propose a schematic model for the accretion and subsequent evolution of Earth and carbonaceous, ordinary chondrite and HED parent bodies based on Si isotopic constrains, illustrated in Fig. 5.11.



**Figure 5.11:** Schematic diagram showing the accretion scenario of different chondritic parent bodies and the Earth. Ordinary-carbonaceous (OC/CC) chondrites and precursors of HED parent bodies were formed farther away from Sun in oxidized conditions where Si behaves strictly lithophilic. Hence no Si isotopic fractionation is expected to occur in such planetary bodies during silicate-metal segregation and as such these planetary bodies preserve pristine  $\delta^{30}$ Si signature of nebula. Contrary to previous scenario, enstatite chondrites were formed near the Sun in reduced environment, where Si behaves siderophilic. The incorporation of lighter isotopes of Si in metal enriches the residual silicate reservoir in heavier isotopes of Si. From such altered gas reservoir, silicates were condensed that subsequently accreted along with the metal to form enstatite chondrite parent body. The similarity in  $\delta^{30}$ Si between BSE and silicate fractions of EH3 chondrite indicates that enstatite chondrite and the Earth

were formed from similar isotope reservoir but they followed different chemical pathway. In initial stages of Earth's accretion, silicon-bearing metals segregated to form the core without much re-equilibration with the silicate counterpart. This left the residual silicate reservoir enriched in heavy Si isotopes, from where forsterite and enstatite were condensed and eventually accreted together to form BSE. Unlike enstatite chondrite formation scenario, the quantitative formation of enstatite via reaction between forsterite and SiO gas could not go to completion in Earth accretion region due to gradually evolving oxygenation. Therefore planetesimals that eventually accreted to form BSE had more proportion of forsterite compared to enstatite chondrite although their isotope composition remained the same.

This study, therefore, provides strong evidence that enstatite chondritic like planetary bodies provided major raw material during Earth's accretion. The widespread occurrence of MgSiO<sub>3</sub> (perovskite) in lower mantle, the redox state of the Earth's deep mantle below 250 km (Frost and McCammon, 2008; Fitoussi *et al.*, 2016) and the similarity of metal to silicate ratio between Earth and E-Chondrite further validates this point. Due to its unique reduced mineralogy, enstatite chondrites are often suggested to have originated closer to the Sun, at around 1 AU (Baedecker and Wasson, 1975; Kallemeyn and Wasson, 1986; Savage and Moynier, 2013). Enstatite chondritic precursor of Earth is in accordance with numerical models, which shows that the major fraction of the Earth forming materials were originated in the innermost region of solar system, not beyond 2.5 AU (Hansen, 2009; Walsh *et al.*, 2011). Based on Ru isotopic systematics and elemental abundance pattern in terrestrial rock samples and meteorites, the most recent publications by Dauphas, 2017 and Gödde and Kleine, 2017 also argue that majority of material that accreted to form the Earth always comprised a large fraction of enstatite chondrite type impactors.

Based on our Si isotope data, we suggest that Earth has undergone a kind of heterogeneous accretion scenario, where light Si isotope bearing metals were formed and accreted earlier than the corresponding silicates with heavier  $\delta^{30}$ Si signature. Although there occurs substantial time lag between formation of metals and silicates in reduced environment corresponding to a temperature difference of 400°C (Larimer and Bartholomay, 1979) but no such time lag exists in oxygenated nebula. According to thermodynamic calculations performed by Grossman, (1972), there hardly occurs a

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temperature difference of 20-30K between first appearance of metallic Fe and silicates (Diopside and Forsterite). Therefore, unlike reduced planetary bodies, it is extremely likely that the metals and silicates were condensed almost simultaneously in planetesimals that formed in oxygenated environment and was differentiated later on due to sinking of heavier metals into the bottom of such partially molten planetary bodies. Therefore, in contrast to reduced planetesimals that underwent a type of heterogeneous accretion, the planetary bodies that were formed in oxygenated environment are likely to have undergone homogeneous accretion.

The similar Si isotope composition in BSE, bulk silicate Moon and silicate fractions of EH3 chondrite provides clue for the formation of all theses planetary bodies including impactor (Theia) in similar isotope reservoir. The heavier  $\delta^{30}$ Si of Moon and its similarity with BSE can only be explained by the derivation of a major fraction of Moon's material from the silicate Earth potentially after the core formation process in Earth had seized completely.

### 5.5.4 Angrite formation in complementary C/O reservoir

Any model to account for the isotope composition of Earth should also explain the heavy Si isotope composition reported in Angrites. Considering overall conserved nebular composition, the process which increases the C/O ratio in the inner reduced nebula must also produce an adjacent region with complementary C/O ratio due to diffusion of oxygen bearing migrators from inner region to the outer region.

Planetary bodies such as angrites, whose Si and O isotopic composition has been found to be similar to Earth is enigmatic and a better understanding of the formation condition of such planetary bodies demands further studies. Nebular fractionation associated with forsterite condensation is suggested to be the reason behind heavy Si isotopic composition in angrite parent bodies (Pringle *et al.*, 2013; Dauphas *et al.*, 2015). This hypothesis is based on the fact that angrites possessing heaviest  $\delta^{30}$ Si and highest Mg/Si ratio compared to any planetary bodies falls on a correlation trend defined by meteorites and BSE on a Mg/Si vs  $\delta^{30}$ Si plot. However, based on available literature data on chemical composition of angrites, BSE and other meteorites (Visscher and Fegley, 2013; Palme and O'Neill 2003; O'Neill, 1991; Lodders, 2000; Lodders and Fegley, 2011; Warren and Kallemeyn, 1990, Warren *et al.*, 1995; Mittlefehldt *et al.*, 2002 and Ringwood, 1960), we have shown that although angrites have the heaviest  $\delta^{30}$ Si among all planetary bodies but its Mg/Si ratio is much lower due to its low Mg and high Si composition (Fig. 5.12). Thus, the chemical composition of angrite does not agree with the trend shown by Dauphas *et al.* (2015) and therefore the association of heavier  $\delta^{30}$ Si of angrites with forsterite condensation is very unlikely. So, there is a need to refine the angrite forming models considering the fact that angrites have lower Mg/Si ratio in terms of chemical composition and not higher Mg/Si ratio that has been predicted based on its heavier Si isotope composition by Dauphas *et al.* (2015).

We believe that angrite parent bodies were formed in a region adjacent to Earth-Enstatite chondrite, where the oxygen fugacity got spiked up due to localized accumulation of water vapor like migrators that was diffused out from reduced enstatite chondrite region. If this is the case then large-scale exchange of gaseous reservoir from reduced nebula into the angrite forming oxidized region provides an explanation for the similar  $\delta^{30}$ Si and  $\Delta^{17}$ O of angrite as that of BSE. Thus, formation of angrite from SiO gas reservoir that has been diffused out of inner solar system could better explain the heavy  $\delta^{30}$ Si composition of angrites rather than forsterite condensation or core formation. Nevertheless, more studies are required to be carried out to establish the validity of our proposed hypothesis to explain the isotopic composition of angrites.



**Figure 5.12:** Correlation of Mg/Si with  $\delta^{30}$ Si value in planetary objects suggesting a link between processes that has fractionated Mg/Si ratio and Si isotopes in planetary materials. The three broad types of meteorites in terms of Si isotopic composition are distinguished by the grey bars. The Mg/Si ratios of meteorites and BSE are atomic ratios calculated from their respective chemical composition (Visscher and Fegley, 2013; Palme and O'Neill 2003; O'Neill, 1991; Lodders, 2000; Lodders and Fegley, 2011; Warren and Kallemeyn, 1990, Warren *et al.*, 1995; Mittlefehldt *et al.*, 2002 and Ringwood, 1960).  $\delta^{30}$ Si values of meteorites are a compilation of data from this study and published values by Armytage *et al.*, 2011; Zambardi *et al.*, 2013. Unlike Dauphas *et al.*, 2015, who postulated angrite to have higher Mg/Si ratio based on angrite's heavier  $\delta^{30}$ Si value, it is clear from this plot that Mg/Si ratio of angrites is lower and similar to enstatite chondrite compared to other chondrites

#### 5.5.5 Silicon content of the Earth's core

The isotopic similarity between enstatite chondrite and the Earth suggests that they were formed in similar silicate reservoir. Our isotopic results depicting the value of  $\delta^{30}$ Si = -0.33 ± 0.11‰ for silicate fraction and  $\delta^{30}$ Si<sub>metal</sub> = -6.94 ± 0.09‰ for metallic fraction from very primitive enstatite chondrite suggests that silicon is not only a robust tracer of the silicate reservoir of Earth but also helps us to understand the composition of Earth's core and thereby the composition of bulk Earth. Since enstatite

meteorites are the only known meteorite group that contains an appreciable concentration (on the order of 2-5 wt%) of silicon in their metallic phases (Ringwood, 1960; 1961), a direct entry of light silicon isotopes to Earth's core from enstatite chondrite like precursor materials during very early stages of planet's formation results in the incorporation of ~2-5 wt% Si in Earth's core. This indicates that at least another light element apart from Si must be present in Earth's core to explain its density deficit relative to pure Fe-Ni alloy. Apart from Si, the contribution of sulfur to the core of Earth is very promising as evinced from the presence of numerous sulfur bearing metallic phases (troilite (FeS), daubréelite (FeCr<sub>2</sub>S<sub>4</sub>)) in enstatite chondrite.

The differences in the relative abundances of Si isotopes between metal (core) and silicate (mantle and crust) are largely being used to constrain the amount Si in Earth's core and elucidate the conditions that prevailed during core segregation (Zieglar *et al.*, 2010). Our Si-isotope results from metal and silicate in metal-rich primitive enstatite chondrites (EH3) could serve as a proxy for Si isotope fractionation during Earth's differentiation.

Assuming that bulk Earth has a chondritic  $\delta^{30}$ Si value, the mass-balance equation stating the relationship between the silicon isotopic compositions of BSE, chondrite and the fraction of Si that resides in Earth's core is given by (Chakrabarti and Jacobsen, 2010b; Zambardi *et al.*, 2013; Fitoussi *et al.*, 2009; Zieglar *et al.*, 2010):

$$\delta^{30} \text{Si}_{\text{BSE}} - \delta^{30} \text{Si}_{\text{CHONDRITE}} = \Delta^{30} \text{Si}_{\text{silicate-metal}} * \text{f}_{\text{Si,CORE}} - - (5.3)$$

where,  $\delta^{30}Si_{BSE}$  and  $\delta^{30}Si_{CHONDRITE}$  are the Si isotopic composition of BSE and chondrites relative to NBS-28 and  $\Delta^{30}Si_{silicate-metal} = \delta^{30}Si_{silicate} - \delta^{30}Si_{metal}$ .  $f_{Si,CORE}$  is the mass fraction of Si present in Earth's core (Chakrabarti and Jacobsen, 2010b).

Since the estimation of Si content in planetary core is highly sensitive to  $\Delta^{30}Si_{silicate-metal}$  value, so it is important to estimate the average values of  $\delta^{30}Si$  in metals and silicates very accurately.

We have documented the first ever-measured  $\Delta^{30}\text{Si}_{\text{silicate-metal}}$  values from primitive enstatite (EH3) chondrites, which are isotopically identical to Earth and are the only chondrite group having appreciable concentration of Si in metals. The average value for silicate phases in enstatite chondrite determined in this study is  $\delta^{30}\text{Si} = -0.33 \pm$ 0.11‰, 2SD. Because it was not possible to micro mill the small metallic phases without contamination from surrounding silicates, so we assume that the most negative Si isotopic value determined in this study reflects the closest estimation of  $\delta^{30}\text{Si}$  value in metals of enstatite chondrite, with  $\delta^{30}\text{Si}_{\text{metal}} = -6.94 \pm 0.09\%$  (Fig. 5.13). This provides a revised estimation of  $\Delta^{30}\text{Si}$  silicate-metal to be 6.61±0.20‰.



**Figure 5.13:** Si isotopic composition of typical silicate, metal and matrices from PCA 91467 (EH3 chondrite).

Although beyond the scope of present study, but anchoring this metal-silicate fractionation factor in various core-forming models could provide a strict constrain on the amount of Si in Earth's core. This is a subject of further research and certainly needs to be revisited again to gain insight into the composition of Earth's core.

### 5.5.6 Implications to Mg/Si ratio of BSE

Silicon and magnesium are the major rock-forming elements of the solar system that combine to form the most diverse suite of silicate minerals known so far. Since the solar abundance ratio of Si and Mg is close to unity and they both have nearly similar condensation temperature, ideally any planetary body should preserve Mg/Si  $\sim 1$ . But the bulk Mg/Si ratios of chondrites and terrestrial planets show a variation in Mg/Si ratio, which has remained one of the most enigmatic aspects of cosmochemistry (Ringwood, 1989; Fitoussi *et al.*, 2009).

It is well known that extremely high temperature prevailed during early evolutionary stage of solar nebula where chemical fractionation was dominated by evaporation, condensation and gas reaction. As the nebula started cooling down, only three minerals were condensed from gaseous phase: Corundum (Al<sub>2</sub>O<sub>3</sub>), Fe-Ni alloy and Forsterite  $(Mg_2SiO_4)$ ; Davis and Richter, (2004). All other known minerals were subsequently formed via the reaction between already condensed minerals with the gas reservoir at different temperature intervals. The reaction between initially condensed forsterite with residual Si-rich gas to form enstatite at lower temperature is one of the most crucial reactions responsible for fractionating Mg/Si among dust and condensates (Chiba et al., 2010). This solid-gas reaction extensively fractionated Mg/Si ratio since the atomic ratio of Mg/Si in the solid changes from 2 (forsterite: Mg<sub>2</sub>SiO<sub>4</sub>) to 1 enstatite (MgSiO<sub>3</sub>). Equilibrium condensation calculation in the system of solar abundance also suggests that the reaction between forsterite with Si rich gas is a very potential reaction that is capable of changing Mg/Si ratios of solid and gas. This is due to the fact that a large fraction of Mg bearing gas condenses into solids by formation of forsterite in a cooling gas reservoir whereas most of Si-bearing gas condenses into solids by formation of enstatite. Therefore enstatite formation via reaction with forsterite and SiO gas largely changes the bulk Mg/Si ratio in condensates from 2 to1.

Since our high precision Si isotopic data from different micro-phases of enstatite chondrite clearly indicates isotopic similarity between BSE and silicate phases of enstatite chondrite, it is likely that the superchondritic Mg/Si ratio of BSE is also

related with the nebular condensation of silicates as Mg/Si ratio correlates with  $\delta^{30}$ Si among meteorites and BSE (Fig. 5.12). Although enstatite chondrites are characterized by lower Mg/Si, Al/Si ratios (~0.65-0.70) compared to chondrites (~1) (Larimer and Anders, 1970; Baedecker and Wasson, 1975) but there are ample evidences which suggest that rather than being depleted in Mg, enstatite chondrites are actually enriched in Si due to incorporation of Si in both silicate and metallic phases. It is worth noticing that the silicate portion of enstatite chondrite comprises primarily of enstatite (MgSiO<sub>3</sub>) where Mg/Si=1. Since enstatite (in the form of perovskite) is the major component of mantle rocks, we believe that mixing of perovskite (MgSiO<sub>3</sub>, Mg/Si = ~1) with forsterite (Mg<sub>2</sub>SiO<sub>4</sub>, Mg/Si = ~2) during earth's accretion could be a likely reason for the origin of super chondritic Mg/Si of BSE (Mg/Si = 1.25).

In condensation sequence of minerals at a high C/O ratio, forsterite appears at least 100K before enstatite (Larimer and Bartholomay, 1979). As the time progresses, enstatite starts appearing at the expense of forsterite through reaction with SiO (or SiS). In other words, initial condensation of silicate in enstatite chondrite forming region is relatively forsterite rich (Mg/Si~2) that evolves through time towards enstatite rich (Mg/Si~1). We believe that the Earth (and Moon) accreted early from forstertite-enstatite rich embryo where enstatite formation could not go to completion whereas in enstatite chondrite forming regions such reaction could go to completion. The presence of both forsterite (Mg/Si = ~2) and enstatite (Mg/Si = ~1) in planetesimals that accreted to form silicate reservoir of Earth explains the superchondritic Mg/Si of BSE.

## 5.5.7 Simultaneous Si and Mg isotope analyses in silicate and matrices of EH3 chondrite: Implications to nebular fractionation *vs.* impact vaporization

To test the involvement of any impact related planetary processes in fractionating Si isotopes, we have carried out Mg isotopic analyses in the same aliquot of silicate and matrices of EH3 chondrite where Si isotopic analyses were performed. For Mg

purification from the same aliquot of meteorite sample, Na were first removed using 75-80 ml 0.2N HNO<sub>3</sub> and elution of 'Mg+cations' was carried out using 20 ml 3N HNO<sub>3</sub>. Further purification of Mg was carried out using 25 ml 1N HNO<sub>3</sub> with 2 ml BioRad cation exchange resin AG 50W-X8 (200–400 mesh) as detailed in Chapter 3 (Sikdar and Rai, 2017).

It is observed that in objects that have experienced high degree of evaporation like CAIs (the first formed objects of the solar system) and evaporative residues from CMAS melt, the degree of Mg isotope fractionation is twice of Si isotope fractionation (Clayton *et al.*, 1988; Davis *et al.*, 1990; Grossman *et al.*, 2000; Sugiura *et al.*, 2004).

Therefore, it is reasonable to expect a higher extent of Mg isotope fractionation than Si isotopes during any large-scale planetary processes that are governed by impact related volatilization and evaporation. Although large mass-dependent Si isotopic fractionation is evident among different phases of enstatite chondrite, the Mg isotopic composition of the silicate and matrix fractions of enstatite chondrite ( $\delta^{26}Mg = -0.31\pm0.08\%$ , 2 SD) is found to be uniform and identical to  $\delta^{26}Mg$  of bulk chondrite and BSE within instrumental uncertainties ( $\delta^{26}Mg = -0.28\pm0.05\%$ ) (Fig. 5.14).

Hence the Si isotopic signatures of BSE are unlikely to have been affected by volatilization and vaporization of silicate vapor during giant interplanetary impacts, parent body alteration, impact erosion of Earth's surface or any such aftermath Earth shaping processes. Similar Si isotope signature in bulk silicate Earth and bulk silicate moon ( $\delta^{30}$ Si= -0.29±0.08‰, Armytage *et al.*, 2011) also suggests that aftermath planetary processes did not induce any substantial Si isotopic shift that could be measured within levels of current instrumental uncertainties.

We, thus conclude that the isotopic composition of Si and Mg in Earth was set during nebular stage where kinetic fractionations were dominant over equilibrium fractionations. Nebular Si isotopic fractionation accompanying condensation of light Si bearing metal from reduced nebula and stripping away of a substantial fraction of gas reservoir is likely to have played a dominant role in causing Si isotope offset between BSE and chondrites rather than equilibrium Si isotopic fractionation during high temperature-pressure core-mantle segregation event. The similarity of Mg and Si isotope composition in silicate fractions of EH3 chondrite with the BSE provides a strong proof suggesting that the Earth has inherited its Si isotopic signature directly from condensation of light Si isotope bearing metals followed by isotopically heavier silicates during its accreting stage from a reduced nebula. Mg isotopes have escaped any such isotope fractionation due to its strict lithophilic behavior in both reduced and oxygenated environment.



**Figure 5.14:** Mg isotopic composition among silicates and matrices of enstatite chondrite appear chondritic and similar to BSE within instrumental uncertainties

## **CHAPTER 6**

## **CONCLUSIONS AND FUTURE SCOPE**

#### 6.1 Summary and conclusions

Enstatite chondrites are a very rare and enigmatic group of meteorites that represent only 2% of total meteorite falls on Earth. Its unique mineralogy suggests that they were formed in a highly reduced environment, closer to the Sun (Mason, 1966; Keil, 1989). The most striking feature of enstatite chondrite is its similarity with terrestrial rock samples with respect to a number of stable isotope systematics such as O, N, Cr, Ni, Mo, Ti, Ca, Os, Ru and Nd etc. The isotopic similarity of enstatite chondrite and BSE is suggested to indicate a generic relationship between enstatite chondrite and the Earth (Javoy *et al.*, 2010).

Since silicon is one of the most abundant elements in the entire solar system, the distribution of silicon isotopes among meteorites and BSE plays a vital role in constraining the actual building blocks of Earth. Assuming that equilibrium Si isotope fractionation has occured between metal and silicate at high temperature prevailing in core of Earth, a number of recent studies have focused on estimating the Si content in Earth's core based on the fact that  $\delta^{30}$ Si of BSE is heavier than chondrite. From the ~0.15‰ offset in  $\delta^{30}$ Si value between chondrites (excluding enstatite chondrite) and BSE, the presence of ~5-16% Si in Earth's core has been suggested (Georg *et al.*, 2007; Fitoussi *et al.*, 2009 Armytage *et al.*, 2011; Zambardi *et al.*, 2013). With respect to silicon isotopes, enstatite chondrites show larger offset from BSE compared to any other groups of meteorites. Accordingly, if the discrepency in  $\delta^{30}$ Si value between enstatite chondrite and BSE is taken into account then the estimated amount of Si in Earth's core changes to ~23%, which is geophysically impossible. Despite having

isotopic similarities for a number of elements, the relatively larger difference in silicon isotopic composition between BSE and bulk enstatite chondrites led Fitoussi and Bourdon, (2012) to preclude enstatite chondrites as a main precursor of Earth-Moon system (Dauphas *et al.*, 2014a).

However, Savage and Bourdon, (2013) have shown that the non-magnetic phases (*i.e.* the silicates) of enstatite chondrites have heavier Si isotope composition than bulk enstatite chondrite. This suggests the possibility of light Si isotopic enrichment in its metallic phases and thus a heterogeneous distribution of Si isotopes within different phases of enstatite chondrite. Therefore, before deeming off enstatite chondrites as a potential building block of Earth, it is extremely vital to have a sound knowledge on the extent of Si isotopic heterogeneity within enstatite chondrite. Savage and Bourdon, (2013) used hand magnets to separate magnetic and non-magnetic fractions of enstatite chondrite. Due to the presence of disseminated metals throughout enstatite chondrite, it is very difficult to sample purest end members of metals and silicates from such meteorite. Apart from *in-situ* Si isotope measurements, micro-milling the metals and silicate fractions followed by their Si isotope analyses is the best alternate option to precisely measure the extent of Si isotope heterogeneity within enstatite chondrite. Our primary objective in this research work was to carry out high precision silicon isotopic measurements in different micro-phases of primitive enstatite (EH3) chondrites (silicates, metals and matrices) to estimate the range of Si isotopic fractionation among its various constituents. Since our work involved handling of micro-phases of meteorites, a new alkali digestion method was developed to digest the extremely small amount of samples in Teflon vial.

Apart from core formation, impact volatilization and evaporation are also suggested as a likely cause to generate the heavier Si isotope composition of the terrestrial samples compared to chondrites. Impact related evaporation and vaporization are expected to cause more extensive fractionation among Mg isotopes compared to Si isotopes as evinced by the Si and Mg isotope composition of CAIs and evaporative residues from CMAS melt (Clayton *et al.*, 1988; Davis *et al.*, 1990; Grossman *et al.*, 2000; Sugiura *et al.*, 2004). Thus, the respective roles played by impact vaporization and core formation to fractionate Si isotopes could be understood by carrying out simultaneous Si and Mg isotope analyses in terrestrial samples, meteorites and phase separates of EH3 chondrites. In order to constrain the origin of Si isotopic fractionation to either nebular *vs* parent body/impact related processes, a number of terrestrial and extra-terrestrial rock samples were analyzed using a newly developed chromatographic protocol that allowed simultaneous purification of Si and Mg from a single aliquot of rock sample (Sikdar and Rai, 2017).

The robustness of the chemical purification procedure and mass spectrometric technique has been assessed by isotope measurements of Si and Mg in seven USGS rock reference powder. All isotopic analyses were carried out using Neptune Plus MC-ICPMS in pseudo-high resolution mode at Physical Research Laboratory, India. During Si and Mg isotopic analyses, the instrumental mass bias was corrected by sample-standard bracketing technique using internationally recognized standards NBS-28 and DSM-3 respectively. The long-term reproducibility of  $\delta^{30}$ Si and  $\delta^{26}$ Mg were found to be better than 0.09‰ and 0.08‰ (2 SD) respectively.  $\delta^{30}$ Si of the terrestrial rock standards analyzed in this study was found to lie in a limited range from -0.21 to -0.28‰ whereas the  $\delta^{26}$ Mg values ranged from -0.12 to -0.87‰.

Silicon isotopic analyses were carried out for 28 bulk meteorites, whose  $\delta^{30}$ Si value ranged from -0.71‰ to -0.38‰. In agreement with previous studies by Georg *et al.* (2007); Armytage *et al.* (2011) and Zambardi *et al.* (2013), we also found that all meteorites display slightly lighter  $\delta^{30}$ Si value compared to BSE. Mg isotopic analyses were carried out in same aliquot of meteorite sample where Si isotopic measurements were performed. The  $\delta^{26}$ Mg value in meteorites was found to range from -0.23±0.09‰ to -0.33±0.08‰, with an average of  $\delta^{26}$ Mg= -0.27±0.07‰. From the isotopic data, it is clear that although broadly homogeneous Mg isotope composition prevails among planetary bodies but isotopes of Si are fractionated. In terms of Si isotope signature, three distinct planetary reservoirs could be distinguished: (i) enstatite chondrite characterized by the lightest  $\delta^{30}$ Si, with EH chondrites being lighter than EL chondrites/aubrites (ii) carbonaceous-ordinary chondrites, HEDs, SNCs, ureilites characterized by pristine  $\delta^{30}$ Si, and (iii) terrestrial rocks, lunar meteorites and angrites displaying a heavier  $\delta^{30}$ Si compared to chondrites. To understand the reason behind the light silicon isotope enrichment in enstatite chondrite, we have micromilled different micro-phases (metals, silicates and matrices) from primitive EH3 chondrites, digested them and purified for silicon using the newly established chromatographic protocol (Sikdar and Rai, 2017). High precision silicon isotopic analyses in the micro-phase separates of enstatite chondrite highlight the presence of significant enrichment of light Si isotopes in metallic phases of enstatite chondrites. Surprisingly, a much heavier  $\delta^{30}$ Si signature was measured in the silicate fractions of enstatite chondrites, which is remarkably similar to the range of silicon isotopic values that has been established for terrestrial rock samples in recent past. Thus, this work has added Si to the long list of elements where an isotopic similarity between enstatite chondrite and BSE has been already documented thereby providing a very strong clue for the formation of Earth and enstatite chondrite from similar isotope reservoir. We have also found homogeneous distribution of Mg isotopes within silicates and matrices of enstatite chondrite, whose range is similar to BSE and bulk chondrites.

Based on results from our present work, the following conclusions can be drawn:

- The similarity in Si and Mg isotopic composition among HEDs, ordinary and carbonaceous chondrites indicate that Si and Mg escaped isotopic fractionation during metal-silicate segregation in oxidized conditions due to its strict lithophilic nature in such environment and hence these planetary bodies preserves pristine Si and Mg isotopic signature of the solar nebula.
- The enstatite chondrites and the Earth were formed near the Sun from a reduced nebula. In such environment, Si started behaving siderophilic and lighter isotopes of Si (δ<sup>30</sup>Si ≤ -6.94±0.09‰) were preferentially partitioned into metals. Condensation of light Si isotope bearing metals in the proximal regions of Sun altered the isotopic composition of residual nebula to heavier side. From such isotopically altered gas reservoir, the silicates ultimately condensed with its characteristic δ<sup>30</sup>Si signature of ~0.1‰ heavier compared to initial carbonaceous chondritic composition. Such isotopically heavy silicates eventually accreted with the early-formed metals to form enstatite chondritic parent bodies.

- The similarity in  $\delta^{30}$ Si value between silicate fractions of enstatite chondrite and bulk • silicate Earth suggests that bulk Earth and Enstatite chondrites were formed in similar silicon isotopic reservoir. Early condensation and segregation of ~2-5 wt% silicon bearing metals without much equilibration with the surrounding silicates was the most prominent process that fractionated Si isotopes during the initial stages of Earth's formation. After a large fraction of core had already formed, the region where Earth's accretion took place became relatively more oxygenated compared to enstatite chondrite. Due to gradual oxygenation, the formation of enstatite via reaction between forsterite and SiO gas could not go to completion in the planetesimals that accreted to form BSE in the second stage. Therefore, the BSE forming planetesimals had relatively more forsterite (Mg/Si = 2) and lesser enstatite than typical enstatite chondrite. This explains the higher Mg/Si ratio of BSE (1.24) compared to enstatite fractions (Mg/Si =1) of EH3 chondrite. Although the pathway of chemical evolution of Earth was changed in the second stage but the isotope characteristics of planetesimals that accreted to form BSE remained similar to that of enstatite chondrite, which was already set in nebula after the incorporation of significant lighter isotopes of Si in metallic fractions.
- We suggest that the Earth had undergone a kind of heterogeneous accretion from reduced nebula where the metals were condensed earlier than the silicates. As a result, a significant amount of core was already formed in Earth before the silicates started appearing. In contrast, the oxidized differentiated planetary bodies like HEDs and SNCs had undergone homogeneous accretion where metals and silicates are likely to have formed almost simultaneously due to their nearly similar condensation temperature. Core formation in such oxygenated planetary bodies took place due to its partial melting followed by segregation of metallic core from surrounding silicates owning to density separation.
- The closer similarity in  $\delta^{30}$ Si composition between lunar and terrestrial samples can be best explained by the formation of a large fraction of Moon's material from the silicate fraction of Earth, potentially after core formation in Earth had seized completely.
- The angrites are likely to have formed in a region where large-scale exchange of residual gaseous SiO took place from adjacent Earth-enstatite chondrite forming region. This explains the similar  $\delta^{30}$ Si and  $\Delta^{17}$ O composition of angrites and BSE.

- The chondritic Mg isotopic signature among silicates and matrices of enstatite chondrites indicate that post accretion events like high-energy impacts; erosion and evaporation did not shift the isotopic signature of Earth. Thus the Earth must have inherited its Si isotopic signature from an initially reduced nebular setting, whereby kinetic Si isotopic fractionation accompanying condensation of light Si bearing metal in nebula have played a vital role in causing the offset between BSE and chondrites rather than equilibrium Si isotopic fractionation during metal-core segregation event.
- An enstatite chondritic Earth model limits the presence of Si in the core of Earth to <5wt%, which requires the presence of at least another light element in Earth's core apart from Si to explain the density deficit of Earth's core relative to pure Fe-Ni alloy.</li>

## **6.2 Future scopes**

- More computational simulation studies are required to minutely understand the exact processes that have caused silicon isotopic alteration of huge silicate reservoir to heavier side relative to starting carbonaceous chondritic composition.
- Further improvements in measurement techniques by the application of both standard sample bracketing and Mg external doping to correct for instrumental mass bias could improve the precision in δ<sup>30</sup>Si measurement allowing the distinction between isotopically close reservoirs.
- In situ silicon isotopic analyses in metallic (perryite, with ~15 wt% Si) and silicate fractions of EH3 meteorites could provide the exact estimation of the extent of silicon isotopic fractionation between metal-silicate in enstatite chondrites. This could be an extremely vital data to calculate the amount of Si in inner and outer core of Earth
- Simultaneous analyses of Si and Mg in chondrules, CAIs and very primitive ordinarycarbonaceous chondrites could shed light on the isotopic evolution of these planetary bodies during very initial stages of solar system formation.
- Application of <sup>60</sup>Fe-<sup>60</sup>Ni and <sup>26</sup>Al-<sup>26</sup>Mg chronometers in metallic and silicate fractions of EH3 meteorites could potentially help in estimating the time lag between silicate and metal formation in reduced nebula.

• Simultaneous study of Si isotopic composition in silicate inclusions and Fe isotopic analyses in metallic portions of iron meteorites (with special focus on iron meteorites that are counterparts of enstatite chondrites) could further constrain the origin of isotopic fractionation to core formation *vs.* nebular fractionation.

## REFERENCES

- Abraham, K. Variation of stable silicon isotopes: Analytical developments and applications in Precambrian geochemistry, *Chemie, Pharmazie und Geowissenschaft, Fachbereich.* 09: 131, 2010.
- Abraham, K., Opfergelt, S., Fripiat, F., Cavagna, A.J., de Jong, T.M.J., Foley, S.F., André, L. and Cardinal, D.  $\delta^{30}$ Si and  $\delta^{29}$ Si determinations on BHVO-1 and BHVO-2 reference materials with a new configuration on a Nu Plasma Multi Collector ICP-MS. *Geostandards and Geoanalytical Research*, **32(2)**: 193-202, 2008.
- Ahrens, L. H., Von Michaelis, H., Erlank, A.J. and Willis, J.P. Fractionation of some abundant lithophile element ratios in chondrites. *Earth and Planetary Science Letters*, 5: 45–46, 1968.
- Albarede, F. and Beard, B. Analytical methods for non-traditional isotopes, Geochemistry of non-traditional stable isotopes. *Reviews in Mineralogy and Geochemistry*, **55**: 113–152, 2004a.
- Albarede, F., Telouk, P., Blichert-Toft, J., Boyet, M., Agranier, A. and Nelson, B. Precise and accurate isotopic measurements using multiple-collector ICPMS. *Geochimica et Cosmochimica Acta*, **68(12)**: 2725-2744, 2004b.
- Allegre, C. J., Manhes, G. and Lewin, E. Chemical composition of the Earth and the volatility control on planetary genetics. *Earth and Planetary Science Letters*, 185: 49–69, 2001.
- Allegre, C. J., Poirier, J. P., Humler, E. and Hofmann, A. W. The chemical composition of the Earth. *Earth and Planetary Science Letters*, **134:** 515–526, 1995.
- Allenby, R. J. Determination of the isotopic ratios of silicon in rocks. *Geochemica et Cosmochemica Acta*, **5:** 40-48, 1954.
- Amelin, Y., Kaltenbach, A., Iizuka, T., Stirling, C. H., Ireland, T., Petaev, M. and Jacobsen, S. B. U–Pb chronology of the Solar System's oldest solids with variable <sup>238</sup>U/<sup>235</sup>U, *Earth and Planetary Science Letters*, **300**: 343–350, 2010.
- Amelin, Y., Krot, A. N., Hutcheon, I. D. and Ulyanov, A. A. Lead isotopic ages of chondrules and calcium-aluminum-rich inclusions. *Science*, **297**: 1678–1683, 2002.

- An, Y. and Huang, F. A review of Mg isotope analytical methods by MC-ICPMS. *Journal of Earth science*, **25**: 822-840, 2014.
- Anders, E., and Grevesse, N. Abundances of the elements: meteoritic and solar. *Geochimica et Cosmochimica Acta*, **53**: 197–214, 1989.
- Anderson, D. L. Composition of the Earth. Science, 243: 367–370, 1988.
- Anderson, D. L. and Isaak, D. G. Another look at the core density deficit of Earth's outer core. *Physics of the Earth and Planetary Interiors*, **131**:19–27, 2002.
- Antonangeli, D., Siebert, J., Badro, J., Farber, D. L. and Fiquet, G. Composition of the Earth's inner core from high-pressure sound velocity measurements in Fe-Ni-Si alloys. *Earth and Planetary Science Letters*, **295**: 292–96, 2010.
- Armytage, R. M. G., Georg, R. B., Savage, P. S., Williams, H. M. and Halliday, A. N. Silicon isotopes in meteorites and planetary core formation. *Geochimica et Cosmochimica Acta*, **75**: 3662–3676, 2011.
- Armytage, R.M.G., Georg, R.B., Williams, H.M. and Halliday, A.N. Silicon isotopes in lunar rocks: implications for the Moon's formation and the early history of the Earth. *Geochimica et Cosmochimica Acta*, **77**: 504–514, 2012.
- Asahara, Y., Frost, D. J. and Rubie, D. C. Partitioning of FeO between magnesiowüstite and liquid iron at high pressures and temperatures: implications for the composition of the Earth's outer core. *Earth and Planetary Science Letters*, 257: 435–449, 2007.
- Badro, J., Cote, A. S. and Brodholt, J. P. A seismologically consistent compositional model of Earth's core, *Proceedings of National Academic of Sciences*, **111(21)**: 7542–7545, 2014.
- Badro, J., Fiquet, G., Guyot, F., Gregoryanz, E., Occelli, F., Antonangeli, D. and d'Astuto, M. Effect of light elements on the sound velocities in solid iron: implications for the composition of Earth's core. *Earth and Planetary Science Letters*, 254: 233–238, 2007.
- Baedecker, P. A. and Wasson, J. T. Elemental fractionations among enstatite chondrites. *Geochemica et Cosmochemica Acta*, **39**: 735–765, 1975.
- Baker, J., Bizzarro, M., Wittig, N., Connelly, J. and Haack, H. Early planetesimal melting from an age of 4.5662 Gyr for differentiated meteorites, *Nature*, **436(7054):** 1127-31, 2005.
- Banerdt, W. B., Dehant, V., Grimm, R., Grott, M., Lognonné, P. and Smrekar, S. Probing the Interiors of Planets with Geophysical Tools, *Encyclopedia of the Solar System*, 2014.

- Baskaran, M. Handbook of Environmental Isotope Geochemistry, ISBN 978-3-642-10637-8, 2012.
- Bergquist, B. A. and Blum, J. D. Mass dependent and independent fractionation of Hg isotopes by photoreduction in aquatic systems, *Science*, **318(584**9): 417-420, 2007.
- Berthet, S., Malavergne, V. and Righter, K. Melting of the Indarch meteorite (EH4 chondrite) at 1 GPa and variable oxygen fugacity: Implications for early planetary differentiation processes. *Geochimica et Cosmochimica Acta*, **73**: 6402–6420, 2009.
- Bigeleisen, J. and Mayer, M. G. Calculation of equilibrium constants for isotopic exchange reactions, *The Journal of Chemical Physics*, **15**: 261-267, 1947.
- Binzel, R.P. and Xu, S. Chips off of asteroid 4 Vesta: Evidence for the parent body of basaltic achondrite meteorites. *Science*, **260**: 186-191, 1993.
- Birch, F. Composition of the earth's mantle. *Geophysical Journal International*, **4**: 295-311, 1961.
- Birch, F. Density and composition of mantle and core. *Journal of Geophysical Research*, **69:** 4377–4388, 1964.
- Birch, F. Elasticity and constitution of the Earth's interior. *Journal of Geophysical Research*, **57:** 227–86, 1952.
- Birch, F. The transformation of iron at high pressures and the problem of the Earth's magnetism. *American Journal of Science*, **238**: 192-211, 1940.
- Bizzarro, M., Baker, J. A., Haack, H. Mg isotope evidence for contemporaneous formation of chondrules and refractory inclusions. *Nature*, **431**: 275–278, 2004.
- Bizzarro, M., Baker, J.A., Haack, H. and Lundgaard, K.L. Rapid timescales for accretion and melting of differentiated planetesimals inferred from <sup>26</sup>Al–<sup>26</sup>Mg chronometry. *The Astrophysical Journal*, **632**: L41–L44, 2005.
- Bonnand, P., H.M. Williams, I.J. Parkinson, B.J. Wood, and A.N. Halliday. Stable chromium isotopic composition of meteorites and metal–silicate experiments: Implications for fractionation during core formation, *Earth and Planetary Science Letters*, **435**: 14-21, 2016.
- Bonsor, A., Leinhardt, Z., Carter, P., Elliott, T., Walter, M. J. and Stewart, S. T. A collisional origin to Earth's non-chondritic composition?, *Icarus*, 247: 291-300, 2015.

- Boujibar, A., Andrault, D., Casanova, N.B., Bouhifd, M.A. and Monteux, J. Cosmochemical fractionation by collisional erosion during the Earth's accretion. *Nature Communications*, **6:** 8295, DOI: 10.1038/ncomms9295, 2015.
- Bourdon, B., Tipper, E. T., Fitoussi, C. and Stracke A. Chondritic Mg Isotope Composition of the Earth. *Geochimica et Cosmochimica Acta*, **74 (17):** 5069– 5083, 2010.
- Bouvier, A. and Wadhwa, M. The age of the solar system redefined by the oldest Pb-Pb age of a meteoritic inclusion. *Nature Geoscience*, **3**: 637–641, 2010.
- Burbine, T. and O'Brien, K. Determining the possible building blocks of the Earth and Mars, *Meteoritics and Planetary Science*, **39(5)**: 667-681, 2004.
- Burbine, T., McCoy, T., Meibom, A., Gladman, B. and Keil, K. Meteoritic parent bodies: Their number and identification. *Asteroids III*, 653-667, 2002.
- Burkhardt, C., Kleine, T., Oberli, F., Pack, A., Bourdon, B. and Wieler, R. Molybdenum isotope anomalies in meteorites: constraints on solar nebula evolution and origin of the Earth. *Earth and Planetary Science Letters*, **312(3)**: 390-400, 2011.
- Canup, R. M. and Asphaug, E. Origin of the Moon in a giant impact near the end of the Earth's formation. *Nature*, **412 (6848):** 708–712, 2001.
- Cardinal, D., Alleman, L.Y., de Jong, J., Ziegler, K., and André, L. Isotopic composition of silicon measured by multicollector plasma source mass spectrometry in dry plasma mode. *Journal of Analytical Atomic Spectrometry*, 18 (3): 213–218, 2003.
- Carignan, J., Cardinal, D., Eisenhauer, A., Galy, A., Rehkämper, M. Wombacher, F. and Vigier, N. A Reflection on Mg, Cd, Ca, Li and Si Isotopic Measurements and Related Reference Materials. *Geostandards and Geoanalytical Research*, 28: 139-148, 2004.
- Carlson, R. W., Boyet, M. and Horan, M. Chondrite barium, neodymium, and samarium isotopic heterogeneity and early earth differentiation. *Science*, **316**: 1175–1178, 2007.
- Caro, G., Bourdon, B., Halliday, A.N., Quitté, G. Super-chondritic Sm/Nd ratios in Mars, the Earth and the Moon, *Nature*, **452**: 336–339, 2008.
- Chabot, N. L., Campbell, A. J., McDonough, W. F., Draper, D. S., Agee, C. B., Humayun, M., Watson, H. C.,Cottrell, E. and Saslow, S. A. The Fe–C system at 5 GPa and implications for Earth's core. *Geochemica et Cosmochemica Acta*, 72

(16): 4146-4158, 2008.

- Chakrabarti, R. and Jacobsen, S. B. The Isotopic Composition of Magnesium in the Inner Solar System. *Earth and Planetary Science Letters*, **293(3–4):** 349–358, 2010a.
- Chakrabarti, R. and Jacobsen, S. B., Silicon isotopes in the inner Solar System: Implications for core formation, solar nebular processes and partial melting. *Geochemica et Cosmochemica Acta*, **74**: 6921–6933, 2010b.
- Chakrabarti, R. Silicon isotopes: from cosmos to benthos, *Current Science*, **108(2)**: 246-254, 2015.
- Chambers, J. Forming Terrestrial Planets, Science, 344: 479-480, 2014.
- Chambers, J.E. and Wetherill, G.W. Planets in the asteroid belt. *Meteoritics and Planetary Science*, **36**: 381–399, 2001.
- Chang, V., Makishima, A., Belshaw, N. and O'Nions, R. K. Purification of Mg from low-Mg biogenic carbonates for isotope ratio determination using multiple collector ICP-MS, *Journal of Analytical Atomic Spectrometry*, **18**: 296-301, 2003.
- Chiba, H., Tachibana, S., Nagahara, H. and Ozawa, K. Reaction experiments of forsterite with Si-rich gas in molecular-beam epitaxity type vacuum furnace, *41<sup>st</sup> Lunar and Planetary Science Conference*, 2531, 2010.
- Chyba, C. F. and Sagan, C. Endogenous production, exogenous delivery and impactshock synthesis of organic molecules: An inventory for the origins of life. *Nature*, **355**: 125–132, 1992.
- Clayton R. N., Onuma N., Ikeda Y., Mayeda T. K., Hutcheon I. D., Olsen E. J. and Molini-Velsko C. Oxygen isotopic compositions of chondrules in Allende and ordinary chondrites. *Chondrules and their Origins*, Lunar and Planetary Institute, Houston, 43, 1983.
- Clayton, D. Some key issues in isotopic anomalies. *Proceedings of Lunar and Planetary Science*, **12**: 1781–1802, 1981.
- Clayton, R. N. and Mayeda, T. K. Correlated oxygen and magnesium isotope anomalies in Allende inclusions, I: Oxygen. *Geophysical Research Letters*, **4(7)**: 295-298, 1977.
- Clayton, R. N. and Mayeda, T. K. Oxygen isotopic compositions of Enstatite chondrites and Aubrites, *Journal of Geophysical Research*, **89**: 245-249, 1984.

- Clayton, R. N. Oxygen isotopes in meteorites. *Annual Review of Earth and Planetary Sciences*, **21**: 115-149, 1993.
- Clayton, R. N., Hinton, R. W. and Davis, A. M. Isotopic variations in the rockforming elements in meteorites. *Philosophical Transactions of the Royal Society* A, 325: 483–501, 1988.
- Consolmagno, G. J. and Drake, M. J. Composition and evolution of the eucrite parent body: evidence from rare earth elements. *Geochemica et Cosmochemica Acta*, 41: 1271–1282, 1977.
- Corgne, A., Keshav, S., Fei, Y. and McDonough, W. F. How much potassium is in the Earth's core? New insights from partitioning experiments. *Earth and Planetary Science Letters*, **256**: 567–576, 2007.
- Corgne, A., Keshav, S., Wood, B. J., McDonough, W. F. and Fei, Y. Metal–silicate partitioning and constraints on core composition and oxygen fugacity during Earth accretion. *Geochimica et Cosmochimica Acta*, **72**: 574–589, 2008.
- Corgne, A., Siebert, J., and Badro, J. Oxygen as a light element: A solution to singlestage core formation. *Earth and Planetary Science Letters*, **288**: 108–114, 2009.
- Cote, A. S., Vocadlo, L. and Brodholt, J. P. Light elements in the core: effects of impurities on the phase diagram of iron. *Geophysical Research Letters*, 35: L05306, 2008.
- Dauphas, N. and Schauble, E. A. Mass Fractionation Laws, Mass-Independent Effects, and Isotopic Anomalies, *Annual Review of Earth and Planetary Sciences*, 44: 709–83, 2016.
- Dauphas, N. The isotopic nature of the Earth's accreting material through time. *Nature*, **541**: 521-524, 2017.
- Dauphas, N., C. Burkhardt, P. H. Warren, and T. Fang-Zhen. Geochemical arguments for an Earth-like Moon-forming impactor. *Philosophical Transactions of The Royal Society- A Mathematical Physical and Engineering Sciences*, **372 (2024)**: 20130244, 2014a.
- Dauphas, N., Chen, J., Zhang, J., Papanastassiou, D., Davis, A. M. and Travaglio, C. Calcium-48 isotopic anomalies in bulk chondrites and achondrites: Evidence for a uniform isotopic reservoir in the inner protoplanetary disk, *Earth and Planetary Science Letters*, 407: 96-108, 2014.
- Dauphas, N., Davis, A. M., Marty, B. and Reisberg, L. The cosmic molybdenumruthenium isotope correlation. *Earth and Planetary Science Letters*, **226**: 465– 475, 2004.

- Dauphas, N., Marty, B. and Reisberg, L. Inference on terrestrial genesis from molybdenum isotope systematics. *Geophysical Research Letters*, 29: 1084–1086, 2002a.
- Dauphas, N., Poitrasson, F., Burkhardt, C., Kobayashi, H. and Kurosawa, K. Planetary and meteoritic Mg/Si and  $\delta^{30}$ Si variations inherited from solar nebula chemistry. *Earth and Planetary Science Letters*, **427**: 326-248, 2015.
- Davis, A. M., Hashimoto, A., Clayton, R. N. and Mayeda, T. K. Isotope mass fractionation during evaporation of Mg<sub>2</sub>SiO<sub>4</sub>. *Nature*, **347**: 655–658, 1990.
- Davis, A.M. and Richter, F.M. Condensation and Evaporation of Solar System Materials. *Treatise on Geochemistry*, Elsevier-Pergamon, Oxford, 1: 407–430, 2003.
- Davis, A.M. Volatile evolution and loss. *Meteorites and the Early Solar System II*. University of Arizona Press, 295–307, 2006.
- Davis, D. R., Chapman, C. R., Greenberg, R., Weidenshilling, S. J. and Harris, A. W. Collisional evolution of asteroids - Populations, rotations, and velocities, University of Arizona Press, 528-557, 1979.
- de Groot, P. A. *Handbook of stable isotope analytical techniques*. Elsevier, **2:** 1398, 2004.
- De La Rocha, C. L. and Bickle, M. J. Sensitivity of silicon isotopes to whole-ocean changes in the silica cycle. *Marine Geology*, **217**: 267-282, 2005.
- De La Rocha, C. L. Measurement of silicon stable isotope natural abundances via multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS). *Geochemistry, Geophysics, Geosystems*, **3:** 1045, 2002.
- De La Rocha, C. L. Opal-based isotopic proxies of paleo-environmental conditions. *Global Biogeochemical Cycles*, **20**: GB4S09, 2006.
- De la Rocha, C. L. Silicon isotope fractionation by marine sponges and the reconstruction of the silicon isotope composition of ancient deep water. *Geology*, 31: 423-426, 2003.
- De La Rocha, C. L., Brzezinski, M. A. and Deniro, M. J. A first look at the distribution of the stable isotopes of silicon in natural waters. *Geochemica et Cosmochemica Acta*, **64**: 2467-2477, 2000.
- De La Rocha, C. L., Brzezinski, M. A. and DeNiro, M. J. Fractionation of silicon isotopes by marine diatoms during biogenic silica formation. *Geochemica et Cosmochemica Acta*, **61(23)**: 5051–5056, 1997.
- De La Rocha, C. L., Brzezinski, M. A., DeNiro, M. J. and Shemesh, A. Siliconisotope composition of diatoms as an indicator of past oceanic change. *Nature*, 395: 680-683, 1998.
- Defouilloy, C., Cartigny, P., Assayag, N., Moynier, F., Barrat, J. A. High-precision sulfur isotope composition of enstatite meteorites and implications of the formation and evolution of their parent bodies. *Geochimica et Cosmochimica Acta*, **172**: 393–409, 2016.
- Delstanche, S., Opfergelt, S., Cardinal, D., Elsass, F., Andre, L. and Delvaux, F. Silicon isotopic fractionation during adsorption of aqueous monosilicic acid onto iron oxide. *Geochemica et Cosmochemica Acta*, **73**: 923–934, 2009.
- Ding, T., Jiang, S., Wan, D., Li, Y., Li, J., Song, H., Liu, Z. and Yao, X. *Silicon Isotope Geochemistry*. Geological Publishing House, Beijing, China, 1996.
- Dodd, R. T. *Meteorites: A petrologic-chemical synthesis*. Cambridge University Press, 337, 1981.
- Douthitt, C. B. The geochemistry of the stable isotopes of silicon. *Geochemica et Cosmochemica Acta*, **46**: 1449-1458, 1982.
- Drake, M. J. and Righter, K. Determining the composition of the Earth. *Nature*, **416**: 39–44, 2002.
- Dziewonski, A. M. and Anderson, D. L. Preliminary reference Earth model, *Physics* of the Earth and planetary interiors, **25**: 297-356, 1981.
- Ebdon, L. An Introduction to Atomic Absorption Spectroscopy. Heyden, London, 1982.
- Ehlers, E.G. and Blatt, H. Petrology: Igneous, Sedimentary and Metamorphic. NewYork, 732, 1982.
- Engström, E., Rodushkin, I., Baxter, D.C. and Öhlander, B. Chromatographic purification for the determination of dissolved silicon isotopic compositions in natural waters by high-resolution multi collector inductively coupled plasma mass spectrometry. *Analytical Chemistry*, **78**: 250–257, 2006.
- Fassel, V.A. and Kniseley, R. N. Inductively coupled plasma. Optical emission spectroscopy, *Analytical Chemistry*, **46** (13):1110A–1120a, 1974.
- Fassel, V.A. Quantitative elemental analyses by plasma emission spectroscopy. *Science*, **202**: 183–191, 1978.

- Faure, G. and Mensing, T. M. *Isotopes: Principles and Applications*, 3<sup>rd</sup> Edition. ISBN: 978-0-471-38437-3, 2004.
- Faure, G. *Principles of isotope geology*. University of Minnesota, Wiley, ISBN: 047125665X, 1977.
- Fegley, B. and Schaefer, L. Spectroscopic signatures of the accretion of Earth-like exoplanets. Bull. *American Astronomical Society*, **37:** 683, 2005.
- Fischer-Gödde, M. and Kleine, T. Ruthenium isotopic evidence for an inner Solar System origin of the late veneer. *Nature*, **541**: 525-527, 2017.
- Fischer, R. A. and Ciesla, F. J. Dynamics of the terrestrial planets from a large number of N-body simulations, *Earth and Planetary Science Letters*, **392**: 28–38, 2014.
- Fitoussi, C. and Bourdon, B. Silicon isotope evidence against an enstatite chondrite Earth. *Science*, **335**: 1477–1480, 2012.
- Fitoussi, C., Bourdon, B. and Wang, X. The building blocks of Earth and Mars: A close genetic link, *Earth and Planetary Science Letters*, **434**: 151-160, 2016.
- Fitoussi, C., Bourdon, B., Kleine, T., Oberli, F. and Reynolds, B.C. Si isotope systematics of meteorites and terrestrial peridotites: implications for Mg/Si fractionation in the solar nebula and for Si in the Earth's core. *Earth and Planetary Science Letters*, **287**: 77–85, 2009.
- Frost, D. J. and McCammon, C. A. The redox state of Earth's mantle. *Annual Review* of *Earth and Planetary Sciences*, **36**: 389-420, 2008.
- Frost, D. J., Liebske, C., Langenhorst, F., McCammon, C. A., Trønnes, R. G. and Rubie, D. C. Experimental evidence for the existence of iron-rich metal in the Earth's lower mantle. *Nature*, **428**: 409–412, 2004.
- Frost, D.J., Mann, U., Asahara, Y., Rubie, D.C. The redox state of the mantle during and just after core formation. *Philosophical Transactions of the Royal Society of London A*, **366**: 4315–4337, 2008.
- Galy, A., Belshaw, N. S., Halicz, L. and O'Nions, R. K. High-precision measurement of magnesium isotopes by multiple-collector inductively coupled plasma mass spectrometry. *International Journal of Mass Spectrometry*, **208**: 89–98, 2001.
- Galy, A., Matthews, M., Halicz, L., Keith, R. and O'Nions, R. K. Mg isotopic composition of carbonate: insight from speleothem formation. *Earth and Planetary Science Letters*, **201**:105-115, 2002.

- Galy, A., Yoffe, O., Janney, P., Williams, R., Cloquet, C., Alard, O., Halicz, L., Wadhwa, M., Hutcheon, I., Ramon, E. and Carignan, J. Magnesium isotope heterogeneity of the isotopic standard SRM980 and new reference materials for magnesium-isotope ratio measurements. *Journal of Analytical Atomic Spectrometry*, 18: 1352–1356, 2003.
- Ganghoffer, J.F., and Rahouadj, R. On the generalized virial theorem for systems with variable mass, *Continuum Mechanics and Thermodynamics*, **28**: 443-463, 2016.
- Gannoun, A., Boyet, M. M., Rizo, H. and Goresy, A. E. <sup>146</sup>Sm–<sup>142</sup>Nd systematics measured in enstatite chondrites reveals a heterogeneous distribution of <sup>142</sup>Nd in the solar nebula. *Proceedings of National Academic of Sciences*, **108**: 7693–7697, 2011.
- Georg, R. B., Halliday, A. N., Schauble, E. A. and Reynolds, B. C. Silicon in the Earth's core. *Nature*, **447**: 1102–1106, 2007.
- Georg, R. B., Reynolds, B.C., Frank, M. and Halliday, A.N. New sample preparation techniques for the determination of Si isotopic compositions using MC-ICPMS. *Chemical Geology*, **235(1–2):** 95–104, 2006.
- Gessmann, C. K., Wood, B. J., Rubie, D. C. and Kilburn, M. R. Solubility of silicon in liquid metal at high pressure: implications for the composition of the Earth's core. *Earth and Planetary Science Letters*, **184**: 367–376, 2001.
- Gödde, M. F. and Kleine, T. Ruthenium isotopic evidence for an inner Solar System origin of the late veneer. *Nature*, **541**: 525-528, 2017.
- Goderis, S. Chakrabarti, R., Debaille, V. and Kodolanyi, J. Isotopes in cosmochemistry: recipe for a solar system. *Journal of analytical atomic spectrometry*, **31(4)**: 841-862, 2016.
- Goldstein, J., Newbury, D.E., Joy, D.C., Lyman, C. E., Echlin, P., Lifshin, E. Sawyer, L. C. and Michael, J. R. Scanning Electron Microscopy and X-Ray Microanalysis, Third Edition by Plenum Press. 2003.
- Grossman, L. and Larimer, J. W. Early chemical history of the solar system. *Reviews* of geophysics and space physics, **12**: 71-101, 1974.
- Grossman, L. Condensation in the primitive solar nebula. *Geochemica et cosmochemica acta*, **36:** 597-619, 1972.
- Grossman, L., Beckett, J. R., Fedkin, A. V., Simon, S. B. and Ciesla, F. J. Redox conditions in the solar nebula: Observational, experimental and theoretical

constraints. *Review in mineralogy and Geochemistry*, Mineralogical Society of America, **68(1)**: 93-140, 2008.

- Grossman, L., Ebel, D. S., Simon, S. B., Davis, A. M., Richter, F. M. and Parsad, N. M. Major element chemical and isotopic compositions of refractory inclusions in C3 chondrites: The separate roles of condensation and evaporation. *Geochimica et Cosmochimica Acta*, 64: 2879–2894, 2000.
- Halliday, A. N. The Origin and Earliest History of the Earth. Planets, Asteriods, Comets and The Solar System, *Treatise on Geochemistry*, **2:** 149-211, 2014.
- Halliday, A. N. The Origin and Earliest History of the Earth. *Treatise on Geochemistry*. Pergamon, Oxford, 509-557, 2003.
- Halliday, A.N., Lee, D.C., Christensen, J.N., Walder, A.J., Freedman, P.A., Jones, C.E., Hall, C.M., Yi, W. and Teagle, D. Recent developments in inductively coupled plasma magnetic sector multiple collector mass spectrometry. *International Journal of Mass Spectrometry and Ion Processes*, 146: 21-33, 1995.
- Handler, M. R., Baker, J. A., Schiller, M., Bennett, V. C. and Yaxley, G. M. Magnesium stable isotopic composition of the Earth's upper mantle. *Earth and Planetary Science Letters*, 282: 306–313, 2009.
- Hansen, B. M. S. Formation of the terrestrial planets from a narrow annulus. *The Astrophysical Journal*, **703**: 1131-1140, 2009.
- Hawkesworth, C. and Schersten, A. Mantle plumes and geochemistry, *Chemical Geology*, **241(3-4)**: 319-331, 2007.
- Heftmann, E. Chromatography. (2nd Ed.) Reinhold Publishing, 1966.
- Heng, C., Moynier, F., Humayun, M., Bishop, M. and Williams, J. T. Cosmogenic effects on Cu isotopes in IVB iron meteorites, *Geochimica et Cosmochimica Acta*, **182**: 145-154, 2016.
- Heng, C., Savage, P. S., Teng, F. Z., Helz, R. T. and Moynier, F. Zinc isotope fractionation during magmatic differentiation and the isotopic composition of the bulk Earth, *Earth and Planetary Science Letters*, **369**: 34-42, 2013.
- Herndon, J. M. Substructure of the inner core of the earth. *The Proceedings of the National Academy of Sciences*, **93:** 646-648, 1996.
- Hewins, R. H. and Herzberg, C. T. Nebular turbulence, chondrule formation, and the composition of the Earth. *Earth and Planetary Science Letters*, **144**: 1–7, 1996.

- Hin, R. C., Fitoussi, C., Schmidt, M. W. and Bourdon, B. Experimental determination of the Si isotope fractionation factor between liquid metal and liquid silicate. *Earth and Planetary Science Letters*, **387**: 55–66, 2014.
- Hoefs, J. *Stable isotope geochemistry*. Springer Science & Business Media, ISBN: 978-3-642-08960-2, 2008.
- Hsu, W. and Ghislaine, C. Mineral chemistry and the origin of enstatite in unequilibrated enstatite chondrites, *Geochimica et Cosmochimica Acta*, **62(11)**:1993-2004, 1998.
- Huang, F., Glessner, J., Ianno, A., Lundstrom, C., Zhang, Z. Magnesium Isotopic Composition of Igneous Rock Standards Measured by MC-ICP-MS. *Chemical Geology*, 268(1–2): 15–23, 2009.
- Huang, F., Wu, Z., Huang, S. and Wu, F. First-principles calculations of equilibrium silicon isotope fractionation among mantle minerals, *Geochimica et Cosmochimica Acta*, **140**: 509–520, 2014.
- Huang, J., Li, S. G., Xiao, Y., Ke, S., Li, W. Y. and Tian, Y. Origin of low  $\delta^{26}$ Mg Cenozoic basalts from South China Block and their geodynamic implications, *Geochimica et Cosmochimica Acta*, **164**: 298-317, 2015.
- Humayun, M., Keil, K., and Bischoff, A. Siderophile elements in metal from Northwest Africa 2526, and enstatite chondrite partial melt residue. 40<sup>th</sup> Proceedings of the Lunar and Planetary Science Conference, 1744, 2009.
- Hutchison, R. *Meteorites: A Petrologic, Chemical and Isotopic Synthesis*. Cambridge University, Cambridge, 506, 2004.
- Hutson, M. and Ruzicka, A. A multi-step model for the origin of E3 (enstatite) chondrites. *Meteoritics and Planetary Science*, **35**: 601–608, 2000.
- Irwin, P. Giant Planets of Our Solar System: Atmospheres, Composition, and Structure. Springer. ISBN: 3-540-00681-8, 2003
- Jacobsen, B., Yin, Q. Z., Moynier, F., Amelin, Y., Krot, A.N., Nagashima, K., Hutcheon, I.D. and Palme, H. <sup>26</sup>Al-<sup>26</sup>Mg and <sup>207</sup>Pb-<sup>206</sup>Pb systematics of Allende CAIs: canonical solar initial <sup>26</sup>Al/<sup>27</sup>Al ratio reinstated. *Earth and Planetary Science Letters*, **272**: 353–364, 2008.
- Jagoutz, E., Palme, H., Baddenhausen, H., Blum, K., Cendales, M., Dreibus, G., Spettel, B., Waenke, H. and Lorenz, V. The abundances of major, minor and trace elements in the Earth's mantle as derived from primitive ultramafic nodules. 10<sup>th</sup> Lunar and Planetary Science Conference, 2031–2050, 1979.

- Javoy, M. Chemical Earth models. *Comptes Rendus de l'Académie des Sciences*, **329**: 537–555, 1999.
- Javoy, M. The integral enstatite chondrite model of the Earth. *Geophysical Research Letters*, **22**: 2219–2222, 1995.
- Javoy, M., Kaminski, E., Guyot, F., Andrault, D., Sanloup, C., Moreira, M., Labrosse, S., Jambon, A., Agrinier, P., Davaille, A. and Jaupart, C. The chemical composition of the Earth: enstatite chondrite models. *Earth and Planetary Science Letters*, 293: 259–268, 2010.
- Javoy, M., Pineau, F. and Delorme, H. Carbon and nitrogen isotopes in the mantle. *Chemical Geology*, **57:** 41–62, 1986.
- Johansen, A., Oishi, J.S., Mac Low, M. M., Klahr, H., Henning, T. and Youdin, A. Rapid planetesimals formation in turbulent circumstellar disk, *Nature*, 448:1022– 1025, 2007
- Kallemeyn, G. W. and Wasson, J. T. Compositions of enstatite (EH3, EH4,5 and EL6) chondrites: implications regarding their formation. *Geochemica et Cosmochemica Acta*, **50**: 2153–2164, 1986.
- Kaminski, K. and Javoy, M. A two-stage scenario for the formation of the Earth's mantle and core, *Earth and Planetary Science Letters*, **365**: 97–107, 2013.
- Keil, K. Enstatite meteorites and their parent bodies. *Meteoritics and Planetary Science*, 24: 195–208, 1989.
- Keil, K. Mineralogical and chemical relationships among enstatite chondrites. *Journal of Geophysical Research*, **73**: 6945–6976, 1968.
- Kempl, J., Vroon, P.Z., van der Wagt, B., Zinngrebe, E., Frost, D.J. and van Westrenen, W. Silicon stable isotope fractionation between metal and silicate at high-pressure, high-temperature conditions as a tracer of planetary core formation, *Netherlands Journal of Geosciences*, 95(2): 113-129, 2016.
- Kempl, J., Vroon, P.Z., Zinngrebe, E. and van Westrenen, W. Si isotope fractionation between Si-poor metal and silicate melt at pressure-temperature conditions relevant to metal segregation in small planetary bodies, *Earth and Planetary Science Letters*, **368**: 61-68, 2013.
- Khan, A. and Deschamps, F. The Earth's Heterogeneous Mantle: A Geophysical, Geodynamical, and Geochemical Perspective, ISBN 978-3-319-15627-9, 2015.

- Khan, A. Inversion of seismic and geodetic data for the major element chemistry and temperature of the Earth's mantle, *Journal of Geophysical Research*, 113, B09308, doi:10.1029/2007JB005239, 2008.
- Kilburn, M. R. and Wood, B. J. Metal–silicate partitioning and the incompatibility of S and Si during core formation. *Earth and Planetary Science Letters*, **152(1)**: 139-148, 1997.
- Kleine, T., Munker, C., Mezger, K., and Palme, H. Rapid accretion and early core formation on asteroids and the terrestrial planets from Hf-W chronometry. *Nature*, **418**: 952-955, 2002.
- Kleine, T., Touboul, M., Bourdon, B., Nimmo, F., Mezger, K., Palme, H., Jacobsen, S. B., Yin, Q. Z., Halliday, A. N. Hf–W chronology of the accretion and early evolution of asteroids and terrestrial planets, *Geochimica et Cosmochimica Acta*, 73: 5150–5188, 2009.
- Kong, P., Tadashi, M. and Ebihara, M. Compositional continuity of enstatite chondrites and implications for heterogeneous accretion of the enstatite chondrite parent body, *Geochimica et Cosmochimica Acta*, **61**: 4895, 1997.
- Krot, A.N., Makide, K., Nagashima, K., Huss, G.R., Ogliore, R.C., Ciesla, F.J., Yang, L., Hellebrand, E.and Gaidos, E. Heterogeneous distribution of <sup>26</sup>Al at the birth of the early Solar System: evidence from refractory grains and inclusions, *Meteoritics and Planetary Science*, **47**: 1948–1979, 2012.
- Larimer, J. W. and Bartholomay, M. The role of carbon and oxygen in cosmic gases: some applications to the chemistry and mineralogy of enstatite chondrites, *Geochemica et Cosmochemica Acta*, **43**: 1455-1466, 1979.
- Larimer, J.W. and Anders, E. Chemical fractionations in meteorites-III. Major element fractionations in chondrites. *Geochemica et Cosmochemica Acta*, **34**: 367–387, 1970.
- Larimer, J.W. The condensation and fractionation of refractory lithophile elements. *Icarus*, **40**: 446–454, 1979.
- Larsen, K.K., Schiller, M. and Bizzarro, M. Accretion timescales and style of asteroidal differentiation in an <sup>26</sup>Al-poor protoplanetary disk, *Geochimica et Cosmochimica Acta*, **176**: 295-315, 2016.
- Lattimer, J. M., Schramm, D. N. and Grossman, L. Condensation in supernova ejects and isotopic anamolies in meteorites, *The Astrophysical Journal*, **219**: 230–249, 1978.

- Lee, D. C. and Halliday, A. N. Accretion of primitive planetesimals: Hf-W isotopic evidence from enstatite chondrites, *Science*, **288**: 1629–1631, 2000.
- Lee, T., Papanastassiou, D. A. and Wasserburg, G. J. Al-26 in the early Solar-System fossil or fuel. *The Astrophysical Journal*, **211:** L107–L110, 1977.
- Lee, T., Papanastassiou, D. A. and Wasserburg, G. J. Demonstration of Mg-26 excess in Allende and evidence for Al-26. *Geophysical Research Letters*, **3**: 41–44, 1976.
- Lehmann, I. P', *Publications du Bureau Central Seismologique International, Série A*, *Travaux Scientifique*, **14**: 87-115, 1936.
- Lehner, S. W., McDonough, W. F. and Németh, P. EH3 matrix mineralogy with major and trace element composition compared to chondrules, *Meteoritics and Planetary Science*, **49(12)**: 2219-2240, 2014.
- Leya, I., Schonbachler, M., Wiechert, U., Krahenbuhl, U. and Halliday, A. N. Titanium isotopes and the radial heterogeneity of the solar system. *Earth and Planetary Science Letters*, **266**: 233–244, 2008.
- Li, J. and Agee, C. B. The effect of pressure, temperature, oxygen fugacity and composition on partitioning of nickel and cobalt between liquid Fe–Ni–S alloy and liquid silicate: implications for the Earth's core formation. *Geochemica et Cosmochemica Acta*, **65**: 1821–1832, 2001a.
- Li, J., Fei, Y., Mao, H. K., Hirose, K. and Shieh, S. R. Sulfur in the Earth's inner core. *Earth and Planetary Science Letters*, **193**: 509–14, 2001b.
- Lie-Wen, X., Yin, Q. Z., Yang, J. H., Wu, F. Y. and Yang, Y. H. High precision analysis of Mg isotopic composition in olivine by laser ablation MC-ICP-MS, *Journal of Analytical Atomic Spectrometry*, **26:** 1773-1780, 2011.
- Liu, S. A., Teng, F. Z., He, Y., Ke, S., Li, S. Investigation of Magnesium Isotope Fractionation during Granite Differentiation: Implication for Mg Isotopic Composition of the Continental Crust. *Earth and Planetary Science Letters*, 297(3–4): 646–654, 2010.
- Liu, Y., Gao, S., Jin, S., Hu, S., Sun, M., Zhao, Z. and Feng, J. Geochemistry of lower crustal xenoliths from Neogene Hannuoba Basalt, North China Craton: Implications for petrogenesis and lower crustal composition. *Geochemica et Cosmochemica Acta*, 65: 2589-2604, 2001.
- Lodders, K. An Oxygen Isotope Mixing Model for the Accretion and Composition of Rocky Planets, Space science reviews, **92(1)**: 341-354, 2000.

- Lodders, K. and Fegley, B. *Chemistry of the Solar System*, Cambridge: Royal Society of Chemistry, 2011.
- Lodders, K. and Fegley, B. The Planetary scientist's companion, Oxford, 400, 1998.
- Lodders, K. Solar system abundances and condensation temperatures of the elements. *The Astrophysical Journal*, **591**: 1220–1247, 2003.
- Luck, J. M., Othman, D. B. and Albarède, F. Zn and Cu isotopic variations in chondrites and iron meteorites: early solar nebula reservoirs and parent-body processes. *Geochimica et Cosmochimica Acta*, **69(22)**: 5351-5363, 2005.
- Luz, B., Barkan, E., Yam, R. and Shemesh, A. Fractionation of oxygen and hydrogen isotopes in evaporating water. *Geochimica et Cosmochimica Acta*, 73(22): 6697-6703, 2009.
- MacDonald, G. J. F. and Knopoff, L. On the chemical composition of the outer core. *Geophysical Journal of the Royal Astronomical Society*, **1:** 284–297, 1958.
- MacPherson, G. J., Davis, A. M., and Zinner, E. K. The distribution of aluminum-26 in the early Solar System-A reappraisal. *Meteoritics*, **30**: 365-386, 1995.
- Maher, K. A., and Stevenson, D. J. Impact frustration of the origin of life. *Nature*, **331:** 612–614, 1988.
- Martin, S., Paton, C. and Bizzarro, M. Evidence for nucleosynthetic enrichment of the protosolar molecular cloud core by multiple supernova events, *Geochimica et Cosmochimica Acta*, **149**: 88-102, 2015.
- Mason, B. The enstatite chondrites. *Geochemica et Cosmochemica Acta*, **30**: 23–39, 1966.
- Mayeda, T. K. and Clayton, R. N. Oxygen isotopic compositions of aubrites and some unique meteorites, 11<sup>th</sup> Proceedings of the Lunar and Planetary Science Conference, 1145-1151, 1980.
- McDonough W. F. and Sun S. S. The composition of the Earth, *Chemical Geology*, **120**: 223–253, 1995.
- McDonough, W. F. and Rudnick, R. L. Mineralogy and composition of the upper mantle, *Reviews in Mineralogy and Geochemistry*, **37**: 139-164, 1998.
- McDonough, W. F. Compositional model for the Earth's core. *Treatise on geochemistry*, 568, 2003.

REFERENCES

- McDonough, W.F. Compositional Model for the Earth's Core, *Treatise on Geochemistry*, **2:** 547-568, 2014.
- McKeegan, K. and Davis, A. Early solar system chronology. *Treatise on Geochemistry*. Pergamon, Oxford, 1-38, 2007.
- McSween, H. Y. Jr. Are carbonaceous chondrites primitive or processed? A review, *Reviews of geophysics and space physics*, **17:** 1059–1078, 1979.
- Meisel, T. C., Leoben, M., Walker, R. J. and Morgan, J. W. The osmium isotopic composition of the Earth's upper mantle. *Nature*, **383**: 517-520, 1996.
- Millet, M.A., Baker, J. A. and Payne, C. E. Ultra-precise stable Fe isotope measurements by high resolution multiple-collector inductively coupled plasma mass spectrometry with a <sup>57</sup>Fe-<sup>58</sup>Fe double spike, *Chemical Geology*, **304-305**: 18-25, 2012.
- Mittlefehldt, D. W. The genesis of diogenite and HED parent body petrogenesis. *Geochemica et Cosmochemica Acta*, **58**: 1537–1552, 1994.
- Mittlefehldt, D. W., Killgore, M. and Lee, M. T. *Meteoritics and Planetary Science Supplement*, **37**: 345, 2002.
- Molini-Velsko, C., Mayeda, T. K. and Clayton, R. N. Isotopic composition of silicon in meteorites. *Geochemica et Cosmochemica Acta*, **50**: 2719-2726, 1986.
- Montmerle, T., Augereau, J.C., and Chaussidon, M. Solar System Formation and Early Evolution: the First 100 Million Years. *Earth, Moon, and Planets*, **98:** 39–95, 2006.
- Morard, G., Siebert, J., Andrault, D., Guignot, N., Garbarino, G., Guyot, F. and Antonangeli, D. The Earth's core composition from high-pressure density measurements of liquid iron alloys. *Earth and Planetary Science Letters*, **373**: 169–178, 2013.
- Morbidelli, A., Marchi, S., Bottke, W. and Kring, D. A Sawtooth-like Timeline for the First Billion Year of Lunar Bombardment. *Earth and Planetary Astrophysics*, arXiv:1208.4624, 2012.
- Moynier, F., Agranier, A. and Hezel, D. Stable isotopic composition of Sr in Earth, Moon, Mars and meteorites. *Earth and Planetary Science Letters*, **300**: 359-366, 2010.
- Moynier, F., Day, J. M. D., Okui, W., Yokoyama, T., Bouvier, A., Walker, R. J. and Podosek, F. A. Planetary-scale strontium isotopic heterogeneity and the age of

volatile depletion of early solar system materials. *Astrophysical Journal*, **758:** 45, 2012.

- Newton, J., Franchi, I.A. and Pillinger, C.T. The oxygen-isotopic record in enstatite meteorities. *Meteoritics and Planetary Science*, **35**: 689–698, 2000.
- O'Brien, D.P., Morbidelli, A., Bottke, W.F. The primordial excitation and clearing of the asteroid belt-revisited, *Icarus*, **191**: 434–52, 2007.
- O'Neill, H.S.C. and Palme, H. Collisional erosion and the non-chondritic composition of the terrestrial planets. *Philosophical Transactions of the Royal Society A*, **366**: 4205–4238, 2008.
- O'Neill, H.S.C. The origin of the moon and the early history of the earth—A chemical model. Part 1: The moon, *Geochimica et Cosmochimica Acta*, **55(4)**: 1135-1157, 1991.
- O'Neill, H.S.C. Theoretical and experimental aspects of isotopic fractionation, *Reviews of mineralogy*, **16**: 1-40, 1986.
- Olesik, J.W. Inductively Coupled Plasma Mass Spectrometers, *Treatise on Geochemistry*, 309-336, 2014.
- Olsen, M. B., Wielandt, D., Schiller, M., Elishevah, M.M.E., Kooten, V. and Bizzarro, M. Magnesium and <sup>54</sup>Cr isotope compositions of carbonaceous chondrite chondrules Insights into early disk processes, *Geochimica et Cosmochimica Acta*, **191**: 118-138, 2016.
- Pack, A., Vogel, I., Rollion-Bard, C., Luais, B. and Palme, H. Silicon in iron meteorite metal. *Meteoritics and Planetary Sciences*, **46**: 1470–1483, 2011.
- Palme, H. and O'Neill, H.S.C Cosmochemical Estimates of Mantle Composition, Reference Module in Earth Systems and Environmental Sciences, Treatise on Geochemistry 2nd Edition, 3: 1-39, 2014.
- Palme, H. and O'Neill, H.S.C. Cosmochemical estimates of mantle composition. *Treatise on Geochemistry: The Mantle and Core*, Elsevier Press, New York, 1– 38, 2003.
- Patel. M. M., Kapadia, M. A. Patel, G. P. and Joshi, J. D. Synthesis, characterization, ion-exchange and antimicrobial study of poly [(2-hydroxy-4methoxybenzophenone) propylene] resin and its polychelates with lanthanides, *Journal of Applied Polymer Science*, **106**: 1307–1317, 2007.

- Patrick J. F., Clymans, W., Fontorbe, G., De La Rocha, C. L. and Conley, D. J. The continental Si cycle and its impact on the ocean Si isotope budget, *Chemical Geology*, **425**: 12-36, 2016.
- Pearson, N. J., Griffin, W. L., Alard, O. and O'Reilly, S.Y. The isotopic composition of magnesium in mantle olivine: records of depletion and metasomatism. *Chemical Geology*, 226(3-4): 115-133, 2006.
- Pfalzner, S., Davies, M. B., Gounelle, M., Johansen, A., Munker, C., Lacerda, P., Portegies, S. Z., Testi, L., Trieloff, M. and Veras, D. The formation of the solar system, *Earth and Planetary Astrophysics*, arXiv:1501.03101v1, 2015.
- Pogge von Strandmann, P. A. E., Elliott, T., Marschall, H. R., Coath, C., Lai, Y. J., Jeffcoate, A. B., Ionov, D. A. Variations of Li and Mg isotope ratios in bulk chondrites and mantle xenoliths. *Geochemica et Cosmochemica Acta*, **75**: 5247– 5268, 2011.
- Poirier, J. P. Light elements in the Earth's core: a critical review. *Physics of Earth and Planetary Interior*, **85:** 319–37, 1994.
- Poitrasson, F. and Zambardi, T. An Earth–Moon silicon isotope model to track silicic magma origins. *Geochemica et Cosmochemica Acta*, **167**: 301–312, 2015.
- Poitrasson, F., Halliday, A. N., Lee, D. C., Levasseur, S. and Teutsch, N. Iron isotope differences between Earth, Moon, Mars and Vesta as possible records of contrasted accretion mechanisms. *Earth and Planetary Science Letters*, 223(3– 4): 253–266, 2004.
- Poitrasson, F., Sylvain, L. and Nadya, T. Significance of iron isotope mineral fractionation in pallasites and iron meteorites for the core-mantle differentiation of terrestrial planets. *Earth and Planetary Science Letters*, **234**: 151-164, 2005.
- Pownceby, M. I., MacRae, C. M. and Wilson, N. C. Mineral characterization by EPMA mapping. *Minerals Engineering*, **20(5)**: 444-451, 2007.
- Pringle, E. A., Moynier, F., Savage, P. S., Badro, J. and Barrat, J. A. Silicon isotopes in angrites and volatile loss in planetesimals. *Proceedings of National Academic* of Sciences, 111: 17029–17032, 2014.
- Pringle, E. A., Moynier, F., Savage, P. S., Jackson, M. G., Moreira, M. and Day, J.M.D. Silicon isotopes reveal recycled altered oceanic crust in the mantle sources of Ocean Island Basalts, *Geochimica et Cosmochimica Acta*, 189: 282-295, 2016.

- Pringle, E. A., Savage, P. S., Badro, J., Barrat, J. A. and Moynier, F. Redox state during core formation on asteroid 4-Vesta, *Earth and Planetary Science Letters*, 373: 75-82, 2013.
- Qin, L., Alexander, C.M.D., Carlson, R.W., Horan, M.F. and Yokoyama, T. Contributors to chromium isotope variation of meteorites. *Geochimica et Cosmochimica Acta*, **74**: 1122–1145, 2010.
- Redd, N. T. Asteroid Belt: Facts and Information, Space.com, 2012.
- Reed, S. J. B. *Electron Microprobe Analysis and Scanning Electron Microscopy in Geology*, Cambridge Univ Press. 1996.
- Regelous, M., Elliott, T. and Coath, C. D. Nickel isotope heterogeneity in the early Solar System. *Earth and Planetary Science Letters*, **272**: 330–338, 2008.
- Rehkämper, M., Frank, M., Hein, J.R., Porcelli, D., Halliday, A., Ingri, J. and Leibetrau, V. Thallium isotope variations in seawater and hydrogenetic, diagenetic, and hydrothermal ferromanganese deposits, *Earth and Planetary Science Letters*, **197(1-2)**: 65-81, 2002.
- Rehkämper, M., Schönbächler, M. and Stirling, C.H. Multiple Collector ICP-MS: Introduction to instrumentation, measurement techniques and analytical capabilities. *Geostandards and Geoanalytical Research*, **25(1)**: 23-40, 2001.
- Reynolds, B. C., Aggarwal, J., Andre, L., Baxter, D., Beucher, C., Brzezinski, M. A., Engstrom, E., Georg, B. R., Land, M., Leng, M. J., Opfergeld, S., Rodushkin, I., Sloane, D., Van den Boorn, S.H.J.M., Vroon, P.Z. and Cardinal, D. An interlaboratory comparison of Si isotope reference materials. *Journal of Analytical Atomic Spectrometry*, 22: 561–569, 2007.
- Reynolds, J. H. and Verhoogen, J. Natural variations in the isotopic constitution of silicon. *Geochemica et Cosmochemica Acta*, **3**: 224-234, 1953.
- Ricolleau, A., Fei, Y., Corgne, A., Siebert, J. and Badro, J. Oxygen and silicon contents of Earth's core from high pressure metal-silicate partitioning experiments, *Earth and Planetary Science Letters*, **310(3)**: 409-421, 2011.
- Righter, K. and Drake, M. J. Core formation in Earth's Moon, Mars and Vesta. *Icarus*, **124**: 513–529, 1996.
- Righter, K. Metal-silicate partitioning of siderophile elements and core formation in the early Earth. *Annual Review of Earth and Planetary Sciences*, **31**: 135–174, 2003.

- Ringwood, A. E. On the chemical evolution and densities of the planets. *Geochimica et Cosmochimica Acta*, **15**: 257–283, 1959.
- Ringwood, A.E. Significance of the terrestrial Mg/Si ratio, *Earth and Planetary Science Letters*, **95(1-2):** 1-7, 1989.
- Ringwood, A.E. Silicon in the metal phase of enstatite chondrites. *Nature*, **186**: 465–466, 1960.
- Ringwood, A.E. Silicon in the metal phase of enstatite chondrites and some geochemical implications. *Geochimica et Cosmochimica Acta*, **25**: 1–13, 1961.
- Ringwood, A.E. The origin of the Earth and the Moon. Springer, New York, 1979.
- Robert, F. and Chaussidon, M. A palaeotemperature curve for the Precambrian oceans based on silicon isotopes in cherts, Nature, **443(7114)**: 969-972, 2006.
- Rosman, K. J. R. and Taylor, P. D. P. Isotopic compositions of the elements, *Pure and Applied Chemistry*, **70(1)**: 217-235, 1997.
- Rubie, D. C., Melosh, H. J., Reid, J. E., Liebske, C. and Righter, K. Mechanisms of metal-silicate equilibration in the terrestrial magma ocean. *Earth and Planetary Science Letters*, 205(3-4): 239–255, 2003.
- Rubie, D. Nimmo, F. and Melosh, H. J. Formation of Earth's Core, *Evolution of the Earth*, **9:** 51-84, 2007.
- Rubin, A. E. Clastic matrix in EH3 chondrite, *Meteoritics & Planetary Science*, **44(4)**: 589-601, 2009.
- Rufu, R., Aharonson, O. and Perets, H. B. A multiple-impact origin for the Moon. *Nature Geoscience*, **10**: 89–94, 2017.
- Rui, L., Wu, P., Yang, L., Hou, X. and Lv, Y. Inductively coupled plasma mass spectrometry-based immunoassay: A review: Inductively Coupled Plasma Mass Spectrometry-based Immunoassay, Mass Spectrometry Reviews, 5(33): 373-393, 2013.
- Russell, S. S., Srinivasan, G., Huss, G. R., Wasserburg, G. J., MacPherson, G. J. Evidence for Widespread <sup>26</sup>Al in the Solar Nebula and Constraints for Nebula Time Scales. *Science*, 273: 757–762, 1996.
- Savage, P. S. and Moynier, F. Silicon isotopic variation in enstatite meteorites: clues to their origin and Earth-forming material. *Earth and Planetary Science Letters*, 361: 487–496, 2013.

- Savage, P. S., Armytage, R. M. G., Georg, R. B. and Halliday, A. N. High temperature silicon isotope geochemistry, *Lithos*, **190-191:** 500-519, 2014.
- Savage, P. S., Georg, R. B., Armytage, R. M. G., Williams, H. M. and Halliday, A. N. Silicon isotope homogeneity in the mantle. *Earth and Planetary Science Letters*, 295: 139–146, 2010.
- Savage, P. S., Georg, R. B., Williams, H. M., Burton, K. W. and Halliday, A. N. Silicon isotope fractionation during magmatic differentiation. *Geochemica et Cosmochemica Acta*, 75: 6124–6139, 2011.
- Savage, P. S., Georg, R. B., Williams, H. M., Turner, S., Halliday, A. N., Chappell,
  B. W. The silicon isotope composition of granites. *Geochemica et Cosmochemica Acta*, 92: 184–202, 2012.
- Savage, P. S., Moynier, F., Chen, H., Shofner, G., Siebert, J., Badro, J. and Puchtel, I. S. Copper isotope evidence for large-scale sulphide fractionation during Earth's differentiation. *Geochemical Perspectives Letters*, 1(1): 53-64, 2015.
- Schaefer, L. and Fegley, B. Application of an Equilibrium Vaporization Model to the Ablation of Chondritic and Achondritic Meteoroids. *Earth, Moon and Planets*, 95(1): 413-423, 2005.
- Schauble, E. A. Applying stable isotope fractionation theory to new systems. *Reviews in Mineralogy and Geochemistry*, **55:** 65–112, 2004.
- Schauble, E.A., Meheut, M. and Hill, P.S. Combining metal stable isotope fractionation theory with experiments. *Elements*, **5**: 369–374, 2009.
- Schiller, M., Baker, J.A. and Bizzarro, M. <sup>26</sup>Al–<sup>26</sup>Mg dating of asteroidal magmatism in the young Solar System, *Geochemica et Cosmochemica Acta*, **74**: 4844–4864, 2010.
- Schiller, M., Connelly, J. N. and Bizzarro, M. Lead and Mg isotopic age constraints on the evolution of the HED parent body. *Meteoritics and Planetary Sciences*, 52(6): 1233-1243, 2017.
- Schiller, M., Dallas, J.A., Creech, J., Bizzarro, M. and Baker, J.A. Tracking the formation of magma oceans in the solar system using stable magnesium isotopes. *Geochemical perspectives letters*, **3**(1): 22-31, 2017.
- Schiller, M., Handler, M. R., Baker, J. A. High-Precision Mg Isotopic Systematics of Bulk Chondrites. *Earth and Planetary Science Letters*, **297(1–2):** 165–173, 2010b.

- Schiller, M., Kooten, E. V., Holst, J. C., Olsen, M. B. and Bizzarro, M. Precise measurement of chromium isotopes by MC-ICPMS. *Journal of analytical atomic spectrometry*, **29(8)**: 1406-1416, 2016.
- Schoenberg, R. and von Blanckenburg, F. Modes of planetary scale Fe isotope fractionation. *Earth and Planetary Science Letters*, **252**: 342–359, 2006.
- Schonbachler, M., Carlson, R. W., Horan, M. F., Mock, T. D. and Hauri, E. H. Heterogeneous accretion and the moderately volatile element budget of Earth. *Science*, **328**: 884–887, 2010.
- Scott, E. and Krot, A. N. Chondrites and their components, *Treatise on Geochemistry*, 143–200, 2003.
- Scott, E. and Krot, A. N. Chondrites and their components. *Meteorites, comets and planets, Treatise on Geochemistry*, **1:** 1–72, 2007.
- Scott, E. and Krot, A. N. Chondritic meteorites and the high-temperature nebular origins of their components. *Chondrites and the protoplanetary disk*, San Francisco: Astronomical Society of the Pacific, 15–53, 2005.
- Sears, D.W., Kallemeyn, G.W., Wasson, J.T. The compositional classification of chondrites: II The enstatite chondrite groups. *Geochemica et Cosmochemica Acta*, **46**: 597–608, 1982.
- Sedaghatpour, F. and Teng, F. Z. Magnesium isotopic composition of achondrites. *Geochemica et Cosmochemica Acta*, **174**: 167–179, 2016.
- Sedaghatpour, F. S., Teng, F. Z., Liu, Y., Sears, D. W. G. and Taylor, L. A. Magnesium isotopic composition of the Moon. *Geochemica et Cosmochemica Acta*, **120**: 1–16, 2013.
- Seitz, H. M., Brey, G. P., Zipfel, J., Ott, U., Weyer, S., Durali, S. and Weinbruch, S. Lithium isotope composition of ordinary and carbonaceous chondrites, and differentiated planetary bodies: bulk solar system and solar reservoirs. *Earth and Planetary Science Letters*, 260(3): 582-596, 2007.
- Shahar, A. and Young, E. D. Astrophysics of CAI formation as revealed by silicon isotope LA-MC-ICPMS of an igneous CAI, *Earth and Planetary Science Letters*, 257(3-4): 497-510, 2007.
- Shahar, A., Hillgren, V.J., Young, E.D., Fei, Y., Macris, C., Deng, L. Hightemperature Si isotope fractionation between iron metal and silicate. *Geochimica et Cosmochimica Acta*, **75**: 7688–7697, 2011.

- Shahar, A., Ziegler, K., Young, E.D., Ricolleau, A., Schauble, E.A. and Fei, Y. Experimentally determined Si isotope fractionation between silicate and Fe metal and implications for Earth's core formation. *Earth and Planetary Science Letters*, 288: 228–234, 2009.
- Sherman, D. M. Stability of possible Fe-FeS and Fe-FeO alloy phases at high pressure and the composition of the Earth's core. *Earth and Planetary Science Letters*, **132**: 87–98, 1995.
- Shukolyukov, A. and Lugmair, G. W. Manganese-chromium isotope systematics of enstatite meteorites, *Geochimica et Cosmochimica Acta*, **68(13)**: 2875-2888, 2004.
- Sikdar, J. and Rai, V. K. Simultaneous chromatographic purification of Si and Mg for isotopic analyses using MC-ICPMS, *Journal of Analytical Atomic Spectrometry*, 32: 822-833, 2017.
- Sikdar, J. and Rai, V. K. Simultaneous determination of Si and Mg isotopic composition in meteorites, 79<sup>th</sup> Annual Meeting of the Meteoritical Society, 6293, 2016.
- Simon, J. I. and DePaolo, D. J. Stable calcium isotopic composition of meteorites and rocky planets. *Earth and Planetary Science Letters*, **289**: 457–466, 2010.
- Simon, N. M., and Beauchemin, D. *Inductively coupled plasma mass spectrometry handbook*. Oxford, Boca Raton, FL, 2005.
- Singh, S., Singh, S. K., Bhushan, R. and Rai, V. K. Dissolved silicon and its isotopes in the water column of the Bay of Bengal: Internal cycling versus lateral transport. *Geochemica et Cosmochemica Acta*, **151**: 172-191, 2015.
- Small, H. Ion Chromatography. Plenum Publishing Corporation, 1990.
- Srinivasan, G., Goswami, J. N. and Bhandari, N. Al-26 in eucrite Piplia Kalan: Plausible heat source and formation chronology. *Science*, **284**: 1348–1350, 1999.
- Srinivasan, G., Whitehouse, M. J., Weber, I. and Yamaguchi, A. The crystallization age of eucrite zircon, *Science*, **317** (5836): 345-7, 2007.
- Steele, R.C.J., Coath, C.D., Regelous, M., Russell, S. and Elliott, T. Neutron-poor nickel isotope anomalies in meteorites. *Astrophysical Journal*, **758**: 59, 2012.
- Steven, G., Chakrabarti, R., Debaille, V. and Kodolányi, J. Isotopes in cosmochemistry: recipe for a Solar System, *Journal of Analytical Atomic Spectrometry*, **31**: 841-862, 2016.

- Stone, J., Hutcheon, I. D., Epstein, S. and Wasserburg, G. J. Correlated Si isotope anomalies and large13C enrichments in a family of exotic SiC grains. *Earth and Planetary Science Letters*, **107**: 570-581, 1991.
- Suess, H. E., and Urey, H. C. Abundances of the elements. *Reviews of Modern Physics*, **39**: 595–599, 1956.
- Sugiura, N., Mizuno, T., Ushikubo, T. and Hiyagon, H. Si and Mg isotope fractionations in melilite in coarse-grained CAIs measured by SIMS. *Geochemical Journal*, **38**: 405-415, 2004.
- Tackley, P. J. Dynamics and evolution of the deep mantle resulting from thermal, chemical, phase and melting effects. *Earth science reviews*, **110**: 1–25, 2012.
- Tang, H. and Dauphas, N. Abundance, distribution, and origin of <sup>60</sup>Fe in the solar protoplanetary disk. *Earth and Planetary Science Letters*, **359**: 248–263, 2012.
- Taylor, H.E. Inductively coupled plasma-mass spectrometry: practices and techniques. Academic Press, 2001.
- Teng, F. Z. Magnesium isotope geochemistry. *Reviews in Mineralogy and Geochemistry*, **82**: 219–287, 2017.
- Teng, F. Z., Dauphas, N. and Watkins, J. M. Non-Traditional Stable Isotopes: Retrospective and Prospective, *Reviews in Mineralogy and Geochemistry*, DOI: 10.2138/rmg.2017.82.1, 2017.
- Teng, F. Z., Li, W. Y., Ke, S., Marty, B., Dauphas, N., Huang, S., Ali, F.Y.W. Magnesium Isotopic Composition of the Earth and Chondrites. *Geochimica et Cosmochimica Acta*, 74(14): 4150–4166, 2010a.
- Teng, F. Z., Li, W. Y., Ke, S., Yang, W., Liu, S. A., Sedaghatpour, F., Wang, S. J., Huang, K. J., Hu, Y., Ling, M. X., Xiao, Y., Liu, X. M., Li, X. W., Gu, H. O., Sio, C. K., Wallace, D. A., Su, B. X., Zhao, L., Chamberlin, J., Harrington, M. and Brewer, A. Magnesium isotopic compositions of international geostandards. *Geostandards and Geoanalytical Research*, **39**: 329-339, 2015a.
- Teng, F. Z., Wadhwa, M. and Helz R. T. Investigation of magnesium isotope fractionation during basalt differentiation: Implications for a chondritic composition of the terrestrial mantle. *Earth and Planetary Science Letters*, 261(1-2): 84-92, 2007.
- Teng, F. Z., Yin, Q. Z., Ullmann, C. V., Chakrabarti, R., Pogge von Strandmann, P.A.E., Yang, W., Li, W. Y., Ke, S., Sedaghatpour, F., Wimpenny, J., Meixner, A., Romer, R. L., Wiechert, U. and Jacobsen, S. B. Interlaboratory comparison of magnesium isotopic compositions of 12 felsic to ultramafic igneous rock

standards analyzed by MC-ICPMS, *Geochemistry, Geophysics, Geosystems*, **16**: 3197-3209, 2015b.

- Thiemens, Mark H. History and Applications of Mass Independent Isotope Effects. *Annual Reviews of Earth and Planetary Sciences*, **34:** 217-262, 2006.
- Thomas, R. Practical guide to ICP-MS: a tutorial for beginners. CRC press, 2013.
- Thompson, M. and Walsh, J. N. A Handbook of Inductively Coupled Plasma Spectrometry, Blackie, Glasgow and London, 1983.
- Tipper, E. T., Bickle, M. J., Galy, A., West, A. J., Pomie's, C. and Chapman, H. J. The short term climatic sensitivity of carbonate and silicate weathering fluxes: insight from seasonal variations in river chemistry. *Geochemica et Cosmochemica Acta*, **70**: 2737–2754, 2006c.
- Tipper, E. T., Galy, A., Gaillardet, J., Bickle, M. J., Elderfield, H. and Carder, E. A. The Mg isotope budget of the modern ocean: constraints from riverine Mg isotope ratios. *Earth and Planetary Science Letters*, **250**: 241–253, 2006b.
- Tipper, E. T., Louvat, P., Capmas, F., Galy, A. and Gaillardet, J. Accuracy of Stable Mg and Ca isotope data obtained by MC-ICP-MS using the standard addition method. *Chemical Geology*, **257(1–2):** 65–75, 2008.
- Trinquier, A., Birck, J. L. and Allegre, C. J. Widespread <sup>54</sup>Cr heterogeneity in the inner solar system. *Astrophysical Journal*, **655**: 1179–1185, 2007.
- Trinquier, A., Elliott, T., Ulfbeck, D., Coath, C., Krot, A. N. and Bizzarro, M. Origin of nucleosynthetic isotope heterogeneity in the solar proto- planetary disk. *Science*, **324**: 374–376, 2009.
- Tsuchiyama, A. and Masao, K. Phase diagrams describing solid-gas equilibria in the system Fe-Mg-Si-O-C-H, and its bearing on redox states of chondrites, *Meteoritics*, **30(4)**: 423-429, 1995.
- Urey, H. The thermodynamic properties of isotopic substances, *The Journal of the Chemical Society*, 562-581, 1947.
- Valdes, M. C., Moreira, M., Foriel, J. and Moynier, F. The nature of Earth's building blocks as revealed by calcium isotopes. *Earth and Planetary Science Letters*, 394: 135–145, 2014.
- Van den Boorn, S. H. J. M., Vroon, P. Z., Van Belle, C. C., Van Der Wagt, B., Schwieters, J. and Van Bergen, M. J. Determination of silicon isotope ratios in silicate materials by high- resolution MC-ICP-MS using a sodium hydroxide

sample digestion method. *Journal of Analytical Atomic Spectrometry*, **21:** 734-742, 2006.

- Van den Boorn, S.H.J.M., Vroon, P. Z. and van Bergen, M.J. Sulfur-induced offsets in MC-ICP-MS silicon-isotope measurements. *Journal of Analytical Atomic Spectrometry*, 24(8): 1111–1114, 2009.
- Visscher, C. and Fegley, B. Chemistry of impact-generated silicate melt-vapor debris disks, *The Astrophysical Journal Letters*, **767:** L12, 2013.
- Wade, J. and Wood, B. J. Core formation and the oxidation state of the Earth. *Earth and Planetary Science Letters*, 236: 78–95, 2005.
- Walsh, K.J., Morbidelli, A., Raymond, S.N., OBrien, D.P., Mandell, A.M. A low mass for Mars from Jupiter's early gas-driven migration. *Nature*, 475: 206–209, 2011.
- Wang, K., Moynier, F., Barrat, J. A., Zanda, B., Paniello, R. C. and Savage, P. S. Homogeneous distribution of Fe isotopes in the early solar nebula, *Meteoritics* and Planetary Science, 48(3): 354-364, 2013.
- Wang, K., Savage, P.S. and Moynier, F. The iron isotope composition of enstatite meteorites: Implications for their origin and the metal/sulfide Fe isotopic fractionation factor. *Geochimica et Cosmochimica Acta*, **142**: 149–165, 2014.
- Wänke, H. and Dreibus, G. Chemical composition and accretion history of terrestrial planets. *Philosophical Transactions of the Royal Society of London A*. **325:** 545–557, 1988.
- Wänke, H. Constitution of the terrestrial planets. *Philosophical Transactions of the Royal Society of London A*, **303**: 287–302, 1981.
- Warren, P. H. and Kallemeyn, G. W. Geochemistry of the LEW87051 Angrite and Other Basaltic Achondrites, *Lunar and Planetary Science Conference*, 21: 1295, 1990.
- Warren, P. H. Stable-isotopic anomalies and the accretionary assemblage of the Earth and Mars: A subordinate role for carbonaceous chondrites. *Earth and Planetary Science Letters*, **311**: 93–100, 2011.
- Warren, P. H., Kallemeyn, G. W. and Mayeda, T. Consortium investigation of the Asuka-881371 angrite: Bulk-rock geochemistry and oxygen isotopes, 20<sup>th</sup> Symposium on Antarctic Meteorites, NIPR, Tokyo, 261-264, 1995.

- Wasserburg, G. J., Lee, T. and Papanastassiou, D. A. Correlated O and Mg isotopic anomalies in Allende inclusions: II. Magnesium. *Geophysical Research Letters*, 4(7): 299-302, 1977.
- Wasserburg, G., Busso, M., Gallino, R., Nollett, K. Short-lived nuclei in the early Solar System: Possible AGB sources. *Nuclear Physics A*, 777: 5–69, 2006.
- Wasson, J. T. and Kimberlin, J. The chemical classification of iron meteorites, 2, Irons and pallasites with germanium concentrations between 8 and 100 ppm, *Geochimica et Cosmochimica Acta*, **31**: 2065-2093, 1967.
- Wasson, J.T. and Wai, C.M. Composition of the metal, schreibersite and perryite of enstatite achondrites and the origin of enstatite chondrites and achondrites. *Geochemica et Cosmochemica Acta*, **34**: 169–184, 1970.
- Wasson, John T. *Meteorites: Classification and properties*. Springer Science and Business Media, **10**: 318, 2012.
- Weidenschilling, S. Formation of planetesimals and accretion of the terrestrial planets, *Space Science Reviews*, **92**: 295–310, 2000.
- Weidenschilling, S.J. Radial drift of particles in the solar nebula: Implications for planetesimals formation, *Icarus*, **165**: 438–443, 2003.
- Weidenshilling, S. J. Formation processes and time scales for meteorite parent bodies. *Meteorites and the early solar system*, Tucson: The Univ. of Arizona Press, 348-371, 1988.
- Weisberg, M. K., Bosenberg, J. S., Kozhusko, G., Prinz, M., Clayton, R. N. and Mayeda, T. K. EH3 and EL3 chondrites: a petrologic-oxygen isotopic study. *Proceedings of the Lunar and Planetary Science Conference* XXVI, 1481–1482, 1995.
- Weiss, B. P. and Elkins-Tanton, L. T. Differentiated planetesimals and the parent bodies of chondrites, *Annual Review of Earth and Planetary Sciences*, **41**: 529–60, 2013.
- Wetherill, G. and Stewart, G. Formation of planetary embryos: Effects of fragmentation, low relative velocity, and independent variation of eccentricity and inclination, *Icarus*, **106**: 190–209, 1993.
- Weyer, S., Anbar, A. D., Brey, G. P., Munker, C., Mezger, K. and Woodland, A. B. Iron isotope fractionation during planetary differentiation. *Earth and Planetary Science Letters*, 240(2): 251–264, 2005.

- Wiechert, U. and Halliday, A. N. Non-chondritic magnesium and the origins of the inner terrestrial planets. *Earth and Planetary Science Letters*, **256**: 360–371, 2007.
- Williams, A. and Frasca, V. Ion-exchange chromatography. *Current protocols in protein science*, 8-2, 2001.
- Willich, P. EPMA A Versatile Technique for the Characterization of Thin Films and Layered Structures. *Electron Microbeam Analysis,* Springer, Vienna, 1-17, 1992.
- Wombacher, F., Eisenhauer, A., Heuser, A., Weyer, S. and Dauphas, N. Separation of Mg, Ca and Fe from Geological Reference Materials for Stable Isotope Ratio Analyses by MC-ICP-MS and Double-Spike TIMS. *Journal of Analytical Atomic Spectrometry*, 24(5): 627–636, 2009.
- Wood, B. J. Accretion and core formation: constraints from metal-silicate partitioning, *Philosophical Transactions of the Royal Society of London A*, **366**: 4339–4355, 2008.
- Wood, B. J., Wade, J. and Kilburn, M. R. Core formation and the oxidation state of the Earth: additional constraints from Nb, V and Cr partitioning. *Geochimica et Cosmochimica Acta*, 72: 1415–1426, 2008.
- Wood, B. J., Walter, M. J. and Wade, J. Accretion of the Earth and segregation of its core. *Nature*, **441(7095)**: 825–833, 2006.
- Wood, J. A. and Morfill, G. E. A review of solar nebula models. *Meteorites and the early solar system*, Tucson: The Univ. of Arizona Press, 329-347, 1988.
- Xiao, Y., Teng, F. Z., Zhang, H. F. and Yang, W. Large magnesium isotope fractionation in peridotite xenoliths from eastern North China craton: product of melt-rock in interaction. *Geochemica et Cosmochemica Acta*, **115**: 241–261, 2013.
- Yang, W., Teng, F. Z. and Zhang, H. F. Chondritic magnesium isotopic composition of the terrestrial mantle: a case study of peridotite xenoliths from the North China craton. *Earth and Planetary Science Letters*, 288: 475–482, 2009.
- Yin, Q., Jacobsen, S. B., Yamashita, K., Blichert-Toft, J., Telouk, P., and Albarede, F. A short timescale for terrestrial planet formation from Hf–W chronometry of meteorites. *Nature*, **418**: 949–952, 2002.
- Youdin, A.N. and Shu, F.H. Planetesimal formation by gravitational instability. *The Astrophysical Journal*, **580**: 494–505, 2002.

REFERENCES

- Young, E. D. and Galy, A. The isotope geochemistry and cosmochemistry of magnesium. *Reviews in Mineralogy and Geochemistry*, **55:** 197–230, 2004.
- Young, E. D., Galy, A. and Nagahara, H. Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance, *Geochemica et Cosmochemica Acta*, **66** (6): 1095-1104, 2002.
- Young, E. D., Manning, C. E., Schauble, E. A., Shahar, A., Macris, C. A., Lazar, C. and Jordan, M. High temperature equilibrium isotope fractionation of nontraditional stable isotopes: Experiments, theory and applications. *Chemical Geology*, **395**: 176-195, 2015.
- Young, E. D., Tonui, E., Manning, C. E., Schauble, E. and Macris, C.A. Spinelolivine magnesium isotope thermometry in the mantle and implications for the Mg isotopic composition of Earth. *Earth and Planetary Science Letters*, 288 (3– 4): 524–533, 2009.
- Zambardi, T., Poitrasson, F., Corgne, A., Méheut, M., Quitté, G. and Anand, M. Silicon isotope variations in the inner solar system: Implications for planetary formation, differentiation and composition. *Geochimica et Cosmochimica Acta*, 121: 67–83, 2013.
- Zeilik, M. A. and Gregory, S. A. *Introductory Astronomy Astrophysics* (4th ed.). Saunders College Publishing. ISBN: 0-03-006228-4, 1998.
- Zhang, J., Dauphas, N., Davis, A. M., Leya, I. and Fedkin, A. The proto-Earth as a significant source of lunar material. *Nature Geoscience*, **5**: 251–255, 2012.
- Zhang, Y. and Yin, Q. Z. Carbon and other light element contents in the Earth's core based on first-principles molecular dynamics, *The Proceedings of the National Academy of Sciences*, **109(48)**: 19579–19583, 2012.
- Zhang, Y., Sekine, T., He, H., Yu, Y., Liu, F. and Zhang, M. Experimental constraints on light elements in the Earth's outer core, *Scientific Reports*, 6: (22473), doi:10.1038/srep22473, 2016.
- Ziegler, K., Chadwick, O. A., Brzezinski, M. A. and Kelly. E. F. Natural variations of δ30Si ratios during progressive basalt weathering, Hawaiian Islands. *Geochemica et Cosmochemica Acta*, **69**: 4597-4610, 2005a.
- Ziegler, K., Chadwick, O. A., White, A. F. and Brzezinski, M. A. δ<sup>30</sup>Si systematics in a granitic saprolite, Puerto Rico. *Geology*, **33**: 817-820, 2005b.
- Ziegler, K., Young, E. D., Schauble, E. A. and Wasson, J. T. Metal-silicate silicon isotope fractionation in enstatite meteorites and constraints on Earth's core formation. *Earth and Planetary Science Letters*, **295**: 487–496, 2010.

REFERENCES

- Zinner, E. and Epstein, S. Heavy Carbon in individual oxide grains from the Murchison meteorite. *Earth and Planetary Science Letters*, **84:** 359-368, 1987.
- Zinner, E., Tang, M. and Anders, E. Interstellar SiC in the Murchison and Murray meteorites: Isotopic composition of Ne, Xe, Si, C, and N, *Geochemica et Cosmochemica Acta*, **53**: 3273-3290, 1989.

## **PUBLICATIONS ATTACHED WITH THESIS**

• Sikdar J. and Rai V.K. Simultaneous chromatographic purification of Si and Mg for isotopic analyses using MC-ICPMS, *Journal of Analytical Atomic Spectrometry*, **32**: 822-833, 2017.

## **CONFERENCE PROCEEDINGS**

- Rai V.K., **Sikdar, J**. and Shukla, A. D. REE and Mo isotopic study of Permo-Triassic sediments from Spiti Himalaya. Abstract no. 2578. '*Goldschmidt conference*'. August 16<sup>th</sup> -21<sup>st</sup>, 2015, Prague, CZ, 2015.
- Sikdar, J. and Rai, V.K. New chromatographic technique for simultaneous extraction of Si and Mg for their isotopic analysis using MC-ICPMS. '29<sup>th</sup> International Symposium on mass spectrometry (ISMAS)' February 2<sup>nd</sup> 6<sup>th</sup>, 2015. Jodhpur, India, 2015.
- Sikdar, J. and Rai, V.K. Simultaneous determination of Si and Mg isotopic composition in meteorites. Abstract No. 6293, '79<sup>th</sup> Annual Meeting of the Meteoritical Society'. August 7-12, 2016, Berlin, Germany, 2016.
- Sikdar, J. and Rai, V.K. Silicon isotopic variation within Enstatite Chondrite. *The XII Torino workshop and IV CSFK Astromineralogy workshop*. July 31<sup>st</sup> – August 5<sup>th</sup>, 2016, Budapest, Hungary, 2016.
- Sikdar, J. and Rai, V.K. Si and Mg isotopic composition in meteorites. "Accretion, Differentiation and early Evolution of the terrestrial planets." May 29<sup>st</sup> to June 3<sup>rd</sup>, 2017, Nice, France, 2017.
- Sikdar, J. and Rai, V.K. The silicon isotopic composition of metals in EH3 chondrite. '*Goldschmidt conference*' to be held from August 13<sup>th</sup> -18<sup>th</sup>, 2017, Paris, 2017.