Zinc and Copper Isotopic Fractionation during Planetary Differentiation

Heng Chen
Washington University in St. Louis

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Zinc and Copper Isotopic Fractionation during Planetary Differentiation

by

Heng Chen

A dissertation presented to the Graduate School of Arts & Sciences of Washington University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

December 2014

St. Louis, Missouri
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Heng Chen

Washington University in St. Louis

December 2014
ABSTRACT OF THE DISSERTATION

Zinc and Copper Isotopic Fractionation during Planetary Differentiation

by

Heng Chen

Doctor of Philosophy in Earth and Planetary Sciences

Washington University in St. Louis, 2014

Professor Bradley Jolliff, Chair

Zinc and copper are two important transition metal elements that are widely involved in every stage of planetary formation and differentiation. Their isotopic ratios are robust tracers used to understand the origin of the Solar System, planetary formation and differentiation processes. In this thesis, I focus on their isotopic behaviors during magmatic processes. I report the Zn isotopic compositions of representative igneous rocks to determine potential isotopic fractionations associated with magmatic processes, and to estimate the bulk silicate Earth value. I report isotopic compositions of various groups of iron meteorites (samples of which represent the core of asteroids) and discuss the data’s implications for volatile history of the parent bodies of these meteorites.

Chapter 1 is a short introduction to this dissertation. I summarize the geochemical properties of Zn and Cu, and discuss why their isotopes are powerful tracers in geochemistry and cosmochemistry studies. Next I introduce some basic knowledge about the meteorites with an emphasis on irons, which represent most of the meteoritic samples used in this thesis. In addition, I discuss the general concepts of mass-dependent and mass-independent isotopic fractionations, as well as Rayleigh distillation during evaporation processes. Finally, I review the isotopic analysis technique of Zn and Cu using anion-exchange chromatography and MC-ICP-MS.
Chapter 2 evaluates Zn isotopic fractionation during magmatic processes and the bulk Earth value. This work has been published in *Earth and Planetary Sciences Letters* (Chen et al., 2013). Non-traditional stable isotopes are new and powerful proxies in the study of planetary formation and differentiation processes. However, their applications are currently limited by our knowledge of how these isotope systems are affected by igneous processes. This is particularly important because most of the materials available from planetary bodies are differentiated igneous rocks, and therefore, it is necessary to understand isotopic behavior during magmatic processes as well as to evaluate the isotopic composition of the bulk Earth for inter-planetary comparison. In order to assess the isotopic behavior of Zn, I precisely measured the Zn isotopic compositions of two suites of igneous rocks (Kilauea Iki lava lake, Hawaii, and Hekla volcano, Iceland). Results show that Zn isotopes can be fractionated as a result of fractional crystallization; however, the isotopic variation is rather limited (< ~0.1 ‰; $\delta^{66}$Zn). I discuss the mechanism of the isotopic fractionation which is most likely associated with inter-mineral equilibrium fractionation. Based on this study and previously published data, I conclude that Earth’s mantle is homogeneous with respect to Zn isotopes and propose the best estimate for the average Zn isotopic composition of bulk silicate Earth is $0.28 \pm 0.05\%_o$.

Chapter 3 focuses on the Zn isotopic compositions of different groups of iron meteorites. This work has been published in *Meteoritics & Planetary Science* (Chen et al., 2013). Volatile and moderately volatile elements (such as Zn) are powerful proxies to study the volatile history of the Solar System because the elemental abundances and isotopic compositions of these elements are sensitive to evaporation and condensation processes. I report the most complete dataset of high-precision Zn isotopic compositions of iron meteorites (n=32; from both fractionally crystallized and silicate-bearing groups) thus far. Our data support the hypothesis
that Zn was derived from a single reservoir or from multiple reservoirs linked by mass-dependent fractionation processes. This project provides useful information for the origin of the volatile depletion observed in some iron groups, the physical and chemical processes of planetary core formation, and the possible genetic relationships among meteorites.

Chapter 4 is a focused study of the Cu isotopic compositions in IVB iron meteorites (the most volatile poor group of iron meteorites) and its application as a neutron dosimeter. This work has been accepted with revisions in *Geochimica et Cosmochimica Acta* (Chen et al., 2014). We found that the Cu isotopic compositions of IVB iron meteorites were significantly modified by neutron capture effects, which leads to a new application of Cu isotopes--a neutron dosimeter used for correction of neutron capture effects on W isotopes (the most powerful radiochronometer in dating the mantle/core segregation events). Combining our Cu data with W isotope ages of IVB irons, we propose a revised core formation age (1.3 ± 1.8 Myr after CAI formation) of the IVB iron meteorite parent body. This age indicates that core/mantle segregation on the IVB iron meteorite parent body occurred very early in Solar System history.

**Bibliography**


CHAPTER 1: INTRODUCTION
1.1. Overview

A quantitative understanding of stable isotope effects by Urey (1947) and Bigeleisen and Mayer (1947) show that the extent of equilibrium isotope fractionation depends mainly on the relative mass difference between the isotopes and on the temperature. Larger fractionation happens between isotopes with a larger relative mass difference in low temperature conditions (e.g. D/H fractionation between liquid water and vapor). Thus it was traditionally thought that transition metal isotopes are too heavy to fractionate at a resolvable level, especially during high temperature processes.

However, the development of MC-ICP-MS (Multiple-Collector Inductively-Coupled-Plasma Mass-Spectrometry) renders it possible to make very precise measurements of isotopic fractionations of transition metal elements (Maréchal et al., 1999; Zhu et al., 2002; Albarède, 2004), which were too small to detect using previous analytical techniques (typically a precision better than 0.05 permil per atomic mass unit on the MC-ICP-MS). The results so far have already afforded new insights into silicate/metal/sulfide/vapor separation during nebular and planetary processes (e.g. Luck et al., 2005; Williams and Archer, 2011), the origin of the Earth, its core and moon (e.g. Georg et al. 2007; Paniello et al., 2012), and mantle-crust evolution (e.g. Dauphas et al., 2007; Teng, et al., 2013).

1.1.1. Zinc and Copper Isotopes

Zinc and Cu are widely involved in the processes of planetary formation and crustal evolution. Their isotopes have been used as geochemical tracers in both experimental and natural work (Albarède, 2004). Copper has two stable isotopes: $^{63}\text{Cu}$ and $^{65}\text{Cu}$, with average natural
abundances of 69.17% and 30.83%, respectively. Zinc has five stable isotopes: $^{64}$Zn (48.63%), $^{66}$Zn (27.90%), $^{67}$Zn (4.10%), $^{68}$Zn (18.75%), and $^{70}$Zn (0.62%) (Wieser and Coplen, 2010).

The combined use of Zn and Cu isotopes has an important advantage because Zn and Cu share many geochemical similarities but also behave distinctly in several aspects.

1) They are both chalcophile elements (Fauer, 1998), but Cu also shows siderophile behavior, while Zn acts as a lithophile element during magmatic differentiation.

2) In natural environments, Zn occurs in only one valence state: Zn$^{2+}$. In contrast, cuprous (Cu$^+$), cupric (Cu$^{2+}$) and native Cu can all occur, which implies that changes in redox condition may induce large Cu isotopic fractionation (Zhu et al., 2002).

3) More importantly, Zn and Cu are two moderately volatile elements, suggesting that their elemental abundances and isotopic compositions could provide some important information about the history of volatile loss (Paniello et al, 2012; Day and Moynier, 2014). During kinetic evaporation processes, lighter isotopes are preferentially lost to vapor phases, leaving the residues enriched in heavy isotopes. Compared with Cu (Tc$_{50\%}$ = 1037K), Zn (Tc$_{50\%}$ = 726K) is more volatile (Lodders, 2003). Owing to their different geochemical affinities, they occur in different species during evaporation (Moynier, et al., 2009a; 2010).

1.1.2. Isotopic Behavior of Metal Elements during Igneous Processes

Studies of isotopic fractionations could help us to understand the history and conditions during the formation and evolution of the Solar System and planets. However, most samples available for study, e.g., planetary crust and iron meteorite samples, also experienced igneous processes that could fractionate isotopes. However, to date it is still not clear how igneous
processes affect the Zn and Cu isotope systems, which impedes the application of these isotope systems in many ways.

It has been reported that no detectable fractionation occurs for Li and Mg isotopes during high-temperature magmatic differentiation (Tomascak et al., 1999; Teng et al., 2007), suggesting that equilibrium fractionation should also be negligible for metal isotopes with smaller relative mass differences. However, recent high-precision data show that Si isotopes fractionate during fractional crystallization as the more evolved lithologies are more enriched in heavy isotopes, which is likely controlled by the vibrational frequency of Si-O bonds in coexisting phases (Savage, et al. 2011). The isotopic behavior of Fe is more complicated. Its isotopic composition is redox-sensitive, and can be fractionated during various magmatic processes, such as partial melting, mineral crystallization, and fluid exsolution (Weyer et al., 2005; Heimann et al., 2008; Teng et al., 2008; Dauphas et al., 2009).

Given the limited study of Zn and Cu isotopes in igneous rocks, it is necessary to apply high-precision analyses to study potential isotopic fractionation during igneous processes that could modify their compositions away from that of their parent bodies. In addition, studying isotopes in a variety of igneous rocks is essential to establish a firm bulk silicate Earth value for inter-planetary comparison.

This thesis presents the Zn and Cu isotopic compositions of terrestrial igneous rocks to study their isotopic behavior during igneous processes. Zinc and Cu isotopes in iron meteorites are also studied to understand mechanisms associated with core formation processes, and to determine the role of volatilization in the histories of iron meteorites.
1.2. Meteorite Classification

Meteorites can generally be divided into two major categories based on their bulk compositions and textures: undifferentiated meteorites (chondrites) and differentiated meteorites (Krot, et al., 2003; Weisberg et al., 2006).

1.2.1. Classification of Undifferentiated Meteorites

Undifferentiated meteorites are considered to be the primitive surviving materials from early Solar System evolution, as they have not been modified due to melting or differentiation of the parent bodies (Eble, 2006). They are composed of varying proportions of mineralogically dissimilar constituents (chondrules, refractory inclusions, metal, sulfide, etc.). Based on primary features, such as bulk chemical composition, mineral composition, and oxygen isotopes, the chondrites are divided into three classes: carbonaceous chondrites, ordinary chondrites, and enstatite chondrites.

The carbonaceous chondrites are characterized by the presence of carbon compounds and are thought to have been formed far from the sun as they have high proportion of volatile compounds. The carbonaceous chondrites are a large clan with many chemical groups: CI, CM, CR, CB, CO, CV, CK, and CH. The second letter refers to a type specimen for each meteorites group. These groups reflect a wide variety of compositions, oxidation states, and petrography. The ordinary chondrites are the most common materials in meteorite collections, constituting more than 85% of observed falls (Weisberg et al., 2006). Ordinary chondrites can be divided into three mineralogically and chemically distinct groupings: H (highest total iron and metal, low iron oxide in the silicates), L (lower total iron and metal, higher iron oxide in the silicates), and LL (low total iron and metal, highest iron oxide content in the silicates) groups. The enstatite
chondrites are characterized by high contents of mineral enstatite (MgSiO$_3$). They are among the most chemically reduced rocks known, with most of their iron occurring as metal or sulfide rather than an oxide (Keil, 1968). The enstatite chondrites are divided into EH (higher enstatite) and EL (lower enstatite) groups.

**Van Schmus - Wood petrologic type**

A chondrite's group is determined by its primary chemical, mineralogical, and isotopic characteristics. Petrologic type is used to indicate the degree to which a chondrite has been affected by the secondary processes of thermal metamorphism and aqueous alteration. The current scheme for describing petrologic types was originally proposed by Van Schmus and Wood (1967), and revised during the following decades (McSween, 1979; Sears et al. 1980). As currently used, Types 3.1 to 6 represent increasing degrees of thermal metamorphism, while types 2 to 1 represent increasing degrees of hydrous alteration in chondrites. The most primitive chondrites are petrologic type 3.

**1.2.2. Classification of Differentiated Meteorites**

Differentiated meteorites are fragments of differentiated solar system bodies that had experienced melt induced by major episodes of heating, along with different degree of volatile loss. Unlike chondrites, the compositions and textures of differentiated meteorites have been affected by melting and crystallization. Differentiated meteorites include three kinds of chemically different meteorites: (stony) achondritic meteorites, stony iron meteorites, and iron meteorites.
The achondrites are stony meteorites that have undergone melting and differentiation. Their precursors are commonly assumed to have had chondritic compositions, although no chondrules existed after melting and differentiation processes (McSween and Huss, 2010). Achondrites can be classified into the following groups: primitive acondrites (similar chemical composition to that of chondirites, but igneous textures, indicative of melting processes; e.g. Ureilites and Brachinites), asteroidal achondrites (e.g. aubrites and HED meteorites), lunar meteorites, and martian meteorites (e.g. SNC meteorites). The stony-irons are meteorites that contain roughly equal proportions of silicates and metal. The stony-irons are divided into pallasites and mesosiderites. Pallasites contain approximately equal amounts of metal (occurs in matrix) and olivine. Mesosiderites are breccias also composed of approximately equal proportions of silicates and iron-nickel metal plus troilite, but the silicate fraction is basalt.

1.2.3. Classification of Iron Meteorites

Iron meteorites formed by separation of molten metal and sulfide from silicates, of which a large number represent samples from the deep interior of differentiated planetary objects. Iron meteorites are our only available analogues to materials found in the core of the Earth and other terrestrial planets (Haack and McCoy, 2004). Although all iron meteorites consist primarily of iron-nickel metal and most of them formed through a similar mechanism, their chemistry, mineralogy, and structure show differences.

Structural classification

Historically, iron meteorites were classified by the macroscopic structure (Buchwald, 1975). The structural classification is based on the presence or absence of the Widmanstätten pattern, which is visible when a polished surface is etched in acid. The Widmanstätten pattern
develops as a two-phase intergrowth of kamacite and taenite, and forms by nucleation and growth of kamacite from taenite during slow cooling of the parent body (Owen and Burns, 1939). This classification is connected with the relative abundance of nickel to iron. The major three categories are:

**Hexahedrites (H):** One-phase kamacite Octahedrites, no Widmanstätten pattern; low nickel (5 – 6.5 wt%).

**Octahedrites (O):** The most common class; visible Widmanstätten pattern; average to high nickel (of 6 – 12 wt%). They are further divided up on the basis of the width of the kamacite lamellae from coarsest to finest.

**Ataxites (D):** Rare; microscopic Widmanstätten pattern; very high nickel (10 – 42 wt%).

**Chemical classification**

With precise chemical compositions available for iron meteorites, chemical classification became more popular and now the standard for iron meteorite classification (Weisberg et al; 2006). This classification is based largely on Ga-Ni, Ge-Ni, and concentrations of other trace elements against that of nickel (Scott and Wasson, 1975). Iron meteorites were originally divided into four large groups labeled as I, II, III, and IV. With more and precise date available, the original four groups were later classified into 14 clusters (Table 1-1). Within each group, members show uniform cooling rate, structure, and mineralogy. Their chemical variations can be modeled as a result of fractional crystallization, indicating that each group might come from a common parent body (Scott and Wasson, 1975; Haack and McCoy, 2004). Up to 15% of
'anomalous members' that do not fit these groups, are treated as ungrouped. These ungrouped iron meteorites may come from up to 50 different asteroids (Goldstein et al., 2009).

Table 1-1. Properties of iron meteorite groups

<table>
<thead>
<tr>
<th>Group</th>
<th>Number</th>
<th>Ni (wt%)</th>
<th>Ga(ppm)</th>
<th>Ge(ppm)</th>
<th>Structure¹</th>
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<td>IAB</td>
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<td>6–60</td>
<td>11-100</td>
<td>25-520</td>
<td>Og-D</td>
</tr>
<tr>
<td>IC</td>
<td>11</td>
<td>6–7</td>
<td>51-61</td>
<td>134-152</td>
<td>Ogg, Og</td>
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<tr>
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<td>45-62</td>
<td>107-185</td>
<td>H, Ogg</td>
</tr>
<tr>
<td>IIC</td>
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<td>37-39</td>
<td>88-114</td>
<td>Opl</td>
</tr>
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<td>IID</td>
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<td>70-83</td>
<td>82-98</td>
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<tr>
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<td>21-28</td>
<td>60-75</td>
<td>Og-Off</td>
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<tr>
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<td>6</td>
<td>11–14</td>
<td>17-29</td>
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<td>/</td>
<td>/</td>
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<td>3-37</td>
<td>Og</td>
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<td>6.3-7.2</td>
<td>0.7-1.1</td>
<td>Ogg, Om</td>
</tr>
<tr>
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<td>1.6-2.4</td>
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</tr>
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<td>0.17-0.27</td>
<td>0.03-0.07</td>
<td>D</td>
</tr>
<tr>
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<td>6–35</td>
<td>/</td>
<td>/</td>
<td>Ogg-D</td>
</tr>
</tbody>
</table>

After Goldstein et al., (2009)

¹ Structure: H, hexahedrite; Ogg, Og, Om, Of, Off – coarsest, coarse, medium, fine, and finest octahedrites; Opl, plessitic octahedrite, D, ataxite.

Detailed study of mineralogy and chemical trends within groups suggests that there are two very different types of groups, which can be related to their different mechanism of formation.
Fractionally crystallized groups include group IIAB, IID, IVA, IVB, etc. They are largely free of silicates, and chemical variations can be explained by chemical fractionation during fractional crystallization of molten iron. These samples are supposedly representatives of the cores of differentiated asteroid parent bodies.

Silicate-bearing groups include IAB, IIICD, and IIE. In contrast to fractionally crystallized groups, silicate-bearing groups contain abundant silicates often in the form of inclusions, and their compositional trends cannot be simply modeled by fractional crystallization alone (Scott, 1972). The origin of these irons is still under debate, but they are most likely the result of impacts (Wasson and Wang 1986; Goldstein et al., 2009).
1.3. Mass-dependent and –independent isotopic Fractionation

1.3.1. Mass-dependent Isotopic Fractionation

From the mass-dependent isotopic fractionation laws by Urey (1947) and Bigeleisen and Mayer (1947), at a constant temperature, the magnitude of isotope fractionation depends on the relative mass differences among different isotopes of one element. For an element with at least three stable isotopes, given a fractionation factor for one pair of these isotopes, the fractionation factor for other pairs of isotopes can be predicted. The general form of mass dependent fractionation law can be expressed as

\[ \alpha_{ij} = (\alpha_{kj})^\beta \]  
\[ \text{Eq.1-1} \]

Where the isotope fractionation factor (\( \alpha \)) between two substances A and B is defined as

\[ \alpha = \frac{R_A}{R_B} \]  
\[ \text{Eq.1-2} \]

\( R_A \) and \( R_B \) are the isotope ratios of two isotopes in two different substances A and B respectively. For \( \alpha_{ij} \) the two isotopes are i and j, e.g. \(^{66}\text{Zn}\) and \(^{64}\text{Zn}\), and for \( \alpha_{kj} \) the two isotopes are k and j, e.g. \(^{68}\text{Zn}\) and \(^{64}\text{Zn}\).

The mass-dependent fractionation includes equilibrium isotope fractionations and kinetic isotope fractionations. The \( \beta \) values are slightly different in these two processes.

**Equilibrium fractionation** occurs in chemically equilibrated systems that comprise two or more phases. It is a quantum-mechanical phenomenon, driven mainly by the slight differences of Gibbs free energy which can convert to vibrational energies of molecules and crystals containing atoms of different masses (Urey, 1947). The magnitude of equilibrium isotope fractionation
rapidly decreases with increasing temperature, because at high temperature the fractionation factor is a function of $1/T^2$. For equilibrium fractionation:

$$\beta_{eq} = \frac{[(1/m_1)-(1/m_2)]}{[(1/m_1)-(1/m_3)]}$$

Eq.1-3

where $m$ refers to the atomic mass of the isotope.

**Kinetic fractionations** are normally associated with fast, incomplete, or unidirectional processes like fast evaporation, thermal/chemical diffusion, and biologically mediated reactions. Young (2002) provide a $\beta_{kin}$ for kinetic isotope fractionation:

$$\beta_{kin} = \frac{\ln(m_1/m_2)}{\ln(m_1/m_3)}$$

Eq.1-4

For Zn isotopes, as $\alpha_{68/64} = (\alpha_{66/64})^{\beta}$, $\beta_{eq}$=1.942 and $\beta_{kin}$ = 1.971 can be obtained respectively.

A majority of mass-dependent isotope variations are reported using “δ” notation, defined as the deviation of a sample’s isotopic ratio from that of a standard (in per mil). The isotopic composition of Zn is expressed as

$$\delta^n{Zn} = \left(\frac{^a{Zn}}{^64{Zn}_{sample}}\right) / \left(\frac{^a{Zn}}{^64{Zn}_{JMC-Lyon}}\right) - 1\right] \times 1000; n=66, 67 or 68$$

Eq.1-5

With the definition of $\delta^n{Zn}$ and fractionation factor ($\alpha$) above, taking the natural logarithm of the fractionation relation (Eq.1-1) gives:

$$\ln[(\delta^{68/64}{Zn}/1000)+1] = \beta \times \ln [(\delta^{66/64}{Zn} /1000)+1]$$

Eq.1-6

As long as the fractionations are relatively small ($\delta^{66/64}{Zn} < 5\%$), there is relation:

$$\delta^{68/64}{Zn} = \beta \times \delta^{66/64}{Zn}$$

Eq.1-7
Therefore, on a $\delta^{68/64}\text{Zn}$ vs. $\delta^{66/64}\text{Zn}$ three isotope plot, mass-dependent isotopic data will fall on a straight line with a slope of $\beta$, depending on whether the fractionation process is a result of equilibrium or kinetic processes. Until now, all the Zn isotopic data measured in the bulk Solar System materials fall on a line with a slope of $\sim 2$, conforming to the mass-dependent fractionation law, and suggest a single common nebular reservoir for Zn (Luck et al. 2005; Moynier et al., 2009b). For the range of Zn isotopic fractionation associated with high temperature processes (usually less than $1\%$), such that current analytical precision is insufficient to distinguish between the kinetic and equilibrium law.

1.3.2. Mass-independent Isotopic Fractionation

Isotopic ‘anomalies’, or mass-independent isotopic deviations from a terrestrial baseline, were found in many meteorites and their components, such as CAIs and chondrules. (Clayton et al., 1973; Birck, 2004; Trinquier, et al., 2007; Leya et al., 2008).

Mass-independent isotope deviations are often reported using “$\varepsilon$” notation, defined in part per 10,000 relative to the composition of the terrestrial reference after internal normalization to a common isotope ratio (to correct for the mass-dependent isotopic fractionation). For example, all of the measured Zn isotope values were first internal-normalized to a $^{68}\text{Zn}/^{64}\text{Zn}$ value of 0.568828 using the exponential law (Maréchal et al., 1999).

$$\varepsilon^n\text{Zn} = \left[\left(\frac{^{n}\text{Zn}}{^{64}\text{Zn}_{\text{sample}}}\right) / \left(\frac{^{n}\text{Zn}}{^{64}\text{Zn}_{\text{MC-Lyon}}}\right) - 1\right] \times 10,000; n=66, 67\ or\ 70$$  \hspace{1cm} \text{Eq. 1-8}

$\varepsilon^n\text{Zn}$ indicates degree of isotopic compositions that differ from the apparently ‘uniform’ terrestrial values. If there is no isotopic anomaly, $\varepsilon^n\text{Zn}$ is 0. The isotopic anomalies found in solar system materials can be attributed to be the result of the following effects:
1) **Nucleosynthetic effects.** The Solar System is comprised of material from a wide range of chemically and isotopically distinct stellar sources. Isotopically diverse materials that were synthesized in other stars and have been preserved in presolar stardust grains show significant isotopic anomalies (Zinner 1998; Yin et al., 2002). The isotopic anomalies observed in some meteorites reflect recorded incomplete mixing of solar nebula (Dauphas et al., 2002; Regelous et al., 2008).

2) **Radioactive decay.** Isotopic variations can be generated by the decay of radioactive nuclides. For example, the short-lived isotope $^{26}$Al ($T_{1/2}=0.7$ m.y.) decays to $^{26}$Mg. As the Al/Mg ratio in the solar system is not homogeneous, for meteorites or meteoritic components with sub (super)-chondritic, the Al/Mg ratio will be characterized by resolvable $^{26}$Mg deficits (surplus) if they formed within a few million years of CAIs (Lee et al., 1977; Jacobsen et al., 2008).

3) **Cosmogenic effects.** In the galactic high-energy environment, cosmic rays can cause spallation reactions and neutron capture reactions in meteorites (Voshage and Feldmann, 1979; Masarik, 1997). These reactions can produce cosmogenic nuclides that lead to changes in the isotopic compositions of the constituent elements.

4) **Mass-independent fractionation (MIF) in physico-chemical processes.** Examples include mass-independent reaction of oxygen isotopes in the stratospheric ozone (Mauersberger, 1981; Thiemens and Heidenreich, 1983); mass-independent fractionation of sulfur observed in the ancient sediments (Farquhar et al., 2000); and mass-independent fractionation led by the nuclear field shift effect found in meteorites (Fuji et al., 2006).
1.4. Isotopic Fractionation during Evaporation Processes

Evaporation is usually a non-equilibrium process that can cause large isotopic fractionation (Criss, 1999). Zinc and Cu are two moderately volatile elements, which exhibit substantial mass loss together with resolvable isotopic fractionation during volatilization in planetary rocks (Paniello, 2012; Moynier, 2009a, 2010), making them powerful tracers of the volatile histories of planets. For example, on the Earth or in primitive meteorites, evaporation is the only process that can fractionate \( \delta^{66}\text{Zn} \) to the magnitude of 1‰ (Day and Moynier, 2014).

Assuming that evaporation of Cu follows a simple Rayleigh distillation law, and the kinetic fractionation factor \( \alpha \) remains constant during the evaporation process, the \(^{65}\text{Cu} / ^{63}\text{Cu} \) ratio \( R \) in the melt is in a simple function of the mass fraction of melt remaining \( (f) \) and \(^{65}\text{Cu} / ^{63}\text{Cu} \) ratio \( (R_i) \) at the beginning of the process ( when \( f=1 \)).

\[
\frac{R}{R_i} = f^{(\alpha-1)} \tag{Eq.1-9}
\]

It is reasonable to assume the kinetic fractionation factor \( (\alpha) \) to be equivalent to the ratio of the gas diffusion coefficient (Criss, 1999), which can be calculated using Graham’s law:

\[
\alpha = \left( \frac{m_{65\text{Cu}}}{m_{63\text{Cu}}} \right)^{0.5} \tag{Eq.1-10}
\]

where \( m_{65\text{Cu}} \) and \( m_{63\text{Cu}} \) refer to the atomic masses of the isotope \(^{65}\text{Cu} \) and \(^{63}\text{Cu} \). If the evaporation of Cu is in molecules, such as CuS or CuO, \( m \) should be the mass of the molecule. It can be inferred from Eq.1-10 that an evaporating species with a higher molecular weight would generate a lower \( \alpha \). If the relationships are converted to delta notation, equation 1-9 for the residue becomes

\[
\delta = \delta_i + (1,000 + \delta_i) \left[ \left( \frac{[\text{Cu}]}{[\text{Cu}_i]} \right)^{(\alpha-1)} - 1 \right] \tag{Eq.1-11}
\]
δ and δᵢ are the δ⁶⁵Cu of the final and initial melt, respectively. [Cuᵢ] represents the concentration before evaporation, and [Cu] represents the concentration after evaporation. The evolution of the expected δ⁶⁵Cu as a function of the remaining fraction of Cu is plotted in Fig1-1.

Rayleigh distillation assumes that the evaporating material is instantly removed in an open system, and that the element in the residue is instantaneously re-homogenized. But in the natural environments many systems do not strictly follow the Rayleigh distillation law.

Isotope fractionation can be limited by slow diffusion in the condensed phases. If diffusive homogenization of isotopes in the melt proceeds more slowly than evaporation, the system deviates from Rayleigh distillation as a diffusion-limited regime is established (Moynier et al., 2009a). In this case, the isotopic composition of the residue also depends on the diffusion coefficient of the element in the condensed phase. For elemental loss, the magnitude of the isotopic fractionation is reduced compared to pure Rayleigh distillation. Moynier et al. 2009a and 2010 found that in tektites Cu is isotopically more fractionated than the elements K and Zn, which are more volatile. This behavior can be explained by the higher diffusion rate of Cu, since for a given evaporation flux, a higher diffusivity will lead to an increase in isotopic fractionation.

Another possible situation is that large equilibrium isotope fractionations can be generated between gaseous and condensed phases. As in equilibrium fractionation, the fractionation factor (αₑq) is smaller than that (αₖᵢ𝑛) in the kinetic fractionation, so partial equilibration of the vapor and condensed phases could reduce isotope fractionation.

Though the overall processes of evaporation and condensation are complex, the light isotopes have the tendency to be enriched in the vapor phase. Over time, the residual condensed phase will progressively become enriched in heavy isotopes.
Figure 1-1. Graph of $\delta^{65}\text{Cu}$ value of residue during Rayleigh distillation in function of the fraction ($f$) of Cu remaining in the residue. The $\delta^{65}\text{Cu}$ of the starting material ($f = 1$) is set to be 0.1‰.
1.5. Analytical Methods

MC-ICP-MS performance can be affected by spectral interferences arising from the sample matrix, such as isobaric interferences, doubly charged ions, and polyatomic ions (Yang, 2009). Sufficient purification is required to overcome the matrix interference. Zinc and Cu were extracted respectively from the dissolved samples using anion exchange chromatography.

1.5.1. Sample Digestion

For a silicate sample, ~50 mg powder was digested in 4-5 ml 3:1 mixture of concentrated HF and HNO3 in a closed teflon beaker under hot lamp at ~120°C for more than 2 days. After drying down, ~3 ml 6N HCl was added and the closed beaker was heated for 1 day. Then the sample was heated at ~120 °C to dryness to expel the fluorine. For a iron meteorite sample, the metallic chip was first cleaned in diluted HCl and deionized water in an ultrasonic bath to get rid of possible rust and surface contamination, and then placed in double distilled 6N HCl / aqua regia in a closed Teflon beaker at ~120°C until complete dissolution. Then the sample was heated to dryness. The final material was dissolved in 1 ml 1.5N HBr (for Zn) or 7N HCl (for Cu) and was ready for anion exchange chromatography.

1.5.2. Anion-exchange Chromatographic Separation

The method for Zn adopts the method described by Moynier et al. (2006) and the method for Cu follows Maréchal et al., 1999 and Luck et al., 2005. As the shape of column and volume of resin used by different groups may vary, it is essential to calibrate the column chemistry using standard solution before running samples. The modified protocols for Zn and Cu are listed on Table 1-2 and 1-3.

Theory for Zn Chromatographic Separation: Zinc can forms ZnBr₃ in diluted HBr
solution, while other cations do not form complexes that bind to AG-1X8 resin. Additional HBr is run through the column to remove most matrix, leaving essentially only the ZnBr⁻, which is strongly bonded to resin in the column. The Zn is then recovered by passing dilute HNO₃ through the column (this changes the speciation of zinc to Zn²⁺, and it is released from the column). For most of the silicate samples, this process is repeated once on a small column, however, for the iron meteorites, which have high Ni and low Zn contents, this process is repeated two times to minimize the matrix, particularly Ni.

<table>
<thead>
<tr>
<th>Table 1-2. Protocol for Zn purification by anion exchange</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eluent</td>
</tr>
<tr>
<td>Step 1: AG1x8 Resin (1 ml)</td>
</tr>
<tr>
<td>1.5N HBr</td>
</tr>
<tr>
<td>Load sample in 1.5N HBr</td>
</tr>
<tr>
<td>1.5N HBr</td>
</tr>
<tr>
<td>0.5N HNO₃</td>
</tr>
<tr>
<td>Step 2: AG1x8 Resin (0.4 ml)</td>
</tr>
<tr>
<td>1.5N HBr</td>
</tr>
<tr>
<td>Load sample in 1.5N HBr</td>
</tr>
<tr>
<td>1.5N HBr</td>
</tr>
<tr>
<td>0.5N HNO₃</td>
</tr>
</tbody>
</table>

Theory for Cu Chromatographic Separation: In highly concentrated HCl, the distribution coefficient of Cu(II) for AG MP-1 anion-exchange resin (100-200 mesh, chloride form) is much higher than most matrix such as Mg, Ti, Ni etc, but lower than Fe and Zn. After the sample is
loaded on the resin, most cations that have weaker affinity for the resins are first removed by 7 ml of 7N HCl+0.001% H₂O₂, and then Cu is collected eluted by the next 19 ml of the same solution (Fig 1-2). After complete recovery of Cu, Fe and Zn can be eluted by diluted HNO₃ and H₂O from the resin. Like the method for Zn purification, this process is repeated once for most of silicate samples, but twice for iron meteorites to minimize the matrix, particularly Ni.

**Table 1-3.** Protocol for Cu purification by anion exchange

<table>
<thead>
<tr>
<th>Eluent</th>
<th>Vol. a</th>
<th>Elements Eluted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1 and 2:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7N HCl</td>
<td>5</td>
<td>conditioning</td>
</tr>
<tr>
<td>Load sample in 7N HCl+0.001%H₂O₂</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>7N HCl+0.001% H₂O₂</td>
<td>7</td>
<td>Matrix (Mg, Ti, Ni etc.)</td>
</tr>
<tr>
<td>7NM HCl+0.001% H₂O₂</td>
<td>19</td>
<td>Cu</td>
</tr>
<tr>
<td>H₂O/ 0.5N HNO₃</td>
<td>30</td>
<td>Matrix (Fe, Zn etc.)</td>
</tr>
</tbody>
</table>

a Volume of eluent in micro liter

As anion-resins fractionate both Cu and Zn isotopes (Maréchal and Albarède et al., 2002), complete recovery is essential. The recovery rate was checked and found to be better than 99% for both Cu and Zn.
1.5.3. MC-ICP-MS Analysis for Cu and Zn Isotopes

In this thesis, all Zn and Cu isotopic ratios were measured by a sample-standard bracketing method using a Thermo-Finnigan Neptune plus MC-ICP-MS at Washington University in St. Louis.

The concentrations of Zn/Cu in the sample solutions were measured first and all samples were then diluted to match the concentration of standard (usually 150 or 200 ppm) in 0.1N HNO₃. Zinc and Cu isotopic ratios were analyzed in low-resolution with the same cup configuration (in Table 1-4). Each sample/standard is measured for 30 cycles with 5s integration time per cycle. Every sample is repeated 2 to 6 times with standard-sample bracketing and the average is reported as the final data for each sample. Zinc isotopic data are reported in standard δ-notation
in per mil relative to standard reference material JMC-Lyon (Eq.1-5), and Cu ratios are report relative to (SRM) NIST 976 (Eq.1-11; Albarède, 2004).

\[
\delta^{n}\text{Zn} = \left( \frac{^{n}\text{Zn}}{^{64}\text{Zn}_{\text{sample}}} / \frac{^{n}\text{Zn}}{^{64}\text{Zn}_{\text{JMC-Lyon}}} \right) - 1 \right) \times 1000; n=66, 67 or 68 \quad \text{Eq.1-5}
\]

\[
\delta^{65}\text{Cu} = \left( \frac{^{65}\text{Cu}}{^{63}\text{Cu}_{\text{sample}}} / \frac{^{65}\text{Cu}}{^{63}\text{Cu}_{\text{NIST 976}}} \right) - 1 \right) \times 1000 \quad \text{Eq.1-12}
\]

After double-column purification, the very low signals of matrix elements yield neglected influence on Cu isotopic measurement. But for some samples, the isobaric interference from $^{64}\text{Ni}$ on $^{64}\text{Zn}$ needs to be corrected in order to obtain accurate Zn isotopic determinations. With nine collection cups on the Neptune MC-ICP-MS, each mass from 62 to 68 can be measured at the same time. Mass 62 is only Ni, so it can be used to evaluate and subtract the interference from $^{64}\text{Ni}$ on $^{64}\text{Zn}$, using natural abundances of Ni isotopes ($^{62}\text{Ni}$ is 3.6345% of Ni isotopes, $^{64}\text{Ni}$ is 0.9256%).

Table 1-4. Positions of collectors (Faraday cups) for Zinc and Copper isotope analysis in MC-ICP-MS

| Cup Number L4 L3 L2 L1 C H1 H2 H3 H4 Isotope \ / | $^{62}\text{Ni}$ | $^{64}\text{Zn}$ | $^{62}\text{Cu}$ | $^{66}\text{Zn}$ | $^{67}\text{Zn}$ | $^{68}\text{Zn}$ | \ / |
|---|---|---|---|---|---|---|---|---|---|---|
| \ | \ | \ | \ | \ | \ | \ | \ | \ | \ |

As the mass bias effect (mass spectrometers favor transmission of heavy isotopes) in the MC-ICP-MS is much larger than in the TIMS (Yang, 2009), so that the natural $^{64}\text{Ni}/^{62}\text{Ni}$ ratio cannot be used directly, and a mass-bias correction procedure must be applied. The mass bias is corrected by using the exponential law (Maréchal et al., 1999; Young, 2002)

\[
\beta_{\text{zn}} = \frac{\ln(R_{Zn}/ r_{Zn})}{\ln(m_{68}/m_{66})} \quad \text{Eq.1-13}
\]

In equation 1-13, $R_{Zn}$ and $r_{Zn}$ are the true and the measured isotopic ratio of $^{68}\text{Zn}/^{66}\text{Zn}$; $m_{68}$ and
are the atomic masses of $^{68}$Zn and $^{66}$Zn, which are 67.925 and 65.926 respectively. Assuming $\beta_{Zn} = \beta_{Ni}$, the measured $^{64}$Ni/$^{62}$Ni ratio ($r_{Ni}$) can be obtained and used to correct $^{64}$Ni interference on $^{64}$Zn following equation 1-14:

$$r_{Ni} = R_{Ni} \left( \frac{m_{64}}{m_{62}} \right)^{\beta_{Ni}} \quad \text{Eq. 1-14}$$

The blank of ~10 ng for Zn and ~5 ng for Cu are negligible with respect to the total amount of Zn and Cu in the samples, which are more than 3μg.
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References


CHAPTER 2:

ZINC ISOTOPE FRACTIONATION DURING MAGMATIC DIFFERENTIATION AND THE ISOTOPIE COMPOSITION OF THE BULK EARTH

Abstract

The zinc stable isotope system has been successfully applied to many and varied fields in geochemistry, but to date it is still not completely clear how this isotope system is affected by igneous processes. In order to evaluate the potential application of Zn isotopes as a proxy for planetary differentiation and volatile history, it is important to constrain the magnitude of Zn isotopic fractionation induced by magmatic differentiation. In this study we present high-precision Zn isotope analyses of two sets of chemically diverse, cogenetic samples from Kilauea Iki lava lake, Hawaii, and Hekla volcano, Iceland, which both show clear evidence of having undergone variable and significant degrees of magmatic differentiation.

The Kilauea Iki samples display small but resolvable variations in Zn isotope composition (0.26‰<$\delta^{66}$Zn<0.36‰; $\delta^{66}$Zn defined as the per mille deviation of a sample's $^{66}$Zn/$^{64}$Zn compositional ratio from the JMC-Lyon standard), with the most differentiated lithologies exhibiting more positive $\delta^{66}$Zn values. This fractionation is likely a result of the crystallization of olivine and/or Fe–Ti oxides, which can both host Zn in their crystal structures. Samples from Hekla have a similar range of isotopic variation (0.22‰<$\delta^{66}$Zn<0.33‰), however, the degree of fractionation caused by magmatic differentiation is less significant (only 0.07‰) and no correlation between isotope composition and degree of differentiation is seen. We conclude that high temperature magmatic differentiation can cause Zn isotope fractionation that is resolvable at current levels of precision, but only in compositionally-evolved lithologies. With regards to primitive (ultramafic and basaltic) material, this signifies that the terrestrial mantle is essentially homogeneous with respect to Zn isotopes. Utilizing basaltic and ultramafic sample analyses, from different geologic settings, we estimate that the average Zn isotopic composition of Bulk Silicate Earth is $\delta^{66}$Zn=0.28±0.05‰ (2s.d.).
2.1. Introduction

Zinc (Zn) is a lithophile and moderately volatile element, with a 50% condensation temperature (T_c) of 726 K (Lodders, 2003). It has five stable isotopes: $^{64}\text{Zn} (49.17\%),$ $^{66}\text{Zn} (27.73\%),$ $^{67}\text{Zn} (4.04\%),$ $^{68}\text{Zn} (18.45\%),$ and $^{70}\text{Zn} (0.61\%),$ with variations in Zn isotope ratios typically expressed relative to the JMC-Lyon Zn standard in parts per thousand (Albarède, 2004), using the delta (δ) notation:

$$\delta^n\text{Zn} = \left[\frac{(n\text{Zn} / 64\text{Zn}_{\text{sample}})}{(n\text{Zn} / 64\text{Zn}_{\text{JMC-Lyon}})} - 1\right] \times 1000; n=66, 67 \text{ or } 68$$

In natural environments, Zn occurs in only one valence state, Zn (II), and therefore Zn isotopes are insensitive to changes in redox condition.

With the development of MC-ICP-MS (Multiple-Collector Inductively-Coupled-Plasma Mass-Spectrometry) over the last 20 yr, high-precision isotopic measurements of Zn are now possible and have been applied to many and varied fields in the geosciences (e.g., Albarède, 2004). For instance, Zn is the second most abundant metal in biological organisms and its uptake and transport can be traced using Zn isotopic measurements (Weiss et al., 2005; Moynier et al., 2009a; von Blanckenburg et al., 2009; Albarède et al., 2011 and Andersen et al., 2011). Since Zn isotopes fractionate during the smelting process, they have also been applied in both archeological and environmental pollution studies (Sivry et al., 2008 and Juillot et al., 2011). Recent work has shown that Zn isotopes are substantially fractionated during evaporation–condensation processes (Moynier et al., 2009b and Moynier et al., 2011) and it has been proposed that Zn isotopes have the potential to provide unique insights into the origin of volatile element depletion in solar system materials. For example, Paniello et al. (2012a) showed that the $\delta^{66}\text{Zn}$ of lunar basalt is ~1‰ heavier than terrestrial basalt, and suggested that this fractionation
occurred during a large-scale evaporation event, likely related to the giant impact origin of the Moon. However the potential to reveal planetary formation and differentiation processes is presently limited by our knowledge of how the Zn isotopic system is affected by igneous processes. Because most materials available for study are differentiated magmatic rocks, potential isotopic fractionation during igneous processes could modify their compositions away from that of their parent bodies.

Since isotopic fractionation is a function of $1/T^2$ (Bigeleisen and Mayer, 1947 and Urey, 1947), it was often assumed that little or no isotopic fractionation occurred during melting and crystallization associated with the formation of planetary crusts. However, technological improvements in mass-spectrometry now allows high precision isotopic measurements, such that such small degrees of isotopic fractionation ($<0.05\%\text{amu}^{-1}$) related to magmatic differentiation can and have been measured for certain elements. For example, both Fe and Si isotopes can fractionate by $\sim0.1\%\text{amu}^{-1}$ during partial melting and fractional crystallization (Weyer and Ionov, 2007; Teng et al., 2008; Schoenberg et al., 2009; Schuessler et al., 2009 and Savage et al., 2011). On the other hand, for some other elements such as Mg and Li, no detectable whole-rock isotopic variations have been observed as a result of magmatic differentiation (Tomascak et al., 1999 and Teng et al., 2007).

In contrast to these element systems, there has been limited investigation into the Zn isotopic compositions of silicate rocks. In an abstract, Ben Othman et al. (2006) reported that mid-ocean ridge basalts (MORB) samples from different ocean basins display little variation away from their average composition of $\delta^{66}\text{Zn}=0.25\%$. Herzog et al. (2009) reported the $\delta^{66}\text{Zn}$ for ten ocean–island basalt (OIB) samples from Reunion Island, which scatter from 0.30 to 0.41%, and two basaltic samples from the Nyiragongo volcano which have $\delta^{66}\text{Zn}$ of 0.22 and 0.37%. The
$\delta^{66}\text{Zn}$ of four andesitic samples from Merapi volcano are homogeneous with values between 0.23 and 0.25‰ (Toutain et al., 2008). Moreover, USGS igneous geostandards from different geologic settings cluster within a narrow range of 0.20–0.40‰ (Chapman et al., 2006; Cloquet et al., 2006; Herzog et al., 2009 and Moynier et al., 2009b). Although this range is limited, given our current analytical precision ($\leq$0.05‰, 2s.d.) it is eminently possible that systematic variations due to igneous processes could be detected. As yet, however, no study has been conducted to investigate this possibility.

In order to investigate the magnitude of Zn isotopic fractionation as a result of magmatic differentiation, and also to evaluate the Zn isotopic composition of the Bulk Silicate Earth (BSE), here we report the Zn isotopic compositions of two sets of samples from Kilauea Iki lava lake, Hawaii, and Hekla volcano, Iceland. These two volcanic systems represent ideal natural laboratories with which to evaluate elemental and isotopic behavior during igneous processes. This is because they both produce samples with a wide range of SiO$_2$ contents from a cogenetic source, which show little evidence for contamination by evolved, geochemically diverse, crustal material (Tomascak et al., 1999; Teng et al., 2007 and Savage et al., 2011).
2.2. Samples and Geological settings

2.2.1. Kilauea Iki

Kilauea Iki lava lake is located in the southeast of Hawaii Island. When the Kilauea volcano erupted in 1959, part of the lava ponded into a pre-existing crater (to the east of the main caldera) to a depth of ~135 m. This, in effect, led to the development of a small, self-roofed, magma chamber. The lava body cooled and crystallized as a closed system during the following decades. Between 1960 and 1988, the interior of the lava lake was sampled by coring from the surface of the lake to the bottom (Helz, 2012).

Kilauea Iki lava lake is an ideal location for studying elemental and isotopic behavior during magmatic differentiation, owing to a number of factors:

1. The system formed from a single eruption, so magmatic differentiation in the lava lake can be treated as a closed system.

2. Large-scale internal differentiation of the lava ceased around 1980 (Helz, 1987), so the total time (less than 30 yr) involved in cooling and crystallization is very short compared to many geological settings. In addition, the lava has a similar composition to the country rock; therefore, chemical modification from assimilation is minor. In addition, Li isotopic studies have shown that geothermal fluids have not significantly affected the chemistry of these samples (Tomascak et al., 1999).

3. The lava lake has been monitored and sampled throughout its existence, so that both the crystallization sequence and thermal history are well documented (Helz, 1987; Helz and Thornber, 1987; Teng et al., 2011 and Helz, 2012).
The original 1959 Kilauea Iki lava consists of picritic tholeiite with an average MgO content of 15.43 wt% (Wright, 1973). The chemical compositions of these fast cooling eruption samples are controlled chiefly by variations in olivine content. Core samples from Kilauea Iki lava lake range from olivine-rich cumulates, through olivine tholeiites, ferrodiabases as well as rare, more silicic veins, with MgO contents ranging from 26.87 to 2.37 wt% (Helz, 1987). Chemically, samples with MgO contents >7.5 wt% were predominantly affected by removal or accumulation of olivine, whilst the more fractionated samples (MgO<7.5 wt%) were produced by segregation of liquid from within coherent, crystal-rich mushes, wherein augite, plagioclase and Fe–Ti oxides had crystallized (Helz, 2012).

The samples utilized by this study include two original eruption lavas (Iki-22, Iki-58) and 8 drill core samples from the interior of the lake, which represent the variety of lithologies so far described. These samples have been well characterized in previous studies for major and trace elements as well as Li, Mg and Fe isotopes (Helz, 1987; Helz, 2012; Tomascak et al., 1999; Teng et al., 2007; Teng et al., 2008; Teng et al., 2011 and Pitcher et al., 2009). Since olivine contents in these samples vary significantly, MgO contents define a large range, from 25.8 to 2.4 wt%. The SiO$_2$ contents range from 44.6 to 57.1 wt%, and Zn concentrations vary from 79 to 165 ppm.

### 2.2.2. Hekla

Hekla volcano is an active fissure volcano, located in the southeast of Iceland, where the South Iceland Seismic Zone and Eastern Volcanic Zone meet. Several prehistoric (7000 BP–2900 BP) eruptions have been identified, which produced large amounts of tephra of mainly felsic and intermediate compositions. Since 1104 A.D., Hekla has had ~20 historic eruptions. The volcano erupted once or twice per century between 1104 A.D. and 1947 A.D. (Thorarinsson,
1967), however, after 1947 A.D., the time interval between eruptions reduced to ~10 yr, and lava volume decreased. The most recent eruption was on February 26, 2000 (Hoskuldsson et al., 2007).

Hekla produces transitional alkali-type eruptive materials with a wide range of SiO$_2$ contents, with lithologies ranging from basalt through basaltic andesite, andesite to dacite and rhyolite (Thorarinsson, 1967). Each eruption begins with a Plinian phase, followed by mixed explosive and effusive activity, ending with an effusive phase, with lava evolving from initial high-Si (rhyolitic or dacitic) to late stage basaltic andesite compositions. The SiO$_2$ contents of initial eruption positively correlate to dormancy interval (Thorarinsson and Sigvaldason, 1972). In Hekla and its vicinity, no hydrothermal system is associated with volcanic activity and Sr, Nd, and O isotope studies suggest contamination from crustal material and geothermal fluids is limited (Sigmarsson et al., 1992). Also, Li isotopic evidence excludes significant chemical alteration from exsolution of fluids from the melt (Schuessler et al., 2009). Potential isotopic fractionation, therefore, should only be the result of high temperature igneous process.

Sigmarsson et al. (1992) suggested that the wide range of silica contents recorded in Hekla lavas are not produced by simple fractional crystallization, and proposed a 3-stage petrogenetic model for Hekla lavas, as follows:

1. Basaltic melt ponds at the base of a shallow magma chamber where it evolves by fractional crystallization to produce basaltic andesite magma.

2. Dacitic melt forms as the result of partial melting of crustal metabasic rocks, caused by the heat from the ponded basaltic magma. Rhyolites evolve from these dacitic melts by fractional crystallization.
(3) Mixing of the basaltic andesite and dacitic melts forms the andesites.

Note that Chekol et al. (2011) question the above model using U-series data, as well as recent seismic evidence (which argues against the presence of a shallow magma chamber; Soosalu and Einarsson, 2004). They propose an alternative model, whereby magma continuously rises from a deeper (near-Moho) reservoir to reside in several isolated lenses of magma at a shallow crustal level, where it undergoes differentiation through AFC (assimilation and fractional crystallization; DePaolo, 1981) processes. In the case of Zn isotopes, however, the acceptance of one model over the other does not alter our interpretation of the data, as will be discussed later.

The samples from Hekla analyzed in this study were collected between 2009 and 2010 and are described, with major and selected trace elements analyses, in Savage et al. (2011). The samples display a wide range of SiO₂ concentrations (46.5–72.1 wt%), and comprise 5 basalts, 4 basaltic andesites, 4 andesites, 3 dacites and 2 rhyolites. Zinc concentrations range from 115 to 168 ppm. These samples have also been analyzed for Si, V and Sr isotope compositions (Savage et al., 2011; Prytulak et al., 2012 and Sutcliffe et al., 2012). One dacite sample which was collected from Iceland, but genetically unrelated to Hekla was also included in this study, as well as the Icelandic basalt USGS geostandard BIR-1.

Finally, we also report the Zn isotopic composition of five additional USGS geostandards: the dunite DTS-1, basalts BCR-1, BCR-2 and BHVO-2, and the andesite AGV-2.
2.3. Analytical Methods

All samples were received as bulk-rock powders, pulverized in agate. Approximately ~50 mg of each sample powder was dissolved in conc. HNO3/HF (1:3) in PTFE containers and heated under a hot lamp for a minimum of 48 h. Subsequently, the samples were dried down and 5 mL of 6 N HCl was added to the residue and heated in a capped beaker for >24 h, to destroy fluoride complexes. Samples were then heated to dryness again.

Purification of Zn was achieved by anion exchange chromatography following the procedure described in Moynier et al. (2006). To separate Zn from the rock matrix, samples were redissolved in 1 mL of 1.5 N HBr and loaded on to columns filled with 0.5 mL of pre-cleaned anion-exchange resin (BioRad AG1-X8, 200–400 mesh), previously conditioned with 2 ml 1.5 N HBr. Matrix elements were eluted by further addition of 1.5 N HBr to the column and Zn was extracted in 0.5 N HNO3. This process was repeated on smaller 0.1 mL columns to further purify Zn. The total procedural blank is ~10 ng, which is negligible with respect to the total amount of Zn contained in the samples (>4 μg).

The collected solutions were heated to dryness and subsequently dissolved in 0.1 N HNO3 for mass spectrometry analysis. All samples were analyzed using a Thermo Scientific Neptune Plus high-resolution MC-ICP-MS at Washington University in St Louis, following the procedures described in Paniello et al. (2012b).
2.4. Results

2.4.1. Measurement Errors and Reproducibility

The internal precision on the measured $^{66}$Zn/$^{64}$Zn ratio (based on more than 3 repeat runs of the same sample solution during a single analytical session) is $\pm 0.04\%$ (2s.d.). In order to evaluate a more robust external precision we processed seven aliquots of sample KI79-1R1-170.9 through the whole procedure (dissolution, chemical purification and mass-spectrometer measurements). The reproducibility taken from these repeat measurements is also $\pm 0.04\%$ (2s.d.; see Table 2-1), comparable to the internal precision data. Also, the Zn isotopic compositions of some widely available and well-characterized USGS standards (DTS-1, BCR-1, BCR-2 BHVO-2, BIR-1 and AGV-2) are listed in Table 2-2 as well as some previously reported analyses. The excellent agreement between our data and literature values demonstrates the robustness of the methods and our analyses.

In order to further test the reproducibility of our sample digestion and analysis techniques, total procedural replicates of 5 Kilauea Iki samples were measured 1 yr after our first measurements. The data (Table 2-1) show that $\delta^{66}$Zn variations between replicates of the same sample are within $\pm 0.03\%$, demonstrating excellent method reproducibility. Finally, in order to rule out possible isotope fractionation caused by incomplete sample digestion of, for example, spinel or oxides, one sample (KI79-1R1-170.9) was also digested in a high pressure Parr bomb. This sample was chosen because it has one of the most fractionated Zn isotope compositions away from “basaltic”, and it exhibits high Fe contents, indicating the presence of oxide phases. Zinc isotope compositions acquired by both regular and bomb digestions are identical within error, indicating our routine digestion method does not induce Zn isotope fractionation.
Table 2-1. Zn isotopic composition of K179-1R1-170.9 to test precision, total seven procedural replicates were prepared and analyzed.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\delta^{66}$Zn</th>
<th>2se</th>
<th>$\delta^{67}$Zn</th>
<th>2se</th>
<th>$\delta^{68}$Zn</th>
<th>2se</th>
<th>n$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>replicate 1</td>
<td>0.34</td>
<td>0.01</td>
<td>0.51</td>
<td>0.02</td>
<td>0.68</td>
<td>0.04</td>
<td>4</td>
</tr>
<tr>
<td>replicate 2</td>
<td>0.34</td>
<td>0.01</td>
<td>0.51</td>
<td>0.03</td>
<td>0.68</td>
<td>0.01</td>
<td>3</td>
</tr>
<tr>
<td>replicate 3</td>
<td>0.34</td>
<td>0.02</td>
<td>0.46</td>
<td>0.08</td>
<td>0.67</td>
<td>0.02</td>
<td>4</td>
</tr>
<tr>
<td>replicate 4</td>
<td>0.36</td>
<td>0.06</td>
<td>0.51</td>
<td>0.09</td>
<td>0.70</td>
<td>0.09</td>
<td>4</td>
</tr>
<tr>
<td>replicate 5</td>
<td>0.31</td>
<td>0.02</td>
<td>0.48</td>
<td>0.05</td>
<td>0.65</td>
<td>0.06</td>
<td>4</td>
</tr>
<tr>
<td>replicate 6</td>
<td>0.33</td>
<td>0.01</td>
<td>0.52</td>
<td>0.05</td>
<td>0.68</td>
<td>0.02</td>
<td>3</td>
</tr>
<tr>
<td>replicate 7</td>
<td>0.32</td>
<td>0.06</td>
<td>0.47</td>
<td>0.08</td>
<td>0.63</td>
<td>0.10</td>
<td>6</td>
</tr>
<tr>
<td>Average</td>
<td>0.33</td>
<td>0.03</td>
<td>0.50</td>
<td>0.06</td>
<td>0.67</td>
<td>0.05</td>
<td>7</td>
</tr>
<tr>
<td>2SD</td>
<td>0.04</td>
<td></td>
<td>0.05</td>
<td></td>
<td>0.05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ n=number of repeat measurement by MC-ICP-MS
Table 2-2. Zinc isotopic composition of USGS geostandards.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta^{66}$Zn</th>
<th>2s.d.</th>
<th>$\delta^{68}$Zn</th>
<th>2s.d.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTS-1</td>
<td>0.29</td>
<td>0.04</td>
<td>0.57</td>
<td>0.06</td>
<td>This study</td>
</tr>
<tr>
<td>BCR-1</td>
<td>0.27</td>
<td>0.04</td>
<td>0.53</td>
<td>0.06</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>0.29</td>
<td>0.12</td>
<td>0.63</td>
<td>0.24</td>
<td>Chapman et al., 2006</td>
</tr>
<tr>
<td></td>
<td>0.32</td>
<td>0.13</td>
<td>0.81</td>
<td>0.22</td>
<td>Cloquet et al., 2006</td>
</tr>
<tr>
<td></td>
<td>0.23</td>
<td>0.08</td>
<td>/</td>
<td>/</td>
<td>Bigalke et al., 2010</td>
</tr>
<tr>
<td>BHVO-2</td>
<td>0.33</td>
<td>0.04</td>
<td>0.65</td>
<td>0.06</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>0.21</td>
<td>0.09</td>
<td>0.50</td>
<td>0.27</td>
<td>Moynier et al., 2010</td>
</tr>
<tr>
<td></td>
<td>0.29</td>
<td>0.09</td>
<td>0.60</td>
<td>0.27</td>
<td>Herzog et al., 2009</td>
</tr>
<tr>
<td>BIR-1</td>
<td>0.31</td>
<td>0.04</td>
<td>0.61</td>
<td>0.06</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>0.26</td>
<td>0.09</td>
<td>0.54</td>
<td>0.27</td>
<td>Herzog et al., 2009</td>
</tr>
<tr>
<td>AGV-2</td>
<td>0.32</td>
<td>0.04</td>
<td>0.62</td>
<td>0.05</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.09</td>
<td>0.55</td>
<td>0.27</td>
<td>Moynier et al., 2010</td>
</tr>
</tbody>
</table>

2.4.2. Sample Data

Zinc isotopic compositions and selected element concentrations of 10 Kilauea Iki samples are reported in Table 2-3 and Fig. 2-1a. The $\delta^{66}$Zn values of Kilauea Iki samples are closely distributed, from 0.26‰ to 0.36‰, with a weighted average of 0.29±0.06‰ (2s.d.; weights calculated using $1/\sigma^2$, where $\sigma$ is the 1 sigma standard deviation). The average composition of erupted and chilled samples is 0.27±0.04‰ (2s.d.), slightly lower than the average value of the three most fractionated samples (0.33±0.05‰).

Zinc isotopic compositions and selected element concentrations of 17 Hekla samples are reported in Table 2-4 and Fig. 2-1b. The total Hekla $\delta^{66}$Zn range is 0.22–0.33‰, with a weighted average value of 0.28±0.06‰ (2s.d.), identical to the average of Kilauea Iki samples. The
average values for each lithology are as follows: $\delta^{66}\text{Zn}_{\text{basalt}} = 0.27 \pm 0.04 \permil$; $\delta^{66}\text{Zn}_{\text{basaltic–andesite}} = 0.25 \pm 0.06 \permil$; $\delta^{66}\text{Zn}_{\text{andesite}} = 0.29 \pm 0.04 \permil$; $\delta^{66}\text{Zn}_{\text{dacite}} = 0.31 \pm 0.03 \permil$; $\delta^{66}\text{Zn}_{\text{rhyolite}} = 0.28 \pm 0.03 \permil$

(all errors are 2σ). Despite the large variations in chemical composition between each lithology, the $\delta^{66}\text{Zn}$ difference between each group is no more than 0.06‰. One Icelandic dacite sample (RHY01-09) which is genetically unrelated to Hekla has a $\delta^{66}\text{Zn}$ of 0.36‰, and the Icelandic basalt geostandard BIR-1 has a $\delta^{66}\text{Zn}$ of 0.31‰; both of these values are identical within error to the Hekla sample set average.
Table 2-3. Zinc isotopic compositions of samples from the Kilauea Iki lava lake, Hawaii.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Description</th>
<th>$\delta^{66}$Zn</th>
<th>$\delta^{67}$Zn</th>
<th>$\delta^{68}$Zn</th>
<th>Zn(μg/g)$^a$</th>
<th>SiO$_2$(%)$^b$</th>
<th>MgO(%)$^b$</th>
<th>n$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI67-3-6.8</td>
<td></td>
<td>0.27</td>
<td>0.41</td>
<td>0.54</td>
<td></td>
<td></td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>KI67-3-6.8 (replicate)</td>
<td>Chilled upper crust</td>
<td>0.24</td>
<td>0.34</td>
<td>0.46</td>
<td>96</td>
<td>44.63</td>
<td>25.83</td>
<td>4</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.26</td>
<td>0.38</td>
<td>0.51</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Iki-22</td>
<td>Eruption sample</td>
<td>0.27</td>
<td>0.42</td>
<td>0.54</td>
<td>81</td>
<td>46.68</td>
<td>19.52</td>
<td>9</td>
</tr>
<tr>
<td>KI79-3-150.4</td>
<td></td>
<td>0.28</td>
<td>0.42</td>
<td>0.56</td>
<td></td>
<td></td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>KI79-3-150.4 (replicate)</td>
<td>Moderate Olivine Content</td>
<td>0.26</td>
<td>0.40</td>
<td>0.53</td>
<td>97</td>
<td>48.44</td>
<td>13.51</td>
<td>3</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.27</td>
<td>0.41</td>
<td>0.55</td>
<td></td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>KIKI67-3-28</td>
<td>Upper Crust, moderate olivine content</td>
<td>0.29</td>
<td>0.43</td>
<td>0.57</td>
<td>104</td>
<td>48.61</td>
<td>12.01</td>
<td>4</td>
</tr>
<tr>
<td>Iki-58</td>
<td></td>
<td>0.27</td>
<td>0.39</td>
<td>0.54</td>
<td></td>
<td></td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Iki-58 (replicate)</td>
<td>Eruption sample</td>
<td>0.27</td>
<td>0.38</td>
<td>0.52</td>
<td>79</td>
<td>49.91</td>
<td>8.08</td>
<td>3</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.27</td>
<td>0.39</td>
<td>0.53</td>
<td></td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>KI75-1-121.5</td>
<td>Olivine-Poor Zone</td>
<td>0.30</td>
<td>0.44</td>
<td>0.59</td>
<td>109</td>
<td>50.00</td>
<td>7.77</td>
<td>4</td>
</tr>
<tr>
<td>KI75-1-75.0</td>
<td>Ferrodiabase segregation vein</td>
<td>0.29</td>
<td>0.42</td>
<td>0.56</td>
<td>126</td>
<td>50.13</td>
<td>5.77</td>
<td>5</td>
</tr>
<tr>
<td>KI79-1R1-170.9</td>
<td></td>
<td>0.33</td>
<td>0.50</td>
<td>0.67</td>
<td></td>
<td></td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>KI79-1R1-170.9 (replicate)</td>
<td></td>
<td>0.34</td>
<td>0.51</td>
<td>0.68</td>
<td></td>
<td></td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>KI79-1R1-170.9 (replicate)$^d$</td>
<td>Differentiated ooze</td>
<td>0.34</td>
<td>0.51</td>
<td>0.67</td>
<td>152</td>
<td>54.59</td>
<td>3.48</td>
<td>3</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.34</td>
<td>0.50</td>
<td>0.67</td>
<td></td>
<td></td>
<td></td>
<td>15</td>
</tr>
</tbody>
</table>

$^a$ Zn concentration in μg/g

$^b$ SiO$_2$ and MgO percentages

$^c$ Sample number

$^d$ Differentiated ooze sample
<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Composition</th>
<th>SiO₂</th>
<th>MgO</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>Na₂O</th>
<th>Al₂O₃</th>
<th>K₂O</th>
<th>P₂O₅</th>
<th>TiO₂</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>1223°C</th>
<th>¹⁸⁷Os/¹⁸⁸Os</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI67-2-85.7</td>
<td>Ooze from partly crystallized segregation vein</td>
<td>0.31</td>
<td>0.47</td>
<td>0.63</td>
<td>165</td>
<td>56.21</td>
<td>2.60</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KI81-2-88.6</td>
<td>Vein within segregation vein</td>
<td>0.34</td>
<td>0.51</td>
<td>0.67</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KI81-2-88.6 (replicate)</td>
<td>Vein within segregation vein</td>
<td>0.37</td>
<td>0.54</td>
<td>0.72</td>
<td>164</td>
<td>57.07</td>
<td>2.37</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.36</td>
<td>0.53</td>
<td>0.70</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a SiO₂ and MgO data for Kilauea Iki samples from Helz et al. (1994)
b Zn data for Kilauea Iki samples from Helz (2012)
c n=number of repeat measurement by MC-ICP-MS
d sample digested in Parr bomb
Table 2-4. Zinc isotopic compositions of samples from the Hekla, Iceland.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Eruption date&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Rock type</th>
<th>δ&lt;sup&gt;66&lt;/sup&gt;Zn</th>
<th>δ&lt;sup&gt;67&lt;/sup&gt;Zn</th>
<th>δ&lt;sup&gt;68&lt;/sup&gt;Zn</th>
<th>Zn (μg/g)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>SiO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
<th>MgO&lt;sup&gt;b&lt;/sup&gt;</th>
<th>n&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEK04-09</td>
<td>1878 A.D.</td>
<td>Basalt</td>
<td>0.26</td>
<td>0.38</td>
<td>0.54</td>
<td>136</td>
<td>46.97</td>
<td>5.53</td>
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</tr>
<tr>
<td>HEK05-09</td>
<td>1913 A.D.</td>
<td>Basalt</td>
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<td>0.37</td>
<td>0.52</td>
<td>136</td>
<td>46.47</td>
<td>5.48</td>
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</tr>
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<td>HEK07-09</td>
<td>1878 A.D.</td>
<td>Basalt</td>
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<td>0.35</td>
<td>0.48</td>
<td>135</td>
<td>46.64</td>
<td>5.57</td>
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<tr>
<td>HEK09-09</td>
<td>1878 A.D.</td>
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<td>0.42</td>
<td>0.57</td>
<td>144</td>
<td>47.01</td>
<td>5.30</td>
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<tr>
<td>HEK12-09</td>
<td>1913 A.D.</td>
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<td>0.40</td>
<td>0.53</td>
<td>139</td>
<td>46.42</td>
<td>5.23</td>
<td>3</td>
</tr>
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<td>1970 A.D.</td>
<td>Basaltic Andesite</td>
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<td>0.42</td>
<td>0.54</td>
<td>164</td>
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<td>2.68</td>
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<td>1991 A.D.</td>
<td>Basaltic Andesite</td>
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<td>Basaltic Andesite</td>
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<td>Dacite (tephra)</td>
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<td>0.44</td>
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<td>0.47</td>
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<tr>
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<td>2800 B.P.</td>
<td>Rhyolite</td>
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<td>0.41</td>
<td>0.55</td>
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<td>71.89</td>
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</tr>
<tr>
<td>HEK03-10</td>
<td>4000 B.P.</td>
<td>Rhyolite</td>
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<td>0.42</td>
<td>0.54</td>
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<td>72.07</td>
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<td>Postglacial</td>
<td>Dacite</td>
<td>0.36</td>
<td>0.54</td>
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<td>96</td>
<td>68.53</td>
<td>0.54</td>
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</tr>
</tbody>
</table>

<sup>a</sup> The ages for the Hekla samples from Savage et al. (2011) established using sample localities from Sigmarsson et al. (1992)
<sup>b</sup> SiO<sub>2</sub>, MgO and Zn data for Hekla samples from Savage et al. (2011), measured by XRF
<sup>c</sup>n=number of repeat measurement by MC-ICP-MS
<sup>d</sup>Icelandic dacitic sample which is genetically unrelated to Hekla

External reproducibilities (2s.d. are estimated to be ±0.04‰ for δ<sup>66</sup>Zn, ±0.05‰ for δ<sup>67</sup>Zn and ±0.05‰ for δ<sup>68</sup>Zn.)
Figure 2-1. (a) Graph of $\delta^{66}$Zn and Zn concentration versus degree of differentiation as represented by MgO content for Kilauea Iki samples. Samples with MgO $>11$ wt% are melt+olivine phenocrysts, whereas those with MgO $<11$ wt% reflect fractional crystallization of olivine (Ol.), followed by augite (Aug.), plagioclase (Plag.), and Fe–Ti oxides (Helz, 1987). (b) Graph of $\delta^{66}$Zn and Zn concentration versus the degree of differentiation as represented by the SiO$_2$ content for Hekla volcanic rocks. One Icelandic dacite sample (RHY01-09), which is genetically unrelated to Hekla, is also plotted (star symbol). The differentiation (via fractional crystallization) and magma mixing regimes, as proposed by Sigmarsson et al. (1992) are also shown (see text for details). The error bars are external uncertainty:±0.04 (2 s.d.). The pink band represents the range of $\delta^{66}$Zn. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
2.5. Discussion

2.5.1. Zn Isotope Fractionation during Magmatic Differentiation

Kilauea Iki Lava Lake formed during one single eruption and internal fractional crystallization has produced a wide range of bulk chemical compositions. Although the samples from Hekla formed during different eruptions over more than 6000 yr, they are believed to be from a cogenetic source (Sigmarsson et al., 1992). Contamination from country rocks and hydrothermal systems is very limited in both igneous systems. Since low temperature alteration may produce notable isotopic fractionation, our samples are specifically chosen for their freshness to avoid interferences from low temperature alteration products (Tomascak et al., 1999; Teng et al., 2007; Teng et al., 2008 and Savage et al., 2011). Therefore, only igneous processes could produce isotopic variability in these samples.

It is interesting, therefore, that the Zn isotopic composition of the Kilauea Iki samples show small but apparently systematic shifts towards heavier $\delta^{66}$Zn values with increasing degree of differentiation. This is borne out by good linear relationships between $\delta^{66}$Zn and MgO ($R^2=0.58$; Fig. 2-1a), SiO$_2$ ($R^2=0.79$; Fig. 2-2), and Zn concentrations ($R^2=0.76$; Fig. 2-3).

It is important to first note that two igneous processes are controlling the chemistry of the Kilauea Iki samples. Samples with MgO$>$~11 wt% have undergone variable degrees of olivine accumulation, which accounts for the wide range of Mg contents (Helz, 1987 and Helz, 2009). The most Mg-rich sample (KI67-3-6.8) does have the lightest Zn isotope composition—this could be an effect of olivine accumulation (Zn is a common trace element in olivine; olivine/melt partition coefficient $\sim$1, http://earthref.org/GERM/), which may be exacerbated by the presence of chromite inclusions in the olivines. These are common and can contain over 1000 ppm Zn.
(Evans and Wright, 1972), and there is also evidence that spinels are isotopically light with respect to Zn (Luck et al., 2005). Inspecting Fig. 2-1a, however, it is apparent that high-Mg samples have a very limited range of Zn isotope compositions ($\delta^{66}$Zn=0.26–0.29‰) over a wide range of MgO (~12–26 wt%) and so it appears that olivine/chromite accumulation has an insignificant effect on the Zn isotope composition of these lavas.

Samples from Kilauea Iki with MgO<~11 wt% formed via fractional crystallization, of olivine, then augite, feldspar and finally Fe–Ti oxides (Helz, 1987). These samples also display a larger range of Zn isotope data ($\delta^{66}$Zn=0.27–0.36‰). This range, which correlates with proxies for magmatic differentiation, suggests that fractional crystallization is fractionating the Zn isotope composition of Kilauea Iki lavas, whereby isotopically light Zn is partitioning into one or more crystallizing phases. Identifying any particular phase is difficult; it is unlikely to be olivine, due to the consistency of the cumulate $\delta^{66}$Zn data and, more importantly, because olivine ceases to form below ~6.5 wt% MgO (Helz, 1987). At this point, Zn begins to exhibit incompatible behavior in the samples (Fig. 2-1a) but, because Zn$^{2+}$ can substitute for Fe$^{2+}$, both augite and Fe–Ti oxides could still host some Zn. The heaviest $\delta^{66}$Zn occurs in samples with MgO<5 wt%, where fractionation of Fe–Ti oxides has contributed to the production of these highly differentiated melts (Helz, 1987; 2009). It should be noted that Fe–Ti oxides typically have a higher mineral/melt Zn partition coefficient than clinopyroxenes in basaltic systems (http://earthref.org/GERM/). This evidence suggests that fractionation of Fe–Ti oxides is a likely cause of Zn isotope fractionation in Kilauea Iki lavas.

An important issue preventing a more quantitative assessment of the above problem is the lack of Zn isotope fractionation factors for common minerals, derived from either ab initio calculations or empirical measurements, in the literature. Also, the small range of $\delta^{66}$Zn values,
which are just outside of analytical uncertainty, limit interpretation within the range of
differentiation, i.e., it is only the most- and least-differentiated samples that are isotopically
resolvable.

In contrast to Kilauea Iki, for the Hekla samples there are no good correlations between Zn
isotopes and proxies for differentiation (Figs. 2-1b and 2-2), despite the large range of lithologies
and SiO$_2$ contents (46.5–72.1 wt%) present in the sample set. Also, $\delta^{66}$Zn variations within the
two fractional crystallization regimes (SiO$_2<$55% and SiO$_2>$67%, Fig. 2-1b) are only 0.07‰ and
0.04‰ respectively, which are barely beyond our analytical uncertainties (±0.04‰). This implies
that no major minerals are significantly fractionating Zn isotopes in this system. This does not
contradict our assertion that crystallization of olivine and/or Fe–Ti oxides may lead to Zn
isotopic fractionation, because compared with Kilauea Iki, Hekla samples are poorer in both
olivine and ilmenite (magnetite is the dominant oxide phase in Hekla lavas).

In addition to equilibrium fractionation, possible kinetic isotope fractionation of Zn isotopes
should also be assessed. It has been observed that, compared to whole-rock isotopic
compositions, Kilauea Iki olivines are enriched in heavier Mg and lighter Fe isotopes, which has
been explained as the result of chemical diffusion during re-equilibration of the olivine with
evolving residual melts (Teng et al., 2011). For our bulk rock samples, there is a fair positive
correlation between $\delta^{56}$Fe and $\delta^{66}$Zn ($R^2=0.43$). As Zn$^{2+}$ and Fe$^{2+}$ have identical charges and
similar ionic radii, they behave similarly during partial melting and magmatic differentiation
(Lee et al., 2010). Also, like Fe$^{2+}$, Zn$^{2+}$ appears to have diffused from melt into olivine in the
Kilauea Iki lavas, due to the re-equilibration of the original forsteritic olivine (Helz, 2012).
Therefore, it could also be hypothesized that, during crystallization of Kilauea Iki lavas, lighter
Zn isotopes were preferentially incorporated into olivine by chemical diffusion, driving the
differentiated melt to slightly heavier Zn isotopic compositions. However, it is very difficult to tease out the contribution of this effect from the effect of fractional crystallization without Zn isotope analysis of olivine grains from Kilauea Iki.

Hekla lavas undergo significant S loss through degassing during eruptions; Moune et al. (2007) estimate that between 78–95% of initial S (in the SO$_4^{2-}$ form) was lost during the 2000 Hekla eruption. Because Zn is chalcophile and moderately volatile, it is possible that volatile loss of Zn, via degassing, could fractionate Zn isotopes (e.g. John et al., 2008). For those samples where there is measurable S loss (S<100 ppm) there is a fair negative correlation ($R^2$=0.30) between $\delta^{66}$Zn and S content. This is consistent with light Zn partitioning into the volatile phase, leaving an isotopically heavy melt. However, given the small range of Zn isotope data in the Hekla samples and the average regression statistics, this hypothesis is somewhat tenuous but could explain some of the variation in the Hekla $\delta^{66}$Zn data.

A final point to make is that, even though igneous processes (fractional crystallization and/or kinetic effects) may lead to resolvable Zn isotope variations, the differences in $\delta^{66}$Zn between primitive and differentiated samples from Kilauea Iki is only 0.10‰. These isotopically heavy samples represent extreme differentiates, which are not typical products within an igneous system. For the samples from Hekla, the $\delta^{66}$Zn range is similar to Kilauea Iki (0.11‰) and the degree of isotopic fractionation caused by magmatic differentiation is even smaller, with the rhyolites having identical Zn isotopic compositions to the basalts in this system. In addition, suites of samples from Merapi volcano (Toutain et al., 2008) and Piton des Neiges volcano (Herzog et al., 2009) all display very restricted $\delta^{66}$Zn variation within a single magmatic system. Based on our study on Kilauea Iki and Hekla, together with these published data, we conclude that Zn isotope fractionation as a result of high-temperature magmatic differentiation is no more
than $\delta^{66}$Zn ±0.10‰.

### 2.5.2. The Average Zn Isotopic Composition of the Earth

The terrestrial crust is created and accreted by melt extraction from the mantle: new material is continually added to the crust through intrusive and extrusive igneous activity (Green, 1972 and McKenzie, 1985). Since Zn isotopic fractionation generated by high temperature igneous processes is limited and only resolvable in extreme differentiates, removal of basaltic melt from the mantle to form crust should not resolvably affect the isotopic composition of the mantle; therefore, the Zn isotopic composition of fresh, mantle-derived melts should represent their source region. Hence, it is appropriate to use mantle-derived ultramafic and mafic rocks to estimate the Zn isotopic composition of the mantle.

Although sourced from different tectonic settings, mantle depths and degrees of partial melting, there are apparently no distinct Zn isotope variations between ocean island basalts (OIB), mid-ocean ridge basalts (MORB), peridotites, and continental flood basalts (CFB; Ben Othman et al., 2006). Considering the limited high temperature isotopic fractionation and long history of mantle convective mixing, the terrestrial mantle can be regarded as homogeneous with respect to Zn isotopes, at current analytical precision. Assuming that Zn exhibited lithophile behavior during Earth's differentiation (a valid assumption based on the predicted range of oxygen fugacities at this time; Dreibus and Palme, 1996), models of Earth's chemical composition assert that Zn is present in only negligible quantities in the core (McDonough and Sun, 1995). In addition, experimental data indicate that Zn behaves even less siderophile at higher pressures (Mann et al., 2009). Therefore, following the assumptions of McDonough and Sun (1995), the Earth's mantle should have the same Zn isotopic composition as the bulk Earth.
We can calculate the Zn isotopic composition of the BSE ($\delta^{66}\text{Zn}_{\text{BSE}}$) following two approaches: (1) based on our analyses only (including Kilauea Iki basalts, mafic samples from Hekla volcano and USGS geostandard samples); (2) by combining our analysis with previously published data (ultramafic and mafic samples only). In order to balance the contribution from different settings, if one location has more than one datum, we use the average value rather than using all samples from one location in the calculation.

The average $\delta^{66}\text{Zn}_{\text{BSE}}$ calculated by the first method is $0.29\pm0.05\%$ (2s.d.). If ultra-mafic and mafic samples measured by Ben Othman et al. (2006) and Herzog et al. (2009), together with well-studied geo-standard samples from other publications are all included, $\delta^{66}\text{Zn}_{\text{BSE}}=0.28\pm0.05\%$ (2s.d.). As an aside, to demonstrate the small range of Zn isotope compositions even in differentiated lithologies, the average Zn composition of all samples analyzed in this study with SiO$_2$ contents >54 wt% is $\delta^{66}\text{Zn}_{\text{BSE}}=0.29\pm0.08\%$ (2s.d.); identical to the $\delta^{66}\text{Zn}_{\text{BSE}}$ values, with only a minor increase in standard deviation. That all these values are statistically indistinguishable demonstrates the homogeneity of Zn isotopes in Earth's mantle. We suggest that the second average ($\delta^{66}\text{Zn}_{\text{BSE}}=0.28\pm0.05\%$) which utilizes more data than the first and avoids using some highly differentiated samples, should be the value adopted for the Zn isotopic composition of the Bulk Silicate Earth, and by corollary, bulk Earth.

2.5.3. Interplanetary Comparison

The compositional differences between extra-terrestrial and terrestrial rocks provide information on planetary formation and differentiation. Here, we compare the Zn isotopic composition of the BSE with the composition of primitive meteorites, which are often regarded as the building blocks of terrestrial planets (e.g., Allègre et al., 1995). Of the primitive meteorites,
carbonaceous and EH enstatite chondrites display a somewhat limited \( \delta^{66}\text{Zn} \) range of 0.15–0.52‰ (Luck et al., 2005 and Barrat et al., 2012); by contrast, ordinary and EL enstatite chondrites display a much larger range in \( \delta^{66}\text{Zn} \) (Fig. 2-4). The \( \delta^{66}\text{Zn} \) BSE value (0.28±0.05‰) falls within the range of carbonaceous and enstatite chondrites (Fig. 2-4), in particular, very similar to the compositions of the CV, CM (carbonaceous) and EH (enstatite) chondrite groups. The large range of Zn isotope compositions observed in the primitive meteorites is thought to be related to variable mixing of isotopically distinct components in the case of the carbonaceous chondrites (Luck et al., 2005), and in the case of the ordinary and EL enstatite chondrites, related to thermal reworking on parent bodies (Moynier et al., 2011). In contrast, the very homogenous Zn isotopic composition of the Earth is most likely the result of large-scale melting, mixing and differentiation events that occurred in the terrestrial mantle during and post-accretion.

In the case of differentiated meteorites, assuming that we can apply our results to other planetary crusts, this means that we can rule out igneous processes as a cause of significant Zn isotopic fractionation in such extra-terrestrial samples as the aubrites and HED (Howardites, Eucrites, Diogenites) meteorites as well as lunar rocks (Moynier et al., 2011, Paniello et al., 2012a and Paniello et al., 2012b; see Fig. 2-5). The Earth and the Moon share a similar composition in many isotopic systems (e.g., Wiechert et al., 2001 and Armytage et al., 2012), which is convincing evidence for their common origin. The exceptions include Fe (\( \delta \sim 0.1\%\text{amu}^{-1} \); Poitrasson et al., 2004), Cl (\( \delta \) up to 12‰ amu\(^{-1} \); Sharp et al., 2010) and Zn (\( \delta \sim 0.5\%\text{amu}^{-1} \); Paniello et al., 2012a) isotopes. While the origin of the Fe isotopic composition of the Moon is still under debate (Poitrasson et al., 2004; Weyer et al., 2005; Schoenberg and von Blanckenburg, 2006 and Dauphas et al., 2009), it is clear that magmatic processes can create Fe isotopic fractionation on the same order as that observed in lunar rocks (Teng et al.,
Chlorine isotope differences between Earth and Moon are ascribed to the absence of H in the Moon, leading to the difference of speciation of evaporated Cl species between the Moon (metal halides) and the Earth (HCl) during basaltic eruptions (Sharp et al., 2010). Therefore, Zn is the only isotope system for which the differences between lunar and terrestrial basalts reflect differences at the planetary scale (Fig. 2-5). The present study confirms that magmatic differentiation does not cause significant isotopic fractionation; therefore, the measured offset between the Earth and the Moon (0.5‰ amu$^{-1}$) most likely reflects volatility effects (Paniello et al., 2012a).
Figure 2-2. Graph of $\delta^{66}$Zn versus SiO$_2$ contents for samples from Kilauea Iki Lava Lake (triangles) and Hekla (diamonds). The dashed line and solid line represent the best-fit linear regression for Kilauea Iki and Hekla samples respectively.
Figure 2-3. Graph of $\delta^{66}$Zn versus Zn concentrations for samples from Kilauea Iki Lava Lake (triangles) and Hekla (diamonds). The dashed line and solid line represent the best-fit linear regression for Kilauea Iki and Hekla samples respectively.
Figure 2-4. Compilation of available Zn isotopic data for primitive meteorites. The blue vertical band represents the $\delta^{66}$Zn value of Bulk Silicate Earth, i.e. 0.28±0.05‰ (2s.d.) calculated in this study. Carbonaceous and ordinary chondrite data are from Luck et al. (2005) and Barrat et al. (2012). Enstatite chondrite data are from Moynier et al. (2011). Piton des Neiges basalt data are from Herzog et al. (2009); Kilauea Iki and Hekla data are from this study. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Figure 2-5. $\delta^{66}$Zn range for the Bulk Silicate Earth (BSE), and for the most isotopically fractionated extra-terrestrial samples including aubrites, EL6 chondrites, lunar basalts and regoliths, as well as terrestrial tektites. The dashed line represents the average Zn isotopic composition of BSE: $\delta^{66}$Zn=0.28±0.05‰ (2s.d.) calculated in this study. Aubrites and EL6 chondrite data are from Moynier et al. (2011); lunar regolith data are from Moynier et al. (2006), Herzog et al. (2009) and Paniello et al. (2012a); lunar basalt data are from Paniello et al. (2012a); and tektite data are from Moynier et al. (2009b).
2.6. Conclusions

We have measured the Zn isotopic composition of two suites of volcanic rocks from Kilauea Iki lava lake and Hekla volcano, in an attempt to investigate Zn isotopic behavior during igneous processes. Although magmatic differentiation has produced a large range of bulk chemical compositions within each of these geological settings, these chemically diverse samples exhibit rather limited Zn isotopic variability. There is some evidence from the Kilauea Iki samples that Zn isotopes can be fractionated toward heavier compositions as a result of fractional crystallization, however, the dearth of Zn isotope fractionation factors for common minerals prevents the identification of the specific phases responsible for fractionation. We also note that kinetic processes, such as Zn diffusion between melt and olivine, or Zn volatile loss in a sulfur-rich phase, could also affect Zn isotopes. Nevertheless, it appears that the maximum Zn isotopic variation induced by high temperature igneous processes is no larger than $\delta^{66}\text{Zn} = -0.10\%$, and we conclude that the Earth's mantle is homogeneous with respect to Zn isotopes. We suggest that the best estimate for the Zn isotope composition of Bulk Silicate Earth is $\delta^{66}\text{Zn} = 0.28 \pm 0.05\% \ (2\text{s.d.})$. Assuming Zn is not partitioned into the core, this value also represents the Zn isotope composition of bulk Earth. Importantly, our results rule out igneous processes as a source of isotopic fractionation in differentiated, volcanic, materials from other planetary bodies, such as differentiated samples from the Moon and Mars.
References


CHAPTER 3:

ZINC ISOTOPIC COMPOSITION OF IRON METEORITES:
ABSENCE OF ISOTOPIC ANOMALIES AND ORIGIN OF THE
VOLATILE ELEMENT DEPLETION

Abstract

High-precision Zn isotopic compositions measured by MC-ICP-MS are documented for 32 iron meteorites from various fractionally crystallized and silicate-bearing groups. The $\delta^{66}$Zn values range from $-0.59\%$ up to $+5.61\%$ with most samples being slightly enriched in the heavier isotopes compared with carbonaceous chondrites ($0 < \delta^{66}\text{Zn} < 0.5$). The $\delta^{66}$Zn versus $\delta^{68}$Zn plot of all samples defines a common linear fractionation line, which supports the hypothesis that Zn was derived from a single reservoir or from multiple reservoirs linked by mass-dependent fractionation processes. Our data for Redfields fall on a mass fractionation line and therefore refute a previous claim of it having an anomalous isotopic composition due to nonmixing of nucleosynthetic products. The negative correlation between $\delta^{66}$Zn and the Zn concentration of IAB and IIE is consistent with mass-dependent isotopic fractionation due to evaporation with preferential loss of lighter isotopes in the vapor phase. Data for the Zn concentrations and isotopic compositions of two IVA samples demonstrate that volatile depletion in the IVA parent body is not likely the result of evaporation. This is important evidence that favors the incomplete condensation origin for the volatile depletion of the IVA parent body.
3.1. Introduction

Iron meteorites are mostly composed of metallic Fe and Ni, and are enriched in siderophile elements compared with chondrites (Mittlefehldt et al., 1998). They are classified into different groups according to their chemical compositions, especially the concentrations of Ga, Ge, and Ir, such that each group of meteorites is presumed to belong to one distinct parent body (Scott and Wasson, 1976; Kracher et al., 1980; Wasson et al., 1980, 2007; Malvin et al., 1984; Wasson and Huber, 2006). However, on the basis of their formation processes, the groups are often divided into two categories: magmatic groups and nonmagmatic groups. The magmatic groups (e.g., IIAB, IICD, IIIAB, IVA), which are largely free of silicates, display smooth elemental trends consistent with a fractional crystallization of a slowly cooling magma, and are thought to represent cores of asteroids, which were formed by fractional-crystallization processes (Scott and Wasson, 1975, 1976; Haack and Scott, 1993). The silicate-bearing groups, which include IAB, IIE, and IIICD, contain abundant silicates and their elemental variations could not be explained by simple fractional crystallization. The origin for silicate-bearing irons is still debated, and models include unique core crystallization involving complex fractional crystallization, nucleation effects, and liquid immiscibility (McCoy et al., 1993), forming as pools of impact-produced melt near the base of a mega-regolith on a chondritic body (Wasson and Wang, 1986), and breakup and reassembly of a partially differentiated object at its peak temperature (Benedix et al., 2000). It is clear that metal in the IAB, IIE, and IIICD groups was once molten; therefore, to avoid ambiguity, the term “silicate-bearing groups” has been adopted to substitute for “non-magmatic groups” in recent years; likewise “fractionally crystallized groups” has been adopted for “magmatic groups” (Haack and McCoy, 2003; Goldstein et al., 2009).

The study of chemical compositions in iron meteorites has been used in the past to constrain
the physical processes which led to the formation of these samples (Scott et al., 1973; Scott and Wasson, 1976; Wasson et al., 1980; Malvin et al., 1984; Albarède et al., 2013). The recent development of multiple-collector inductively coupled-plasma mass-spectrometry (MC-ICP-MS) has allowed for high-precision measurements of nontraditional stable isotopes. These isotope ratios have been used as new tracers to study planetary formation and differentiation: Si (Georg et al., 2007; Fitoussi and Bourdon, 2012; Pringle et al., 2013; Savage and Moynier, 2013), Fe (Poitrasson et al., 2004; Wang et al., 2012), Ni (Moynier et al., 2007), Cu (Luck et al., 2003; Williams and Archer, 2011; Bishop et al., 2012), Zn (Luck et al., 2005; Moynier et al., 2007; Paniello et al., 2012a), Ge (Luais, 2007), Cd (Wombacher et al., 2008), and Sr (Moynier et al., 2010).

Zinc is a lithophile element, which is preferentially retained in the silicate phases during planetary differentiation; therefore, Zn concentrations in fractionally crystallized irons are generally very low (<5 ppm) compared with the carbonaceous chondrites (>50 ppm). Models of Earth's chemical composition assert that Zn is present in only negligible quantities in the core (McDonough and Sun, 1995). Zinc is also a moderately volatile element with a condensation temperature of approximately 726 K (Lodders 2003). It has five stable isotopes: $^{64}\text{Zn}$ (49.17%), $^{66}\text{Zn}$ (27.73%), $^{67}\text{Zn}$ (4.04%), $^{68}\text{Zn}$ (18.45%), and $^{70}\text{Zn}$ (0.61%). In terrestrial rocks, Zn shows a narrow range of isotopic variations (Chen et al. 2013), indicating that isotopic fractionation during magmatic differentiation is rather limited (no more than 0.05 permil/amu for basaltic magma; Chen et al. 2013). Volatilization is the most important planetary formation process that can significantly fractionate isotopes with preferential loss of the light isotopes in the gas phase, leading to mass-dependent isotopic variability (Albarède 2004; Paniello et al. 2012a; Chen et al. 2013). Previous studies have used Zn isotope ratios to determine the impact-induced
volatilization (Moynier et al. 2006; Paniello et al. 2012a, 2012b). Comparing the Zn isotope compositions in iron meteorites may help further our understanding of the physical and chemical conditions involved in the variation in the volatile element abundance among different groups. So far, all Zn isotopic fractionations measured in bulk solar system materials have followed a mass-dependent law (Moynier et al., 2009). One remarkable exception is the Redfields iron meteorite, for which Ghidan and Loss (2011) reported surprisingly large isotopic anomalies. These isotopic anomalies were interpreted to be the consequences of an incomplete mixing of nucleosynthetic products, similar to what have been observed in the unusual FUN refractory inclusions from the Allende chondrite (Völkening and Papanastassiou, 1990). However, such large isotopic anomalies are unexpected in differentiated materials such as iron meteorites; therefore, this observation, if correct, would have important consequences on our understanding of the homogenization of nucleosynthetic products and the preservation of isotopic anomalies during planetary differentiation.

Presently, there are very few works that focus on the isotopic composition of Zn in iron meteorites (Luck et al., 2005; Ghidan and Loss, 2011) and none has measured the composition of the Zn-poor IVA group. This is mostly because of the very low Zn concentrations (few ppm) in most iron meteorites and even down to 0.1 ppm in the IVA group. Our goal in this work is to study high-precision Zn isotopic compositions of a variety of iron meteorite groups including IVAs to learn more about the planetary processes that had operated on their parent bodies and about the origin of the volatile depletion observed in some iron groups.
3.2. Sample Description

A total of 32 samples from 10 meteorite groups were analyzed by MC-ICP-MS: seven IAB, four IIC, three IIB, six IID, three IIE, one IIF, three IIIAB, one IIIE, one IIIF, two IVA, and one ungrouped (see Table 3-1). These meteorite samples were obtained in the form of metal chips. For all the irons, large chips with no visible sulfides and silicate inclusions were selected. Some of these samples were cut in half for Cu and Zn isotope analysis, respectively, and the Cu isotope compositions were reported in Bishop et al. (2012). Zn data of Campo del Cielo, Casas Grandes, and Charcas obtained from Luck et al. (2005) were incorporated to further characterize the group IAB and IIIAB.
3.3. Methods

To extract an adequate amount of Zn (>300 ng) for isotopic analysis, 0.2 up to 2.0 g chips were obtained from each sample based on the Zn concentration estimated from previous literature. As low-temperature alteration and biological processes could generate detectable Zn isotopic fractionation (Albarède, 2004), our samples were specifically selected from polished interior slices, free from fusion crust or from oxidation products. Metallic chips were first cleaned in diluted HCl, and then in deionized water in an ultrasonic bath to get rid of surface contamination. Cleaned samples were placed in double-distilled 6 mol/L HCl in closed Teflon beakers at approximately 120 °C until complete dissolution.

Zinc was extracted from the solution following the anion-exchange chromatography procedure described in Moynier et al. (2006). The dissolved solute was dried under a heating lamp and then redissolved in 1.5 N HBr. The sample's solution was loaded on to the teflon columns, which were preloaded with AG-1X8 (200–400 mesh) resin and cleaned with alternating cycles of 0.5 HNO₃ and H₂O. The sample matrices were cleaned up by an additional 1.5 mol L⁻¹ HBr step, while the remaining Zn was finally collected from the column in 0.5 mol L⁻¹ HNO₃. In a similar manner, two more passes through smaller columns were performed on the collected Zn solution for better purification result, especially to remove any traces of Ni. As in 1.5 mol L⁻¹ HBr, neither Fe nor Ni forms anionic complexes; these elements are not retained by the resin and thus there is no danger of losing Zn due to the saturation of the column (Maréchal and Albarède, 2002), even when approximately 2 g of IVA meteorites were loaded. This analytical method allows us to measure the Zn isotopic composition of even the most Zn-poor samples. In addition, the small volumes of acid used in this method could keep a low blank (<10 ng).
All Zn isotope analyses were performed on a Thermo-Finnigan Neptune MC-ICP-MS at Washington University in St. Louis following the procedure described in Paniello et al. (2012a).

Samples were introduced into the mass spectrometer in 0.1 mol L\(^{-1}\) HNO\(_3\) via a CPI PFA nebulizer attached to a glass spray chamber. The Zn concentration in each sample was determined by comparing the voltage peak heights of \(^{64}\text{Zn}\) with that of a standard with known concentration (200 ppm). Then all samples and standards were adjusted to the same concentration (200 ± 20 ppm) for mass spectrometer analysis. Isotope intensities were collected simultaneously in static mode using a multiple faraday collector array. Thirty integrations of 5 s duration were acquired during sample measurements with an associated internal error on the \(^{66}\text{Zn}/^{64}\text{Zn}\) of about 3–6 × 10\(^{-6}\). Typically, 150 ng Zn was used for each measurement. Ni interferences on mass 64 are corrected using \(^{62}\text{Ni}\), with a mass bias correction applied on the \(^{64}\text{Ni}/^{62}\text{Ni}\) ratio (\(^{64}\text{Ni}/^{62}\text{Ni} = 0.25467\)). The Zn isotopic ratios are expressed as parts per 1000 deviations relative to the “Lyon” standard JMC-Lyon, which is the most broadly used standard for normalizing Zn isotopes:

\[
\delta^x\text{Zn} = \left(\frac{\delta^x\text{Zn}_{\text{sample}}}{\delta^x\text{Zn}_{\text{JMC-Lyon}}} - 1\right) \times 1000; \text{ with } x = 66, 67, \text{ or } 68.
\]

The internal precision on \(\delta^{66}\text{Zn}\) (based on more than three repeat runs of the same sample solution during a single analytical session) is <±0.03% (2 SE). Replicate analyses of the same sample, carried out during different sessions, were performed for most of the samples. To evaluate a more robust external precision, we processed eight or more analyses (full procedural replicates) for some samples with high concentrations such as Anako and Canyon Diablo. The 2 × standard error (2 SE) of the sample estimated from these replicates gives ±0.03‰ for \(\delta^{66}\text{Zn}\), ±0.05‰ for \(\delta^{68}\text{Zn}\), and ±0.07‰ for \(\delta^{68}\text{Zn}\) for Anoka, which is the sample with largest number of
replicates (see Table 3-2). The total blank (<10 ng) is negligible compared with the amount of Zn present in the samples (>300 ng). The long-term uncertainty in concentration is about ±10%.
3.4. Results

Zinc concentrations are reported in Table 3-1. The samples are generally in good agreement with those found in previous studies. Moreover, Zn concentrations of the same group members consistently fall within the same range: 22–45 ppm for IAB, 0.1–0.5 ppm for IIB and IIC, 0.4–2.7 ppm for IID, 0.8–1.1 ppm for IIE, 1.4–11 ppm for IIIAB, and 0.17–0.67 ppm for IVA. As expected, members of the silicate-bearing groups IAB and IIE are generally richer in Zn than the fractionally crystallized groups. Gnowangerup (IIIAB) is the only sample that has an abnormally high concentration of Zn (34 ppm) compared with the rest of the fractionally crystallized irons.

The $\delta^{66}\text{Zn}$ and $\delta^{68}\text{Zn}$ measurements of all samples are reported in Table 3-1 and plotted on Fig. 3-1. As expected, all samples fall on a mass-dependent fractionation line with a slope of 1.981 ($R^2 = 0.999$) on the three-isotope plot. In contradiction to Ghidan and Loss (2011), this study shows that Redfields' Zn isotopic composition is mass-dependent just like any other bulk meteorite analyzed so far. The ranges of $\delta^{66}\text{Zn}$ values significantly overlap for the different meteorite groups, with the isotopically heaviest sample being the IIE Watson ($\delta^{66}\text{Zn} = 5.61\%$o) and the lightest being the III AB Casas Grandes ($\delta^{66}\text{Zn} = −0.59\%$o as measured by Luck et al. 2005). Correspondingly, members of the groups IIE are most enriched in heavy isotopes and members of IIIAB are most enriched in light isotopes. The two members of the IVA group analyzed here (Gibeon and Yanhuitlan) show very low Zn concentrations (0.17 and 0.66 ppm), and almost identical isotope values ($\delta^{66}\text{Zn} = 0.07$ and 0.06$\%$o), which fall in the range of carbonaceous chondrites.
Table 3-1. Isotopic compositions and concentrations of Zn in iron meteorites. The isotopic composition is reported using the δ notation (parts per 1000 deviation from a terrestrial Zn standard JMC 3-0749 L) while the Zn concentrations are in ppm. The external reproducibility (2σ) of δ⁶⁶Zn, δ⁶⁷Zn and δ⁶⁸Zn are 0.03‰, 0.07‰ and 0.06‰, respectively. Cu isotopic compositions (%) and Zn concentrations from literatures are also listed for comparison.

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<th>δ⁶⁷Zn</th>
<th>δ⁶⁸Zn</th>
<th>[Zn] ppm</th>
<th>Lit. [Zn] ppm</th>
<th>Lit. δ⁶⁵Cu (a)</th>
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Notes: (a) \(\delta^{65}\)Cu is from Bishop et al. (2012). (b) Zn isotopic compositions and concentrations are from Luck et al. (2005). (c) Ghidan and Loss (2011). (d) Rosman and De Laeter (1974).

Samples are provided by: ME = The Field Museum, Chicago; M= Oscar Monnig Meteorite Collection, Texas Christian University; USNM= United States National Museum, Washington DC; ASU= Arizona State University, Tempe; BM= Natural History Museum, London; NHMV= Natural History Museum, Vienna; OHWAM= Western Australia Museum, Perth.
Table 3-2. Zn isotopic composition of Anoka and Canyon Diablo to test precision, total 9 and 8 procedural replicates were prepared and analyzed. se = standard error.

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3.5. Discussion

3.5.1. Mass-dependent Fractionation and Redfields

Ghidan and Loss (2011) reported the Redfields iron meteorite to have an anomalous Zn isotopic composition, stating its deviation from the Zn standard IRMM 3702 to be $5.6 \pm 0.4$ for $\delta^{66}\text{Zn}$, $4.4 \pm 3.6$ for $\delta^{67}\text{Zn}$, and $21.0 \pm 0.9$ for $\delta^{68}\text{Zn}$ in unspiked samples. When normalized to $^{68}\text{Zn}/^{64}\text{Zn}$, the isotope $^{66}\text{Zn}$ anomaly would be approximately $-52\epsilon$ units, which is significantly larger than the largest anomaly found in CAIs (+16.7$\epsilon$ in Allende FUN inclusion; Völkening and Papanastassiou, 1990). In this work, we find the Zn isotopic composition of Redfields to be consistent with mass-dependent fractionation, with its isotopic deviations from the standard JMC 3-0749 L to be $0.55 \pm 0.03$, $0.83 \pm 0.05$, and $1.10 \pm 0.07$ for $\delta^{66}\text{Zn}$, $\delta^{67}\text{Zn}$, and $\delta^{68}\text{Zn}$, respectively. Mass-dependent fractionations are expected when the heavier isotopes show larger fractionation effects with $\delta^{68}\text{Zn} = 2 \times \delta^{66}\text{Zn}$ and $\delta^{67}\text{Zn} = 1.5 \times \delta^{66}\text{Zn}$, which is exactly what we observed. Therefore, Zn isotopic fractionation in Redfields is totally mass-dependent. Moreover, the Zn concentration of Redfields measured in this study (6.8 ppm) is very close to the isotope dilution measurement (7.2 ppm) by Ghidan and Loss (2011) ensuring that our Zn purification technique is working correctly. The difference in isotopic compositions might be due to the heterogeneity of the samples or problem with measurement and data analysis. However, extreme isotopic heterogeneity within a single iron meteorite that could lead to a large magnitude of anomalies as in this case is unlikely.

With the improvement of analytical precision, isotope anomalies of several refractory siderophile elements, e.g., Ni (Regelous et al., 2008; Steele et al., 2011), Mo (Burkhardt et al., 2011), Ru (Chen et al., 2010) have been found in iron meteorites. However, these isotope anomalies in iron meteorites are barely at the limit of the analytical resolutions, and smaller than
what have been observed in CAIs and bulk chondrites. Until now, Zn isotopic anomalies have only been found in FUN calcium-aluminum-rich inclusions (CAIs) (Völkenning and Papanastassiou, 1990; Loss et al., 1994) and these mineral scale anomalies are ascribed to incomplete mixing of the products of stellar nucleosynthesis in the early solar system. Given the fact that Zn isotopic anomalies have never been observed in bulk chondrites and other differentiated meteorites (Moynier et al., 2009) and that iron meteorites are not a major Zn reservoir (due to the lithophile behavior of Zn), it would be very unlikely that iron meteorites would have preserved such large magnitude of Zn isotopic anomalies after early solar system mixing and asteroid differentiation. In addition, previous works on Zn isotopes also pointed out that the sources for terrestrial, lunar, Martian, and meteoritic zinc all come from a single reservoir or from multiple reservoirs linked by mass-dependent fractionation processes (Luck et al., 2005; Herzog et al., 2009). All of our samples forming a straight line on the three-isotope plot (Fig. 3-1) support these conclusions.

Recent studies have observed that neutron irradiation from cosmic rays can alter the isotopic compositions of some elements in iron meteorites (Walker, 2012); for example, neutron capture reactions create detectable Pt and Os anomalies in some irons with long exposure ages (Wittig et al., 2013; Kruijer et al., 2013). However, it is unlikely that the isotopic anomalies observed by Ghidan and Loss (2011) are the result of neutron irradiation, because the Zn isotope composition in most cosmic-ray damaged samples (e.g., Carbo [IID] with cosmic-ray exposure age of 850 Ma) is mass-dependent.

3.5.2. δ^{65}Cu versus δ^{66}Zn Correlation

Although Zn and Cu are both moderately volatile elements, Zn is more volatile ($T_c = 726$ K)
than Cu ($T_c = 1037$ K; Lodders 2003). Because of the difference in volatility, the range of isotope fractionation induced by evaporation-condensation processes on Zn is generally larger than that of Cu (Luck et al., 2005; Moynier et al., 2007). In the plot of $\delta^{66}$Zn against $\delta^{65}$Cu (Fig. 3-3), group IICD and IIIAB show loose negative trends, while group IAB shows a resolvable positive trend, which is opposite to that observed by Luck et al. (2005). This discrepancy might be due to the limited number of samples analyzed in Luck et al. (2005) compared with the present study. It is also possible that local heterogeneities in composition may render the difference in the $\delta^{66}$Zn – $\delta^{65}$Cu trend, however, Zn (this study) and Cu (Bishop et al., 2012) isotope measurements were conducted from the same parent chip, indicating the positive trend by our data should be reliable. The positive trend in the IAB group is likely the result of evaporation, as Cu and Zn are both moderately volatile elements; therefore, the Zn and Cu isotopes should be affected at the same time. It is also noted that the variations of Zn isotopes in this group are larger than Cu, which is consistent with elemental difference in volatility. Isotopic fractionation during metal/silicate fractionation is also a possibility and has been shown to occur for elements such as Si (Georg et al., 2007). There are presently no experiments of Zn isotopic fractionation during metal/silicate partitioning and it is therefore not possible to exclude metal/silicate partitioning as a source of isotopic fractionation. However, it has been shown (Savage et al., 2013) that Cu isotopes are not fractionated to a large extent (<0.1 permil/amu) by metal/silicate fractionation and therefore the correlation between Zn and Cu isotopes suggests a similar origin for the isotopic variability, which may not be metal/silicate fractionation.

3.5.3. The Silicate-Bearing Groups IAB and IIE

Compared with the asteroid-core magmatic groups, the silicate-bearing iron meteorites are isotopically more fractionated in Zn. Although the silicate-bearing irons experienced melting
during their history, magmatic process is not likely the mechanism for the large isotopic variations, as it has been known that Zn isotopic fractionation during fractional crystallization is rather limited (Ben Othman et al., 2006; Chen et al., 2013). Until now, the origin of silicate-bearing groups is still under debate, but different theories agree that impact occurs at one stage of their formation (Wasson and Wang, 1986; Benedix et al., 2000; Wasson and Kallemeyn, 2002; Yang et al., 2008). It is reasonable that severe impacts contribute to volatile loss accompanied by isotopic mass-dependent fractionation, leaving the heavier isotopes in the residue (Scott and Wasson, 1975; Wasson and Wang, 1986). Our data show that IAB and IIE members are the isotopically heaviest samples in Zn. Furthermore, the positive $\delta^{66}\text{Zn} - \delta^{65}\text{Cu}$ trend of IAB (Fig. 3-3) and negative correlation between Zn concentration and $\delta^{66}\text{Zn}$ of IAB and IIE (Fig. 3-2) also support the mass-dependent evaporation with depletion in Zn and preferential loss of lighter isotopes to the vapor phase.

The IIE group can be divided into two subgroups: the old IIE (4.1 Ga) and the young IIE (3.7 Ga) due to their difference in Ar-Ar ages (Niemeyer, 1980; Snyder et al., 2001), which were possibly formed due to a localized impact that reset the ages and removed volatile elements such as Mn from the silicate melt (McDermott et al., 2012). It has been found that these two subgroups have distinct nitrogen isotopic compositions (Mathew et al., 2000). The Zn isotope compositions of the young and old IIE samples also show the difference. The young group (of which Watson is a representative) has lower Zn abundance than that of the old group (0.8 ppm in Watson compared to 1.1 ppm and 1.05 in Weekeroo Station and Artlington, respectively). Watson ($\delta^{66}\text{Zn} = 5.61$) is also significantly enriched in heavy isotopes compared with the members of the old group ($\delta^{66}\text{Zn} = 2.08$ for Weekeroo Station; $\delta^{66}\text{Zn} = 2.19$ for Arlington). This observation in Zn agrees well with another moderately volatile element Ge ($T_c = 825$ K). The IIE
group shows the largest variations in Ge isotopic compositions among iron meteorites, and the young group samples also have lower concentration of Ge than old group, together with distinct heavier Ge isotopes (Luais, 2007).

In summary, the silicate-bearing groups seem to be more isotopically fractionated, most likely due to their different formation processes (volatilization by impacts) compared with the fractionally crystallized groups primarily yielded by high-temperature fractional-crystallization processes.

3.5.4. The Fractionally Crystallized Groups

The magmatic iron meteorites are commonly thought to have formed by fractional crystallization of the metallic cores of asteroid-sized bodies; therefore, they generally have low lithophile element abundances. The variations in Zn isotopic composition of fractionally crystallized irons are smaller than those of silicate-bearing groups, and there is no distinct difference between groups. However, group IIIAB seems to be the exception with high Zn concentration and two members being the isotopically lightest irons analyzed so far. However, this could be questioned as the data for the isotopically lightest samples (Casas Grandes and Charcas) were analyzed in a different study (from Luck et al., 2005).

Within the same fractionally crystallized group, the elemental variations are mainly controlled by fractional crystallization during cooling, which can be reflected on scattering diagrams of elemental concentrations against Ni, Au, Ir, etc. (Wasson, 1999; Walker, 2012). Au is an incompatible element with concentration increasing during crystal–liquid fractionation in iron meteorites. As total ranges of Au are usually larger than Ni within the iron meteorite group, but the relative analytical uncertainties are even lower (Wasson and Kallemeyn, 2002), Au has
been widely used as an indicator of fractional crystallization (Wasson, 1999; Wasson and Huber, 2006). In a δ^{66}Zn versus Au content plot (Fig. 3-4), there is no within-group correlation for these groups, indicating that fractional crystallization of metallic liquid does not fractionate Zn isotopes.

The IIIAB group has one member (Gnowangerup) with very high Zn concentration (34 ppm) compared with the rest of its group members (1–10 ppm), and yet its isotope compositions (δ^{66}Zn = 0.46‰) are not that distinct. Meanwhile, the group IID member Wallapai has significantly less Zn (0.4 ppm; δ^{66}Zn = 1.08‰) compared with the rest of its group (average 2 ppm), but does not show significant isotopic differences from other IID irons (0.97 < δ^{66}Zn < 1.56‰). Due to strong fractionation during evaporation-condensation processes (Albarède, 2004; Paniello et al., 2012a), the Zn isotopic composition of IVA members (Gibeon and Yanhuitlan) can aid in better understanding the origin of volatile depletion. The IVA irons are among the oldest iron meteorites and differentiated materials known in the solar system (Blichert-Toft et al., 2010; Kruijer et al., 2013) and are drastically depleted in moderately volatile elements (Wasson and Richardson, 2001). The continuity of the chemical trends in the IVA group indicates that IVA irons come from a single metallic body that fractionally crystallized (Wasson and Richardson, 2001). Our data show that the IVA samples are depleted in Zn (0.17 and 0.66 ppm), while their isotope compositions are undifferentiated (δ^{66}Zn = 0.06 and 0.07) compared with carbonaceous chondrites (0 < δ^{66}Zn < 0.50; Luck et al., 2005; Barrat et al., 2012). Similarly, despite the depletion of Cu, the Cu isotopic compositions of the IVA iron meteorites (−1.83‰ < δ^{65}Cu < −0.35‰; Bishop et al., 2012) also fall in the range of carbonaceous chondrites (−1.51‰ < δ^{65}Cu < 0.07‰; Luck et al., 2003; Barrat et al., 2012). It seems premature to propose an isotopically light precursor such as L/LL group chondrites (Clayton and Mayeda,
1996; Wang et al., 2004) for IVA iron meteorites, as most of the chondrites have heavier Zn and Cu isotope compositions than IVA irons (Luck et al., 2003, 2005). Therefore, volatile depletion in the IVA parent body is probably not due to partial kinetic evaporation induced by impact; should it have been the case, we would see an enrichment in the heavier isotopes. Our results rather favor a parent body of the IVA group members already depleted in the volatile element via an incomplete condensation of volatile elements.

It is important to note that the origins and histories of volatile loss of many iron meteorite groups are still under debate, and the conclusions obtained by different methods and from different authors can be antithetic (Haack and McCoy, 2003; Goldstein et al., 2009). Our work provides new constraints from an isotopic perspective on this issue; however, we give no unequivocal answer for iron meteorite petrogenesis and further work is still required.
Figure 3-1. $\delta^{66}$Zn versus $\delta^{68}$Zn for different groups of iron meteorites. All samples fall onto the line of mass-dependent fractionation (with slope of 1.98). UNGR = Ungrouped meteorites.
Figure 3-2. Zn concentration versus $\delta^{66}$Zn plot. Only group IAB+IIE shows a definite negative trend; other groups show no correlation. UNGR = Ungrouped meteorites.
Figure 3-3. $\delta^{66}$Zn versus $\delta^{65}$Cu plot. The silicate-bearing group IAB shows resolvable positive trends, while the fractionally crystallized groups IIC and IID show loose negative trends. Other groups' trends are not definable due to lack of members. UNGR = Ungrouped meteorites.
Figure 3-4. $\delta^{66}$Zn versus Au plot. The absence of correlation suggests that fractional crystallization of metallic liquid does not fractionate Zn isotopes. UNGR = Ungrouped meteorites.
3.6. Conclusion

We measured Zn isotopic compositions of seven IAB, four IIC, three IIB, six IID, three IIE, one IIF, three IIIAB, one IIIE, one IIIF, two IVA, and one ungrouped (Redfields) iron meteorites. The range of isotopic composition among the groups is large, ranging from the isotopically heaviest sample Watson ($\delta^{66}\text{Zn} = 5.61\%$) to the lightest Casas Grandes ($\delta^{66}\text{Zn} = -0.59\%$ as measured by Luck et al. 2005). All of the samples support mass-dependent fractionation by forming a linear trend on the three-isotope plot (Fig. 3-1). The negative correlation between Zn concentration and $\delta^{66}\text{Zn}$ of the silicate-bearing groups IAB + IIE (Fig. 3-2) is consistent with mass-dependent evaporation with preferential loss of lighter isotopes. The positive trend of IAB and IIE on the $\delta^{66}\text{Zn}$-$\delta^{65}\text{Cu}$ plot is also expected as Cu and Zn are both moderately volatile elements (Fig. 3-3).

Compared with the silicate-bearing groups, fractionally crystallized iron meteorites show smaller isotopic variations within group, which is consistent with previous observations that Zn isotopic fractionation during magmatic differentiation is limited (Ben Othman et al. 2006; Chen et al. 2013). Our data for the two IVA samples suggest that volatile depletion in the IVA parent body is not likely the result of evaporation and favor an incomplete condensation hypothesis instead. Overall, investigating the Zn isotopic composition of iron meteorites has afforded important insights, leading to a better understanding of the origin and evolution of these meteorites.
References


CHAPTER 4:

COSMOGENIC EFFECTS ON Cu ISOTOPES IN IVB IRONS:
IMPLICATION FOR $^{182}$Hf-$^{182}$W CHRONOMETRY

This chapter has been submitted to Geochimica et Cosmochimica Acta and is in revision: H. Chen, M.C. Bishop, M. Humayun, J.T. Williams, F. Moynier, Cosmogenic effects on Cu isotopes in IVB irons: implications for $^{182}$Hf-$^{182}$W chronometry. GCA (in revision).
Abstract

The short-lived $^{182}\text{Hf}^{-182}\text{W}$ isotope system ($t_{1/2} = 8.9 \pm 0.1$ Myr) is a widely used chronometer to date metal/silicate segregation events that occur early in Solar System history. However, its application is impeded in iron meteorites with long cosmic ray exposure ages, because $\varepsilon^{182}\text{W}$ values (per ten thousand deviation of the $^{182}\text{W}/^{184}\text{W}$ ratio from a terrestrial standard) are lowered by neutron capture processes during exposure to galactic cosmic ray (GCR) irradiation, yielding spuriously older ages. In this study, we use Cu isotopes to correct for cosmogenic effects on W isotopes based on the rationale that IVB irons have high Ni/Cu ratios and that $^{65}\text{Cu}/^{63}\text{Cu}$ ratios are significantly modified by the neutron capture reaction, $^{62}\text{Ni}(n,\gamma)^{63}\text{Ni}(\beta^-)^{63}\text{Cu}$.

We measured the Cu isotope composition of 12 out of the 14 known IVB iron meteorites. Our results show that $\delta^{65}\text{Cu}$ values (per mil deviation of the $^{65}\text{Cu}/^{63}\text{Cu}$ ratio from the NIST-976 standard) of IVB iron meteorites display a large range (-5.84‰ < $\delta^{65}\text{Cu}$ < -0.24‰). These Cu isotopic data show linear correlations with W, Pt, and Os isotope ratios, which are also very sensitive to GCR neutron capture processes. This demonstrates that $\delta^{65}\text{Cu}$ in IVB irons is majorly modified by neutron capture and can be used as a neutron dosimeter for neutron capture effects on $^{182}\text{W}$.

By coupling Cu-Os-Pt isotope data we obtain the pre-exposure Cu isotopic composition of IVB irons ($\delta^{65}\text{Cu} = -0.3 \pm 0.4$ ‰), which falls in the range of chondrites (-1.51‰ < $\delta^{65}\text{Cu}$ < 0.07‰). We correct the influence from GCR-induced burn-out from the correlation between W and Cu isotopes to give a pre-exposure $\varepsilon^{182}\text{W}$ value of -3.34 ± 0.16, which corresponds to a $^{182}\text{Hf}^{-182}\text{W}$ age of core segregation for the IVB iron meteorite parent body of 1.3 ± 1.8 Myr after formation of Calcium-Aluminum-rich Inclusions (CAIs). This corrected $^{182}\text{Hf}^{-182}\text{W}$ age of IVB
iron meteorites indicates that core formation in the IVB iron meteorite parent body occurred very early in the Solar System’s history.
4.1. Introduction

The $^{182}\text{Hf}^{182}\text{W}$ system ($t_{1/2} = 8.9 \pm 0.1$ Myr; Vockenhuber et al., 2004) has proven to be a very important short-lived chronometer for dating metal-silicate differentiation events, which occurred in the first 60 Myrs of the Solar System's history (Yin et al., 2002; Kleine et al., 2002; Schoenberg et al., 2002; Kleine et al., 2004; Jacobsen, 2005; Kleine et al., 2009; Moynier et al., 2010a). Both Hf and W are refractory elements (Lodders, 2003), with abundances that are typically assumed to be chondritic in most bulk planetary bodies. These two elements are strongly fractionated during metal/silicate segregation. Hafnium is a lithophile element which is preferentially retained in the silicate phases, while W is a moderately siderophile element which is partitioned into the metal. Core/mantle differentiation leads to strong fractionations between Hf and W, with very low Hf/W ratios in the metallic core and high Hf/W ratios in the silicate mantle. Planetary bodies for which core/mantle differentiation occurred while $^{182}\text{Hf}$ was still extant (~in the first 60 Myrs of the Solar System), have a core with lower $\varepsilon^{182}\text{W}$ (relative deviation of the ratio of $^{182}\text{W}$ to a stable W isotope from a terrestrial standard in parts per $10^4$) and a mantle with a higher $\varepsilon^{182}\text{W}$ when compared to chondrites. The magnitude of the effect can be used to date the time of the Hf/W fractionation (Yin et al., 2002; Kleine et al., 2002; Kleine et al. 2004; Moynier et al., 2010a).

Magmatic iron meteorites are believed to be samples of the metallic cores of small planetary bodies (Scott, 1972). Precise Hf–W ages of metal segregation can be calculated by comparing the $\varepsilon^{182}\text{W}$ of iron meteorites to the solar system initial value determined for Calcium-Aluminum-rich Inclusions (CAIs). The pioneering work on the W isotope composition of iron meteorites goes back to Harper and Jacobsen (1996) and Lee and Halliday (1996). In the study conducted by Horan et al. (1998) five groups of iron meteorites displayed $\varepsilon^{182}\text{W}$ values within a range of -
5.1 and -3.1. Following studies improved the analytical precision and confirmed that magmatic iron meteorites have variable negative $\varepsilon^{182}{\text{W}}$ (Kleine et al., 2005; Lee, 2005; Markowski et al., 2006a; Schersten et al., 2006; Qin et al., 2008). What is worth noting is that some of the $\varepsilon^{182}{\text{W}}$ values are lower (e.g., $\varepsilon^{182}{\text{W}} = -4.10 \pm 0.02$ for Tlacotepec (IVB) and $\varepsilon^{182}{\text{W}} = -4.09 \pm 0.08$ for Carbo (IID); Qin et al., 2008) than the initial $\varepsilon^{182}{\text{W}}$ of the CAIs (-3.51 ± 0.10) acquired from an isochron on Allende (CV chondrite) CAIs and corrected for nucleosynthetic anomalies (Burkhardt et al., 2012), and would imply that IVB meteorites are older than CAIs (Qin et al., 2008). The implication that metal–silicate differentiation in some planetesimals predated the formation of CAIs is puzzling as CAIs are considered to be the oldest condensed material in the solar system (Grossman, 1972; Gray et al., 1973).

It has been found that the abnormally low $\varepsilon^{182}{\text{W}}$ in some iron meteorites not only reflects lack of radiogenic contributions from $^{182}{\text{Hf}}$ decay, but also superimposed neutron capture effects that result from exposure to galactic cosmic rays (GCR) (Masarik, 1997; Leya et al., 2003; Markowski et al., 2006a). When subjected to intense GCR irradiation, particles with energies of several MeV or more may induce nuclear reactions, including spallation and secondary neutron capture reactions in meteorites. The first major nuclide in the W-Au mass region, $^{182}{\text{W}}$ has no major source for production (Wittig, et al., 2013), but can be burned out by the following neutron capture reaction:

$$^{182}{\text{W}} + n \rightarrow ^{183}{\text{W}}$$

Most iron meteorites have cosmic ray exposure ages of several hundred Myrs, much longer than stony meteorites (Voshage and Feldmann, 1979; Voshage, 1984). The longtime neutron
capture burn-out could lower the $\varepsilon^{182}$W values of iron meteorites, thus yielding the apparently older ages relative to CAIs.

In order to accurately determine the timing of the metal segregation relative to the formation of CAIs, it is necessary to find an adequate method to correct for these cosmogenic effects. Previous correction for $^{182}$W burn-out relied on noble gases and/or exposure age as GCR exposure proxies (Markowski et al., 2006b; Qin et al., 2008). However, spallation reactions in noble gases peak near the surface of a meteoroid, whereas neutron capture reactions increase with depth, peaking between 0.5 and 1 m below the exposure surface (Masarik, 1997; Leya et al., 2003; Qin et al., 2008; Kruijer et al., 2012; Wittig et al., 2013). Therefore, noble gases do not provide direct neutron dosimetry. This has driven the search for in situ neutron dosimeters.

Recent studies have found that neutron capture effects also modify the isotopic compositions of other siderophile elements in iron meteorites (Huang and Humayun, 2008; Walker, 2012); for example, neutron capture reactions (reactions 2 and 3) create detectable $^{192}$Pt and $^{190}$Os excesses coupled with $^{189}$Os deficits (Wittig et al., 2013; Kruijer et al., 2013). These siderophile elements have comparable responses to secondary neutrons to W, so cosmogenic Pt and Os isotopic anomalies have been applied as in situ neutron dosimeters for W isotope correction (Walker, 2012; Kruijer et al., 2013; Wittig et al., 2013).

$$^{191}\text{Ir} + n \rightarrow ^{192}\text{Ir} (\beta^-) \rightarrow ^{192}\text{Pt} \quad \text{(Reaction 2)}$$

$$^{189}\text{Os} + n \rightarrow ^{190}\text{Os} \quad \text{(Reaction 3)}$$

Copper is a moderately volatile element ($T_c=1037$ K; Lodders, 2003), which follows a chalcophile /siderophile behavior during magmatic processes (Righter et al., 2009). It has two
stable isotopes: $^{63}$Cu (69.17%) and $^{65}$Cu (30.83%) and even though very limited data have been published on the natural fractionation of Cu isotopes in terrestrial rocks, it seems that Cu has a very limited isotopic fractionation during igneous processes (Ben Othman et al., 2006). In a survey of the Cu isotopic composition of iron meteorites, Bishop et al. (2012) observed that IVB irons (n=3) have distinctly negative $\delta^{65}$Cu (~ -2‰; $\delta^{65}$Cu defined as the per mille deviation of a sample’s $^{65}$Cu/$^{63}$Cu compositional ratio from that of the NIST-976 standard), which deviates from the values of carbonaceous chondrites (-1.51 ‰ < $\delta^{65}$Cu < 0.07 ‰; Luck et al., 2003; Barrat et al., 2012) and other iron meteorite groups (-1.83 ‰ < $\delta^{65}$Cu < 0.99 ‰; Luck et al., 2005; Bishop et al., 2012). Among iron meteorites, the IVB group is the most volatile depleted with low concentrations of moderately volatile elements (e.g. Ga, Ge, and Cu) coupled with high concentrations of Ni (16 – 18 wt.%) and other refractory elements (e.g. Ir, Re) (Campbell and Humayun, 2005; Walker et al., 2008). The depletion in the heavy isotope suggests that evaporation was unlikely the mechanism that led to the volatile depletion observed in IVB group. Bishop et al. (2012) proposed a precursor with a non-chondritic Cu isotopic composition for the IVB parent body to explain the unique Cu isotopic composition. This explanation contradicts with the prediction by Campbell and Humayun (2005) that angrite meteorites represent the silicate portion of IVB parent body.

Most IVB iron meteorites have been extensively exposed to GCR, with exposure ages between 200 and 950 Myrs (Voshage and Feldmann, 1979). The average $\varepsilon^{182}$W (-3.57 ± 0.10, excluding Tlacotepec) for IVB irons is barely within the error of CAI initial $\varepsilon^{182}$W (-3.51 ± 0.10), indicating the influence from long-time GCR-exposure (Qin et al., 2008). Among all the Ni isotopes, $^{62}$Ni has the largest thermal capture cross section (14.5 barns) and epithermal resonance integral (6.6 barns) (Mughabghab, 2003), so a potential neutron capture reaction, $^{62}$Ni(n,γ)$^{63}$Ni(β$^-$...
$^{63}\text{Cu}$ might have produced excessive $^{63}\text{Cu}$ in these IVB irons due to extremely high Ni/Cu ratio (3 orders of magnitude higher than the CI ratios), leading to some very low $\delta^{65}\text{Cu}$ values. If this speculation is confirmed, Cu isotopes might have the potential to be developed as a new neutron dosimeter for $\varepsilon^{182}\text{W}$ correction.

In the present study, we measured Cu isotopic composition of 12 IVB iron meteorites from the same samples analyzed for W, Os and Pt isotope composition (Wittig et al., 2013) and found a good correlation between Cu and W isotopes, as well as with recently published Pt and Os data which are shown to be modified by GCR neutron capture process. We use these data to correct for the neutron capture effect on W isotopes and propose a core/mantle segregation age in the IVB iron parent body.
4.2. Samples

In order to test our assumption that Cu isotopes in IVB iron meteorites have been modified by GCR, the Cu isotopic composition of 12 of the 14 known IVB iron meteorites were measured by Multiple-Collection Inductively-Coupled-Plasma Mass-Spectrometry (MC-ICP-MS). Since neutron capture effects vary with depth within a meteorite body, these samples were taken within 2 mm from the samples for which Os, Pt, and W isotopic composition have been reported by Wittig et al. (2013). This sample set, based on previously reported cosmic ray exposure age data (Voshage and Feldmann, 1979) and W isotope compositions (Kleine et al., 2005; Markowski et al., 2006; Qin et al., 2008; Wittig et al., 2013) is likely to cover a wide range in degrees of GCR irradiation.

In addition, we also report the Cu isotopic composition of 7 USGS geostandards (dunite DTS-1, peridotite PCC-1, andesite AGV-2, and basalts BCR-1, BCR-2, BIR-1, and BHVO-2) in order to test the reproducibility of our technique, as well as to provide more data on the Cu isotopic composition of the Earth.
4.3. Analytical Methods

Based on estimated Cu concentration, 0.5 – 1 g of metal was cut and polished for isotopic analysis. Metallic chips were first cleaned in diluted HCl, and then rinsed with deionized water in an ultrasonic bath to get rid of surface contamination. Cleaned samples were digested in aqua regia in PTFE containers under hot lamps for > 48 hours until complete dissolution. Purification of Cu was achieved by anion exchange chromatography following the procedure described in Maréchal et al. (1999) and Bishop et al. (2012). The samples were loaded in 7 mol/L HCl on 1.6 mL of anion-exchange resin (AGMP1). Matrix elements were eluted by 7 ml of 7 mol/L HCl and Cu was extracted by further addition of 19 ml of 7 mol/L HCl. This process was repeated twice to further purify Cu.

Copper isotopic compositions were measured on a Thermo-Finnigan Neptune Plus MC-ICP-MS at Washington University in St. Louis following the procedure described in Weinstein et al. (2011) and Bishop et al. (2012). Samples were introduced into the mass spectrometer in 0.1 mol/L HNO₃ via a CPI PFA nebulizer attached to a glass spray chamber. All samples and standards were adjusted to the same concentration (150 ± 10 ppm) for mass spectrometer analysis. Isotope measurements were performed using standard-sample bracketing to correct for any instrumental drift over time. Isotope intensities were collected simultaneously in static mode using a multiple faraday collector array. Twenty-five integrations of 5 s duration were acquired during sample measurements with an associated internal error on the $^{65}\text{Cu}/^{65}\text{Cu}$ of about $2.4 \times 10^{-6}$. Copper isotopic composition is expressed in δ permil units with respect to the standard NIST-976 as:

$$\delta^{65}\text{Cu} = \left( \frac{^{65}\text{Cu}/^{63}\text{Cu}_{\text{sample}}}{^{65}\text{Cu}/^{63}\text{Cu}_{\text{NIST-976}}} - 1 \right) \times 1000$$
The blank of the total procedure (dissolution and chemical purification) is < 5 ng, which is negligible compared with the total amount of Cu present in the samples (> 300 ng). The external reproducibility (2 s.d.) of the $\delta^{65}$Cu is 0.10 for iron meteorites (see Bishop et al., 2012).

The Ni and Cu concentrations were determined by laser ablation ICP-MS at Florida State University following the method described in Williams and Humayun (2013).
4.4. Results

The Cu isotopic compositions of well-characterized USGS standards (DTS-1, PCC-1, AGV-2, BCR-1, BCR-2, BIR-1, and BHVO-2) are listed in Table 4-1 together with some previously reported analyses. The good agreement between our data and literature values demonstrates the robustness of the methods and of our analyses. These geostandard samples have very similar Cu isotopic compositions within the errors, showing a typical terrestrial composition, which scatters around 0 ‰ (Albarède, 2004; Ben Othman et al., 2006).

The Ni and Cu concentration and Cu isotopic composition for each of the 12 IVB iron meteorites are presented in Table 4-2, together with corresponding W, Pt, and Os isotope data by Wittig et al., (2013). The IVB iron meteorites exhibit a small range of Ni (15.68–17.87 wt.%) and Cu concentration (1.26–1.79 ppm), with Ni/Cu ratios (9.9–12.9×10^4) ~ 10^2 times higher than those in other groups of iron meteorites studied by Bishop et al. (2012).

Although small nucleosynthetic ε^{184}W anomaly has been confirmed in IVB irons, the nucleosynthetic effects are negligible on ε^{182}W (Qin et al., 2008; Kruijer et al., 2013; Wittig et al., 2013). The δ^{65}Cu values of IVB irons are widely scattered between -0.24 and -5.84 ‰, with an average of -2.78 ‰. Compared with chondrites and other groups of iron meteorites, IVB irons have a much larger δ^{65}Cu span, and most of them display significant enrichment in ^{63}Cu isotopes (or depletion in ^{65}Cu). Of the IVB iron meteorites, Weaver Mountains is the least modified by GCR-induced ^{182}W burn-out and has the highest δ^{65}Cu value, falling within the range of chondrites and other iron meteorites. In contrast, Tlacotepec, one of the most cosmic ray-damaged samples, has the lightest δ^{65}Cu measured in this study, of -5.84 ‰, which deviates the most from average chondrite composition.
Table 4-1. Copper isotopic composition of USGS geostandards.

<table>
<thead>
<tr>
<th>Geostandard</th>
<th>$\delta^{65}$Cu</th>
<th>2s.d.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCR-1</td>
<td>0.21</td>
<td>0.09</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>0.07</td>
<td>0.08</td>
<td>Archer and Vance (2004)</td>
</tr>
<tr>
<td>BCR-2</td>
<td>0.20</td>
<td>0.09</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>0.22</td>
<td>0.08</td>
<td>Bigalke et al., (2010)</td>
</tr>
<tr>
<td></td>
<td>0.18</td>
<td>0.08</td>
<td>Bigalke et al., (2011)</td>
</tr>
<tr>
<td>BIR-1</td>
<td>0.04</td>
<td>0.09</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>-0.02</td>
<td>0.10</td>
<td>Li et al., (2009)</td>
</tr>
<tr>
<td>BHVO-2</td>
<td>0.13</td>
<td>0.09</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.07</td>
<td>Moynier et al., (2010b)</td>
</tr>
<tr>
<td>AGV-2</td>
<td>-0.02</td>
<td>0.09</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.11</td>
<td>Moynier et al., (2010b)</td>
</tr>
<tr>
<td>PCC-1</td>
<td>0.17</td>
<td>0.09</td>
<td>This study</td>
</tr>
<tr>
<td>DTS-1</td>
<td>0.08</td>
<td>0.09</td>
<td>This study</td>
</tr>
</tbody>
</table>
Table 4-2. Cu, W, Os, and Pt isotope data of IVB iron meteorites

<table>
<thead>
<tr>
<th>Location</th>
<th>δ⁶⁵Cu⁹²⁺</th>
<th>n</th>
<th>Ni (wt.%)</th>
<th>Cu (ppm)</th>
<th>Ni/Cu (10⁴)</th>
<th>Re (ppm)</th>
<th>ε¹⁸²W</th>
<th>ε¹⁸⁹Os</th>
<th>ε¹⁹⁰Os</th>
<th>ε¹⁹²Pt</th>
<th>2s.d.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cape of Good Hope</td>
<td>-2.40</td>
<td>2</td>
<td>15.68</td>
<td>1.30</td>
<td>12.0</td>
<td>3.06</td>
<td>-3.6</td>
<td>0.18</td>
<td>-0.32</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>Dumont</td>
<td>-4.53</td>
<td>2</td>
<td>16.30</td>
<td>1.27</td>
<td>12.9</td>
<td>2.63⁸</td>
<td>-3.85</td>
<td>0.06</td>
<td>-0.23</td>
<td>0.07</td>
<td>0.26</td>
</tr>
<tr>
<td>Hoba</td>
<td>-1.53</td>
<td>3</td>
<td>16.43</td>
<td>1.31</td>
<td>12.6</td>
<td>2.43</td>
<td>-3.61</td>
<td>0.09</td>
<td>-0.06</td>
<td>0.03</td>
<td>0.00</td>
</tr>
<tr>
<td>Iquique</td>
<td>-1.96</td>
<td>2</td>
<td>15.99</td>
<td>1.39</td>
<td>11.5</td>
<td>3.21</td>
<td>-3.55</td>
<td>0.03</td>
<td>-0.25</td>
<td>0.05</td>
<td>0.18</td>
</tr>
<tr>
<td>Kokomo</td>
<td>-4.30</td>
<td>2</td>
<td>16.29</td>
<td>1.27</td>
<td>12.9</td>
<td>3.15</td>
<td>-3.55</td>
<td>0.12</td>
<td>-0.25</td>
<td>0.06</td>
<td>0.15</td>
</tr>
<tr>
<td>Santa Clara</td>
<td>-2.26</td>
<td>3</td>
<td>17.64</td>
<td>1.68</td>
<td>10.5</td>
<td>1.81</td>
<td>-3.64</td>
<td>0.06</td>
<td>-0.34</td>
<td>0.01</td>
<td>0.14</td>
</tr>
<tr>
<td>Skookum</td>
<td>-3.47</td>
<td>3</td>
<td>17.83</td>
<td>1.63</td>
<td>11.0</td>
<td>1.37</td>
<td>-3.59</td>
<td>0.17</td>
<td>-0.16</td>
<td>0.00</td>
<td>0.19</td>
</tr>
<tr>
<td>Tawallah Valley</td>
<td>-2.89</td>
<td>2</td>
<td>17.66</td>
<td>1.77</td>
<td>10.0</td>
<td>1.37</td>
<td>-3.72</td>
<td>0.17</td>
<td>-0.24</td>
<td>0.10</td>
<td>0.06</td>
</tr>
<tr>
<td>Tinnie</td>
<td>-1.54</td>
<td>2</td>
<td>17.69</td>
<td>1.79</td>
<td>9.9</td>
<td>1.53</td>
<td>-3.57</td>
<td>0.07</td>
<td>-0.05</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Tlacotepec</td>
<td>-5.84</td>
<td>3</td>
<td>16.06</td>
<td>1.26</td>
<td>12.7</td>
<td>3.10</td>
<td>-4.21</td>
<td>0.13</td>
<td>-0.64</td>
<td>0.06</td>
<td>0.39</td>
</tr>
<tr>
<td>Weaver Mountains</td>
<td>-0.24</td>
<td>3</td>
<td>17.87</td>
<td>1.65</td>
<td>10.9</td>
<td>1.40</td>
<td>-3.33</td>
<td>0.12</td>
<td>-0.03</td>
<td>0.01</td>
<td>0.06</td>
</tr>
<tr>
<td>Warburton Range</td>
<td>-2.42</td>
<td>2</td>
<td>17.84</td>
<td>1.77</td>
<td>10.1</td>
<td>1.23</td>
<td>-3.42</td>
<td>0.16</td>
<td>0.02</td>
<td>0.06</td>
<td>0.05</td>
</tr>
</tbody>
</table>

a) External reproducibilities (2 s.d.) are estimated to be ± 0.10 ‰ for δ⁶⁵Cu
b) n=number of repeat measurements by MC-ICP-MS
c) Re data for IVB iron meteorites from Walker et al. (2008)
d) ε¹⁸²W, ε¹⁸⁹Os, ε¹⁹⁰Os, and ε¹⁹²Pt data from Wittig et al. (2013)
e) Uncertainties of Wand Os isotope data are given as standard error of the mean (2se_m) derived from replicate measurements of the same digestions
f) Uncertainties of Pt isotopes are given as in-run standard deviation (2s.d.)
g) data from Campbell and Humayun (2012)
4.5. Discussion

4.5.1. Copper Isotope Fractionation during Low-temperature Alteration Processes

Low-temperature alteration and biological processes could generate significant Cu isotopic fractionations (Albarède, 2004). For example, iron and copper minerals from supergene profile of the Bayugo porphyry copper-gold deposit yielded δ\(^{65}\)Cu values between -3.4 and +6.9 ‰ (Braxton and Mathur, 2011). Precise Re–Os isotopic systematics (Walker et al., 2008) and siderophile element abundances (Campbell and Humayun, 2005; Walker et al., 2008) confirm that the IVB parent body remained a chemically closed system after crystallization, excluding the interference from late-stage alteration. In addition, our samples were specifically selected from polished interior slices, free from fusion crust or from oxidation products. Each sample was polished to remove sawn surfaces. Therefore, isotopic variations in these samples were not influenced by late-stage alteration.

4.5.2. Copper Isotope Fractionation during Evaporation Processes

Copper is a moderately volatile element with a 50 % condensation temperature (T\(_{c}\)) of 1037 K (Lodders, 2003). Previous studies have observed that Cu isotopes are substantially fractionated during evaporation-condensation processes (Herzog et al., 2009; Moynier et al., 2010b). The IVB irons contain the lowest concentrations of moderately volatile elements among all iron meteorite groups, which either reflects high nebular temperatures when their parent body accreted or volatile loss during one or more impacts (Rasmussen et al., 1984; Campbell and Humayun, 2005). During evaporation process, light isotopes of an element are preferentially lost into the vapor, leaving the residual phase enriched in heavy isotopes (Humayun and Clayton, 1995; Humayun and Cassen, 2000). This is what has been observed in shock-melted rocks.
(Albarède et al., 2004), especially in the tektites (hypervelocity impact glasses) that are among the terrestrial samples with the heaviest Cu isotopic composition ($\delta^{65}$Cu up to 6.99‰; Moynier et al., 2010b), although no such fractionation of potassium ($T_c = 1006$ K) isotopes is observed in tektites or in impact melts (Humayun and Clayton, 1995; Humayun and Koeberl, 2004). In contrast, IVB irons are significantly depleted in heavy Cu isotopes, which is opposite to what is expected from an evaporation process (Fig. 4-1). In addition, the absence of correlation between $\delta^{65}$Cu and Cu concentration also argues against the volatile loss by vaporization (Fig. 4-2). Therefore, our new data agree with the conclusions by Bishop et al. (2012) that partial vaporization did not fractionate Cu isotopes in IVB irons, and that the severe depletion of Cu and other moderately volatile elements in IVB irons must have been induced by other mechanisms.

4.5.3. Copper Isotope Fractionation during Igneous Processes

Although the volatile history and accretion processes of IVB parent body are still under debate (Campbell and Humayun, 2005; Walker et al., 2008; Yang et al., 2010), the variations of chemical compositions within the IVB group can be successfully modeled as a result of simple crystallization of the metallic liquid in a closed system (Walker et al., 2008). Previous studies have suggested that isotopic fractionations observed in iron meteorites might have been created during the partitioning of Cu between metal and silicates (Luck et al., 2003; Moynier et al., 2007). However, magmatic fractionation is unlikely to account for the Cu isotopic variations observed in IVB irons for the following reasons:

Firstly, no such large span of $\delta^{65}$Cu has been measured in any other group of magmatic iron meteorites, which exhibit similar or even larger ranges of fractional crystallization (Goldstein et al., 2009). Studies have shown that most of the iron groups display relatively homogeneous Cu
isotopic composition (δ⁶⁵Cu variation < 1 ‰) within each group (Bishop et al., 2012). Among all the major iron meteorite systems, IVB group has the simplest chemical evolution that resulted from crystallization of a metallic liquid (Walker et al., 2008), so it is unlikely that magmatic differentiation could fractionate δ⁶⁵Cu up to 5.6 ‰ in IVB irons.

Second, the δ⁶⁵Cu variation in IVB irons is independent of magmatic evolution. Rhenium (Re) is a highly compatible element, of which the concentration decreases with increasing degree of fractional crystallization, and thus it has been applied as an indicator of magmatic differentiation in iron meteorites (Walker et al., 2008). The δ⁶⁵Cu is poorly correlated with the Re concentration (Fig. 4-3, R² = 0.16), indicating no direct correlation between δ⁶⁵Cu and the degree of crystal-liquid differentiation.

Finally, published Cu isotopic data of igneous rocks showed that the isotopic fractionation induced by magmatic differentiation is rather limited. The δ⁶⁵Cu values of igneous standards derived from different geological settings (see Table 4-1) and unaltered igneous rocks acquired by previous studies are narrowly scattered between -0.1 and 0.3 ‰ (Albarède, 2004; Ben Othman et al., 2006; Li et al., 2009; Savage et al., 2013). This range is much smaller than what was measured in IVB irons (5.6 ‰). Therefore we conclude that it is unlikely that high temperature magmatic processes could induce δ⁶⁵Cu fractionation up to the scale of 5.6 ‰ as observed in IVB irons.

4.5.4. Nucleosynthetic Effects in Iron Meteorites

Copper has only two stable isotopes, and thus it is impossible to differentiate mass-dependent and mass-independent fractionation (e.g. nucleosynthetic effect and radioactive decay). For some transition metal elements, mass-independent variations have been observed in
iron meteorites. e.g. Ni (Regelous et al. 2008), Cr (Trinquier et al. 2007), Mo (Dauphas et al. 2002), and Ru (Chen et al. 2010) isotopes. These isotopic anomalies are most likely the results of the heterogeneous distribution of isotopes in the Solar System at the time when iron meteorite parent bodies formed. However, the magnitudes of nucleosynthetic effects in iron meteorites are rather small (< 0.1‰ amu\(^{-1}\)), and some are merely beyong current analytical uncertainties. For example, the total ranges of \(\varepsilon^{60}\text{Ni}_{58/61}\), \(\varepsilon^{62}\text{Ni}_{58/61}\), and \(\varepsilon^{64}\text{Ni}_{58/61}\) in iron meteorites (including IC, IIAB, IIIAB, IVA, IVB) are only 0.14, 0.36, and 0.69 respectively (Steele et al., 2011). Therefore, it can be inferred that even if Cu isotopes were not well mixed in the Solar System by the time of IVB parent body formation, the magnitude of nucleosynthetic effect on \(\delta^{65}\text{Cu}\) should be less than 0.1 ‰, which is negligible compared to the range of Cu isotopes in IVB irons. Williams and Archer (2011) also concluded that the Cu isotopic variations in iron meteorites are not the result of nucleosynthetic effect or radioactive decay.

### 4.5.5. Neutron Capture Effects on Cu Isotopes during GCR-exposure

From the arguments above, we exclude that nucleosynthetic effects, low-temperature alteration, high temperature volatilization, and magmatic differentiation processes could account for such large range of Cu isotope compositions measured in IVB irons. IVB iron meteorites have large GCR exposure ages of 200-950 Myrs (Voshage and Feldmann, 1979; Herzog, 2007). When exposed to GCR irradiation, secondary neutrons produced by cosmic ray spallation in iron meteorites are captured by siderophile element nuclei. For \(^{62}\text{Ni}\), there is the following reaction:

\[
^{62}\text{Ni} + n \rightarrow ^{63}\text{Ni} (\beta^-) \rightarrow ^{63}\text{Cu} \quad \text{---------}(\text{Reaction 4})
\]

\(^{62}\text{Ni}\) captures neutron to produce \(^{63}\text{Ni}\); since \(^{63}\text{Ni}\) (\(t_{1/2}: 100.1\) y) is unstable, it quickly decays to \(^{63}\text{Cu}\).
Although both $^{63}\text{Cu}$ and $^{65}\text{Cu}$ can also be burned out by capturing secondary neutrons (Reaction 5), the direct effect is negligible compared to the production of cosmogenic $^{63}\text{Cu}$ from $^{62}\text{Ni}$, because $^{63}\text{Cu}$ and $^{65}\text{Cu}$ have relatively insignificant neutron capture cross section, and the $^{62}\text{Ni}/^{63}\text{Cu}$ ratio is as high as $5\times 10^3$ in IVB irons.

$$^{63}\text{Cu} + n \rightarrow ^{64}\text{Cu} (\beta^+) \rightarrow ^{64}\text{Ni} (61\%) \text{ or } ^{64}\text{Cu} (\beta^-) \rightarrow ^{64}\text{Zn} (39\%)$$

(Reaction 5)

Given the long exposure to GCR, the accumulated $^{63}\text{Cu}$ from $^{62}\text{Ni}$ burn-out leads to a resolvable decrease in $^{65}\text{Cu}/^{63}\text{Cu}$ value in IVB iron meteorites. It should be pointed out that the total burn-out on $^{62}\text{Ni}$ is too small ($<0.001\%$; calculated from $\delta^{65}\text{Cu}$ deviation) to be detected by measuring Ni isotopic ratios under current analytical precisions ($\sim 0.05\%$; Moynier et al. 2007; Regelous et al. 2008), even in the most irradiation-damaged sample, such as Tlacotepec. Thus, variations in $\delta^{62}\text{Ni}$ are not expected to be affected measurably by direct GCR burning of the Cu isotopes.

The deviation of $\delta^{65}\text{Cu}$ from the pre-exposure value depends on Ni/Cu ratio and the dosage of secondary neutrons. The higher the Ni/Cu ratio and longer the galactic cosmic ray exposure is, the larger the deviation from the pre-exposure value would be. The IVB irons contain the exceptionally low concentrations of moderately volatile elements (e.g. Ga, Ge, and Cu) and high Ni contents (16 – 18 wt.%), with Ni/Cu ratios generally 2 orders of magnitude higher than those for other iron groups. Therefore the deviations of $\delta^{65}\text{Cu}$ induced by GCR irradiation in IVB irons are expected to be 2 orders of magnitude larger than other iron meteorite groups, given the same cosmic-ray exposure history. For example, among all the samples measured by Bishop et al. (2012), Ni/Cu ratios of IVB group members are $\sim 100$ times or even higher than in other groups. Given the $\delta^{65}\text{Cu}$ variation of 5.6‰ between the most (Tlacotepec) and the least cosmic ray-
damaged sample (Weaver Mountains) in IVB group, it is easy to be calculate that even in a iron meteorite (non-IVB) with a as large exposure-age as Tlacotepec (945 ± 55 ma; Voshage and Feldmann, 1979), the $\delta^{65}$Cu shift induced by GCR irradiation is no more than 0.1‰, which is barely beyond our current analytical uncertainties. This explains why significantly negative $\delta^{65}$Cu only appears in IVB group and variations of other iron meteorite groups are limited and close to the range defined by chondrites. However, several low-volatile ungrouped irons with long exposure ages, e.g., Deep Springs (Scott, 1978; Qin et al. 2008) might also exhibit large $\delta^{65}$Cu deviations.

4.5.6. Pre-exposure $\delta^{65}$Cu Value Derived from Correlated Cu–Os–Pt Isotope Systematics

In IVB iron meteorites, $\delta^{65}$Cu values display an apparent positive correlation with $\varepsilon^{189}$Os and negative correlations with $\varepsilon^{190}$Os and $\varepsilon^{192}$Pt that were measured on the sample taken within 2 mm from our samples (Fig. 4-4), with Weaver Mountain and Tlacotepec representing the least and most irradiated samples. This is consistent with our assumption that $\delta^{65}$Cu of IVB irons were modified by neutron capture effects. Assuming that Cu, Pt, and Os have comparable responses to secondary neutrons, the pre-exposure $\delta^{65}$Cu can be obtained from the linear correlation between Cu and Os, as well as Pt isotopes. As cosmogenic $\varepsilon^{192}$Pt anomalies are dependent on Ir/Pt ratios (see Reaction 2), which display relatively large variation in IVB group (0.46-1.00 with an average of 0.74; Walker et al., 2008), it is necessary to eliminate the $\varepsilon^{192}$Pt bias from chemical difference (Kruijer et.al., 2013). In $\delta^{65}$Cu vs. $\varepsilon^{192}$Pt space, all $\varepsilon^{192}$Pt values are normalized to a common Ir/Pt value (average value 0.74) based on the neutron capture modal. Like $\varepsilon^{192}$Pt, $\delta^{65}$Cu deviation caused by GCR also depends on chemical composition (Ni/Cu ratios; See Reaction 4), and therefore should theoretically be normalized to a common Ni/Cu value. But due to limited Ni/Cu variations in IVB irons and larger uncertainties arising from a pre-exposure $\delta^{65}$Cu
assumption for normalization, we choose not to normalize $\delta^{65}\text{Cu}$. In contrast, $\varepsilon^{189}\text{Os}$ and $\varepsilon^{190}\text{Os}$ show anti-correlation (Wittig et al., 2013), with little dependence on the chemical composition (see Reaction 3), so no normalization is needed. In each systematics, the dashed line is the best-fit regression to the correlation, calculated using Isoplot (Ludwig, 2013). The intercepts to the pre-exposure $\varepsilon^{189}\text{Os}$, $\varepsilon^{190}\text{Os}$, and $\varepsilon^{192}\text{Pt}$ values (by definition 0, since the data are internally normalized) represent the pre-exposure $\delta^{65}\text{Cu}$ value. The $\delta^{65}\text{Cu}$ vs. $\varepsilon^{189}\text{Os}$ (Fig. 4-4 A), $\delta^{65}\text{Cu}$ vs. $\varepsilon^{190}\text{Os}$ (Fig. 4-4 B), and $\delta^{65}\text{Cu}$ vs. $\varepsilon^{192}\text{Pt}$ (Fig. 4-4 C) correlation yield pre-exposure $\delta^{65}\text{Cu}$ values of $-0.3 \pm 1.8$ (95% conf.), $-0.5 \pm 1.2$ (95% conf.), $-0.1 \pm 1.2$ (95% conf.) respectively, with an average $\delta^{65}\text{Cu}$ of $-0.3 \pm 0.4$ (2 s.d.). The corrected Cu isotopic composition for the IVB iron meteorites falls in the range defined by other iron meteorite groups as well as chondrites (Fig. 4-5). Therefore, our results imply that volatile depletion in IVB meteorites did not fractionate Cu isotopes, and thus the observed depletion was probably not produced by evaporation processes. Recent measurements of nucleosynthetic anomalies in Ni ( Regelous et al., 2008), Mo (Burkhardt et al., 2011), Ru (Chen et al., 2010), and W (Qin et al., 2008; Kruijer et al., 2012; Wittig et al., 2013) isotopes show that IVB irons have the largest isotopic anomalies among iron meteorites, similar to the scales observed in chondrites. The IVB irons also show a chondritic pre-exposure Cu isotope composition given our current analytical precision (Fig. 4-5).

4.5.7. Pre-exposure $\varepsilon^{182}\text{W}$ and Chronology of IVB Iron Meteorites

The Cu and W isotope systematics of the IVB iron meteorites are presented in Figure 4-6. The IVB iron meteorites display a linear correlation between $\delta^{65}\text{Cu}$ and $\varepsilon^{182}\text{W}$, indicating comparable responses to secondary neutrons between Cu and W. Since the pre-exposure $\delta^{65}\text{Cu}$ has been obtained, Cu isotopes could provide a neutron dosimeter for correcting $\varepsilon^{182}\text{W}$ isotope compositions for cosmogenic effects. The back-projection of the linear regression fit to the pre-
exposure $\delta^{65}$Cu (-0.3 ± 0.4) yields a pre-exposure $\varepsilon^{182}$W value of -3.34 ± 0.16 (2 s.d.), which is in good agreement with the values of -3.42 ± 0.09 (Wittig et al., 2013) and -3.26 ± 0.06 (Kruijer et al., 2013) obtained by Pt and Os neutron dosimeters.

A model age of metal segregation in IVB iron meteorite parent body relative to the formation of CAIs can be calculated using the relation:

$$\Delta t_{\text{CAI-sample}} = \frac{1}{\lambda} \times \ln \left( \frac{(\varepsilon^{182}\text{W}_{\text{CAI}} - \varepsilon^{182}\text{W}_{\text{chondrite}})}{(\varepsilon^{182}\text{W}_{\text{sample}} - \varepsilon^{182}\text{W}_{\text{chondrite}})} \right)$$

Where $\varepsilon^{182}\text{W}_{\text{CAI}} = -3.51 ± 0.10$ is CAI initial W isotopic composition determined from the Hf–W isochron corrected for nucleosynthetic anomalies (Burkhardt et al., 2012), which represents the solar system initial value; $\varepsilon^{182}\text{W}_{\text{chondrite}} = -1.9 ± 0.1$ is the present-day W isotopic composition of carbonaceous chondrites (Yin et al., 2002; Kleine et al., 2004); $\varepsilon^{182}\text{W}_{\text{sample}}$ is the W isotopic composition of iron meteorites; $\lambda$ is the decay constant of $^{182}$Hf (0.078 ± 0.002 My$^{-1}$) (Vockenhuber et al., 2004). The pre-exposure $\varepsilon^{182}$W of the IVB irons of -3.34 ± 0.16 corresponds to a Hf–W age of core segregation of 1.3 ± 1.8 (2 s.d.) Myr after CAI formation. The recalculated IVB iron meteorites Hf–W age of 1.3 ± 1.8 Myr is identical to those for most groups of iron meteorites (~2 Myr after CAI formation; Qin et al., 2008). This indicates that core formation in the IVB iron meteorite parent body was coeval with chondrule formation as given by Al–Mg and Mn–Cr ages (1.3 – 3.2 Myr after CAIs) for chondrules from carbonaceous (CO and CR) and ordinary (L and LL) chondrites (Kita et al., 2000; Kunihiro et al., 2004; Yin et al., 2006; Moynier et al., 2007b; Rudraswami and Goswami, 2007; Kurahashi et al., 2008).
Figure 4-1. $\delta^{65}\text{Cu}$ range for the bulk silicate Earth (BSE), tektites, lunar basalts and soils, chondrites, and IVB iron meteorites. The dashed line represents the average Cu isotopic composition of BSE: $\delta^{65}\text{Cu} = 0.07 \pm 0.12$ ‰ (2 s.d.; Savage et al., 2013). Lunar soil and basalt data are from Moynier et al. (2006) and Herzog et al. (2009); tektite data are from Moynier et al. (2010b); and chondrite data are from Luck et al. (2003) and Barrat et al. (2012). The IVB data are from this study before cosmogenic neutron capture corrections.
Figure 4-2. $\delta^{65}\text{Cu}$ versus Cu concentration for IVB iron meteorites. The external uncertainty is $\pm 0.10$ (2 s.d.) for $\delta^{65}\text{Cu}$.

Figure 4-3. $\delta^{65}\text{Cu}$ versus the degree of crystal-liquid differentiation as represented by the Re concentration for IVB iron meteorites. The external uncertainty is $\pm 0.10$ (2 s.d.) for $\delta^{65}\text{Cu}$. Re data are from Walker et al. (2008), except for Dumont which were determined by Campbell and Humayun (2005).
Figure 4-4. Correlation of $\delta^{65}$Cu (this study) with GCR-modified isotopes (Wittig et al., 2013) (A) $\varepsilon^{189}$Os, (B) $\varepsilon^{190}$Os, and (C) $\varepsilon^{192}$Pt in IVB iron meteorites. In each panel, the dashed line
represents the best-fit linear regression line calculated using Isoplot (Ludwig, 2003) and projection to the x-axis intercept of 0 yields the pre-GCR irradiation $\delta^{65}\text{Cu}$ of the IVB iron meteorite group (black bar, 2 s.d.). Error bars on symbols represent the uncertainties (see Table 2). Uncertainty of $\delta^{65}\text{Cu}$ is 0.10‰, which is not resolvable in this figure set due to large span of Cu variation.

Figure 4-5. Comparison of Cu isotopic composition between primitive meteorites and pre-exposure IVB iron meteorites. The yellow band represents the $\delta^{65}\text{Cu}$ value of Bulk Silicate Earth, i.e. 0.07 ± 0.12 ‰ (2 s.d.; Savage et al., 2013). Carbonaceous and ordinary chondrites data are from Luck et al. (2003) and Barrat et al. (2012).
Figure 4-6. Correlation of $\varepsilon^{182}$W (Wittig et al., 2013) with in situ neutron dosimeter $\delta^{65}$Cu measured on the same samples of IVB iron meteorites. The dashed line represents the best-fit linear regression line. Projection at the x-axis intercept of pre-GCR $\delta^{65}$Cu (0.56 ± 0.23 ‰; shown by the yellow band) yields the pre-GCR $\varepsilon^{182}$W (-3.34 ± 0.16; 2 s.d.) of the IVB iron meteorite group. The blue band represents the CAI initial $\varepsilon^{182}$W (-3.51 ± 0.10) estimated by Burkhardt et al., (2012). The outlier is Kokomo.
4.6. Conclusions

This study presents Cu isotopic composition for 12 of the 14 known IVB iron meteorites. IVB magmatic iron meteorites show significant Cu isotopic variations (-5.84 ‰ < δ$^{65}$Cu < -0.24 ‰) that result from neutron capture on $^{62}$Ni induced during cosmic ray exposure. The δ$^{65}$Cu displays clear negative correlations with ε$^{192}$Pt and ε$^{190}$Os and positive correlations with ε$^{189}$Os and ε$^{182}$W, with Weaver Mountains representing the least and Tlacotepec representing the most irradiation-damaged samples. The δ$^{65}$Cu–ε$^{192}$Pt, δ$^{65}$Cu–ε$^{190}$Os, δ$^{65}$Cu–ε$^{189}$Os correlations defined by the IVB irons yield an average pre-exposure δ$^{65}$Cu of -0.3 ± 0.4 (2 s.d.), which agrees well with the Cu isotopic composition of other iron meteorite groups and falls within the range of carbonaceous chondrites. The pre-exposure ε$^{182}$W value derived from the δ$^{65}$Cu–ε$^{182}$W correlation is -3.34 ± 0.16, corresponding to a Hf–W age of core segregation of 1.3 ± 1.8 (2 s.d.) Myr after the formation of CAIs. This corrected Hf–W age of IVB iron meteorites is close to that of most magmatic iron meteorites (1.5 – 3 Myr) and thus consistent with earlier conclusions that accretion of the parent bodies occurred very early in Solar System history. This study reveals the utility of using Cu isotopes as in situ neutron dosimeters to quantify the effects of secondary neutron capture reactions on ε$^{182}$W in iron meteorites with high Ni/Cu ratios.
References


