

Mass dependent isotopic fractionation of molybdenum in the solar system



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Abstract

Mass dependent isotope fractionation of stable isotopes between meteorites and planetary materials has been used to assess processes that occurred during formation of Earth and its core. However, thus far little is known about the mass dependent isotope fractionation of Mo in the solar system, and at high temperatures in the Earth, in particular during mantle processes. Molybdenum is a refractory and moderately siderophile element. The processes that might have fractionated Mo in the early solar system include condensation and evaporation of dust grains, metal-silicate segregation, core crystallization, silicate and sulphide melting and aqueous alteration.

In order to investigate the processes fractionating Mo isotopes, it is first necessary to assess how much fractionation takes place during mantle melting, estimate the isotopic composition of the bulk silicate Earth, and then make comparisons with primitive and differentiated meteorites. I present double spike Mo isotope data for forty-two mafic and seven ultramafic samples from diverse locations, and nineteen extra-terrestrial samples. The $\delta^{98/95}\text{Mo}$ values of all the terrestrial samples (normalized to NIST SRM 3134) exhibit a significant range from $+0.53\pm 0.21$ to $-0.56\pm 0.09\text{‰}$. The compositions of mid-ocean ridge basalts (MORBs) ($+0.03\pm 0.07\text{‰}$, 2s.d.) and ultramafic rocks ($+0.38\pm 0.15\text{‰}$, 2 s.d.) are relatively uniform and well resolved, providing evidence of fractionation associated with partial melting. In contrast intraplate and ocean island basalts (OIBs) display significant variability within a single locality from MORB-like to strongly negative (-0.56‰). The most extreme values measured are for nephelinites from the Cameroon Line and Trinidad, which also have anomalously high Ce/Pb and low Mo/Ce relative to normal oceanic basalts. The observed relationships between $\delta^{98/95}\text{Mo}$ and Ce/Pb, U/Pb and Mo/Ce provide evidence that sulphide plays a critical role in retaining Mo in the mantle and fractionating its isotopic composition in basaltic magmas. If residual sulphides are

responsible the Mo isotopic composition, Mo budget of the bulk silicate Earth will be misrepresented by values estimated from basalts. On this basis a revised best estimate of the Mo content in the bulk silicate Earth (BSE) ranging between 251 to 268 ppb is derived, approximately 6 times higher than previously assumed, and similar to the levels of depletion in refractory siderophile elements such as W, Ni and Co. This significantly ameliorates the argument for Mo removal via late stage sulphide extraction to the core.

The Mo isotopic composition of the BSE (0.35‰) is distinct from the $\delta^{98/95}\text{Mo}$ values found in primitive and iron meteorites. Although Mo isotopic fractionation varies between different phases within a single iron meteorite, and occurs during fractional crystallization in asteroidal cores, most iron meteorites have $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ (-0.14 to -0.06‰) that are similar to ordinary and CI carbonaceous chondrite (-0.12 to -0.09‰). This range of $\delta^{98/95}\text{Mo}$ is not only significantly lighter than the BSE, but also enstatite chondrites, which have $\delta^{98/95}\text{Mo}$ values of 0.04 to 0.13‰. Several possible explanations are proposed. (A) Core-mantle differentiation fractionates Mo isotopes. The recently proposed Mo effect of sulphide liquid removal is likely to be minor because this should have generated a light Mo isotope composition for the BSE. However, isotopic fractionation associated with metal-silicate partitioning may be responsible for the heavy Mo in the BSE. (B) A distinct isotopic composition for the late material that contributed Mo to the BSE. Enstatite chondrites (or other putative groups of chondrites with a heavy Mo isotope composition) and sulphur-rich components form the cores of impacting bodies are the most likely candidates that could deliver heavy Mo to Earth. (C) The Mo isotopic composition of the Solar System is heterogeneous in a mass dependent fashion such that heavier Mo isotopes are enriched in the section of the disk from which Earth accreted. There are some difficulties behind each of these models and further work is needed to determine which is correct.

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For
Mum, Dad, and Kuan-Ying

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CHAPTER ONE



Introduction

1.1 Solar System evolution

The primary aim of this project is to apply the established Mo isotopic measurement technique to a range of terrestrial and extra-terrestrial samples, in order to investigate high temperature mass dependent Mo isotopic variation within the Earth's interior as well as elsewhere in the Solar System. Mass dependent isotope fractionation between meteorites and planetary materials has been used before to assess processes that occurred during formation of the Earth and to give information about the formation of the core in particular (Georg et al., 2007). In the following some general background is provided about Solar System evolution.

1.1.1 The beginning of the Solar System

The cosmological Big Bang and stellar nucleosynthesis are the most significant causes of for the origins of elements comprising the Universe. The lightest elements H, He, and Li are probably the only elements synthesized during the Big Bang (Burles et al., 2001; Cyburt et al., 2002). After that, nuclear processes inside stars and supernovas are thought to have produced most of the elements and their isotopes.

Generally, the materials that built the Solar System are believed to be derived from a nebular gas and dust cloud (Figure 1.1). The observation with long wave-lengths indicates molecular hydrogen gas, helium, and molecules such as carbon monoxide comprise dense interstellar molecular clouds, and then become precollapse clouds.

These dense cloud cores resist collapse while their magnetic fields and other factors (e.g. thermal pressure and centrifugal force) provide support. However, gravity can prevail and then self-gravitational collapse happens onto one of the dense molecular cloud cores. This then forms a protosun and solar nebula (Boss, 2007).

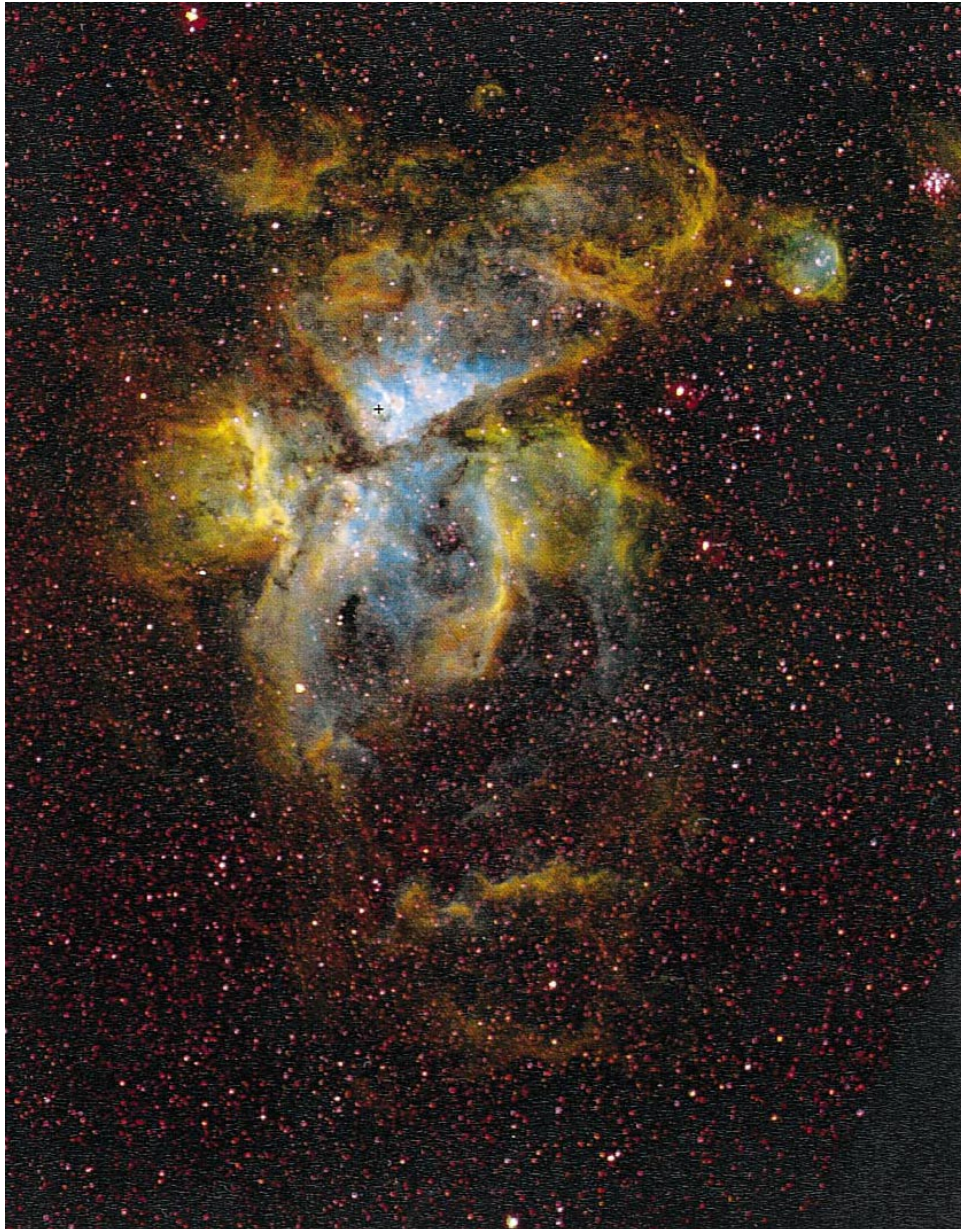


Figure 1.1 Composite three-color optical image of ionized gas in Carina Nebula (NGC 3372), a region of star formation. Carina Nebula is estimated distance between 6,500 and 10,000 light years from Earth, and it is one of the most remarkable aggregates of unusually massive stars known in the Galaxy (Smith et al., 2000).

1.1.2 Planetary formation

It is thought that at the beginning of our Solar System, part of the cloud collapsed, and most of its mass fell to the centre while the remaining material formed a rotationally supported disk or protoplanetary nebula. Some parts of the protoplanetary disks get quite hot because of (a) radiation from the central star, and (b) release of gravitational energy as gas falls inwards through the disk (Kenyon et al., 1993). While the system was cooling down, solids and perhaps liquids began to condense, and then refractory inclusions probably formed close to the protosun at an early stage. Calcium-aluminium rich inclusions (CAIs) are thought to be formed in very high-temperature condition during this stage, therefore, CAIs are generally recognized as being the oldest objects produced in our Solar System (MacPherson, 2007) (Figure 1.2).

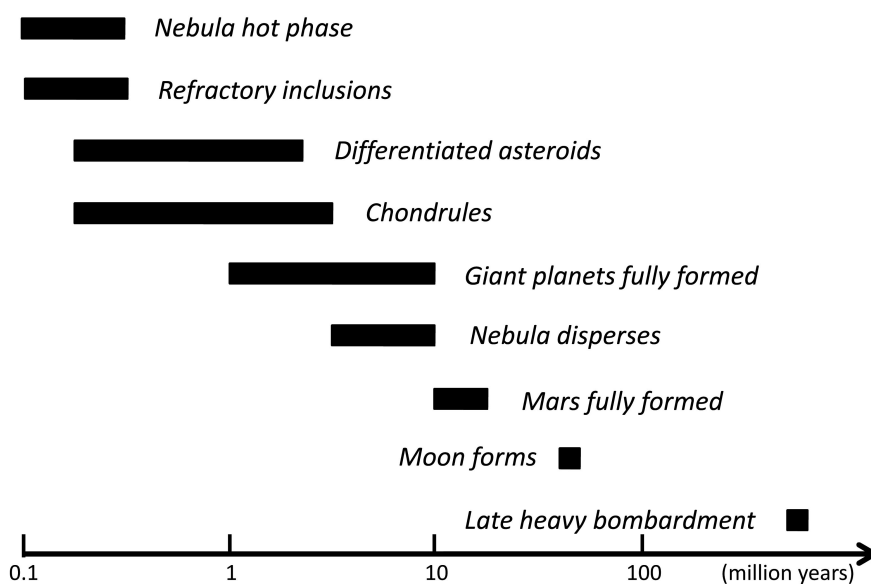


Figure 1.2 Key milestones related to planet formation with approximate timing (Chambers, 2007).

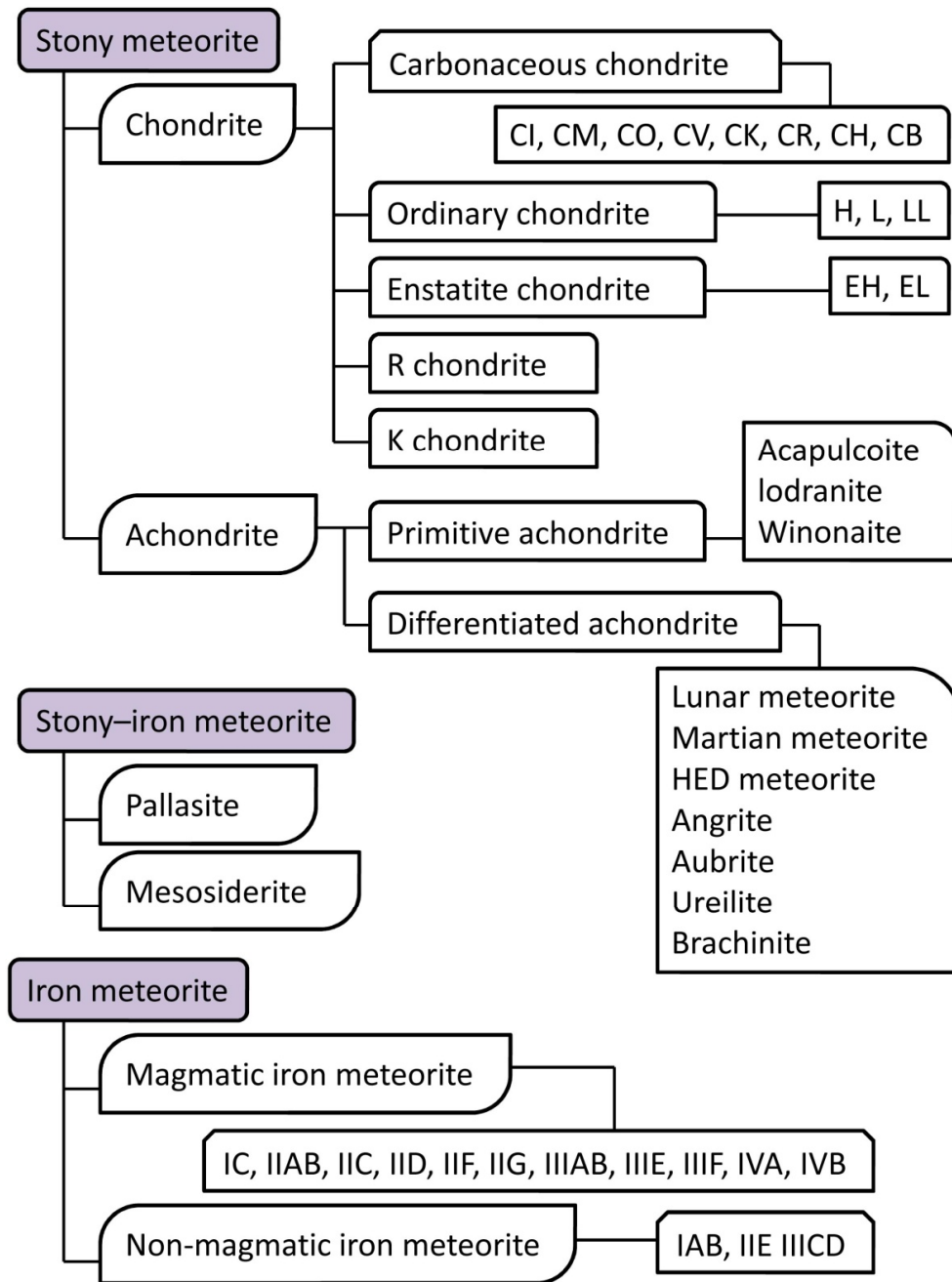


Figure 1.3 Classification of meteorites. (after Krot et al., 2007)

The next stage of planet formation is thought to be the formation of planetisimals. Chondritic material began to gather together due to gravitational drift towards the centre of the nebular accumulating dust. Then such aggregations accumulated to form objects with a dimension of kilometre (Halliday, 2003). (How this earliest stage

of accumulation occurred is unclear.) Once objects reach about a kilometre in size accretion proceeds by “runaway growth.” The largest bodies would have increased their size through further gravitationally driven collisions at a rapid and increasing rate. Initially, hundreds of moon-sized bodies would have been produced in about 2×10^4 years (Wetherill and Stewart, 1989). Subsequently, objects roughly the size of Mercury to Mars were built over timescales on the order of $\sim 10^5$ years (Wetherill and Stewart, 1989). The giant planets formed further out and along similar lines as runaway growth in the terrestrial-planet formation. Larger planetary embryos of giant planets were produced at 5–10AU, and it takes about 2Myr to grow to the mass of Jupiter (Hubickyj et al., 2005). For the terrestrial planets, it took $\sim 10^7$ years to reach nearly their full size, and terrestrial planets might also continue accreting with large planetesimals for another 10^8 years, which means some of them might have “giant impacts” involved in their later accretion stages (Chambers, 2001).

1.1.3 Meteorite

The differentiation of the Earth and its tectonic activity have erased most of the early geological record. Therefore, geochemistry is particularly important for understanding how Earth formed. It is generally believed that primitive chondritic meteorites provide information about undifferentiated bulk Earth compositions because they match the relative composition of the Sun for non volatile elements. Differentiated meteorites provide information about asteroidal and planetary

evolution more broadly (Allègre et al., 1995; McDonough, 2003; Palme and O'Neill, 2007). More than 1.7×10^4 meteorites are currently known; based on their texture, they are classified into three major groups, stony meteorites, stony – iron meteorites, and iron meteorites (Figure 1.3).

1.1.3.1 Stony meteorite

1.1.3.1.1 Chondrite

Chondrites were formed by the accretion of particles present in the primitive Solar System and are thought to not have been greatly modified by melting or differentiation of a parent body. Therefore, the components of chondrites could contribute the best clues when studying the origin of the Solar System. The major components of chondrites are chondrules, FeNi-metal, refractory inclusions (CAIs and amoeboid olivine aggregates (AOAs)), and fine-grained matrix material. CAIs are the oldest objects in chondrites excluding presolar grains (Amelin et al., 2002), and they are composed of Al-, Ti-, Ca-rich FeO poor oxide and silicate minerals, which are predicted to condense from a cooling gas of solar composition at high temperatures ($> 1,200\text{--}1,300\text{K}$) (Ireland and Fegley, 2000). Chondrules probably formed over several million years as molten or partially molten droplets. They are round objects in chondrites with igneous textures and are mainly composed of olivine and low-calcium pyroxene crystals set in a feldspathic glass or microcrystalline matrix

(Scott and Krot, 2007).

Based on their mineralogy, petrology, bulk chemistry and oxygen isotopic compositions, and proportions of various chondritic components, fifteen chondrite groups have been recognized. They can be divided into three major classes: carbonaceous chondrite, ordinary chondrite, and enstatite chondrite. Actually only parts of carbonaceous chondrites are rich in carbon, and nowadays, carbonaceous chondrites are defined on their refractory elemental abundances. Ivuna-like (CI) chondrite is a special group, not only because they lack chondrules. There are only five CI chondrites being known so far, and according to their composition, they are the most primitive meteorites and provide the best match to the solar photosphere (Palme and Jones, 2003).

More than 80% of all meteorites are ordinary chondrites, and they are divided into three groups (H, L, and LL), which refer to their metallic iron and bulk iron contents. Compared to carbonaceous chondrites, CAIs are rarely found in ordinary chondrites. Enstatite chondrites are so named because of their abundant enstatite-rich chondrules. They are grouped into EH and EL types with different contents of metallic iron. As with ordinary chondrites, CAIs are also a rarity in enstatite chondrites. They have a unique mineralogy indicating they were formed under extremely reducing conditions, and their bulk oxygen isotopic compositions follow along the terrestrial fractionation line quite close to the composition of the Earth and Moon (Clayton et

al., 1984).

1.1.3.1.2 Achondrite

Achondrites are silicate rich meteorites that do not contain chondrules. Although all achondrites have gone through differentiation, they still can be simply divided into “differentiated” and “primitive” achondrites. Primitive achondrites are generally thought to be ultrametamorphosed chondrites, or might be residues that had undergone very low degrees of partial melting. Therefore, primitive achondrites would have igneous or metamorphic textures and approximately chondritic bulk compositions (Krot et al., 2007). Martian and Lunar meteorites are sub-groups of differentiated achondrites, but differentiated achondrites mainly consist of HED (howardite, eucrite and diogenite) meteorites, which are believed to originate from the crust of asteroid 4 Vesta. Several lines of evidence including oxygen isotopic compositions and Fe/Mn ratios of pyroxenes shows that HED meteorites originated from same asteroidal parent body (Drake, 2001), and they should be impact ejecta of 4 Vesta (McCord et al., 1970). More recently, the Dawn mission has provided new evidence for this parent body–meteorite linkage between Vesta and HED meteorites. A global lithologic maps of Vesta based on Dawn mission’s Visible InfraRed (VIR) Spectrometer indicate pyroxene compositions and abundances like those of HEDs (Ammannito et al., 2013). Other observations and constraints of Vesta such as unique space weathering, chronology of surface units and impact history, dimensions of the

core, etc. are all consistent with characteristics of HED meteorites (McSween et al., 2013).

1.1.3.2 Iron meteorite

Iron meteorites are composed mainly of metallic alloys of iron and nickel. Although less than 6% of meteorite falls are constituted by iron meteorites, they offer a rare chance to probe into the deep interior of differentiated planetary objects. While melting happened within planetesimals, lighter silicate magmas or solids and metallic liquids segregated from each other, and then dense liquids would sink to form the cores of these bodies. Widmanstätten patterns are the most distinguished texture in iron meteorites, which are intergrowths of several different Fe-Ni phases originating as iron cores cooled slowly. These exquisite patterns can provide important information on the sizes of the iron meteorite parent bodies and their thermal evolution (Haack and McCoy, 2007).

Most iron meteorites can be classified into 13 groups according to their bulk chemical components, and they can be divided into “magmatic” and “nonmagmatic” groups. Chemical compositions of magmatic iron meteorite groups indicate they might form in the cores of differentiated asteroids by fractional crystallization. However, in nonmagmatic iron meteorites, the broad ranges in Ni, Ga, and Ge make their formation harder to explain by simple fractional crystallization of a metallic core

(Scott, 1972; Scott and Wasson, 1975), and many models for their origins are proposed (e.g. McCoy et al., 1993; Wasson and Kallemeyn, 2002).

1.2 Stable isotope geochemistry

Stable isotope geochemistry, which is the research about non-radiogenic and non-nucleogenic variations of the isotopic compositions of elements in natural rocks, minerals, and fluids, began to be explored more than fifty years ago. A number of light elements, including H, C, N, O, and S, were the first subjects of the field of stable isotope geochemistry. These “traditional” stable isotope elements play a key role in contributing clues for climate change, evolution of life, chemical and physical processes happened during Solar System formation, and biological processes, etc. Some other elements (e.g. Mg, Si, Ti, Cr, Fe, Zn, Cu, Ge, and Mo) are also geochemically important, but the isotopic variations of these elements in natural samples are generally quite small and therefore analysis of isotope variations of these elements was limited analytically. However, these “non-traditional” stable isotope elements are now more routinely analysed because of the improvement of analytical instrumentation (e.g. multi-collector inductively-coupled plasma mass spectrometry, MC-ICP-MS) in the last decades.

Conveniently, variations in stable isotope ratios are typically reported in “delta notation”, in which the isotopic difference is presented as the deviation of an isotopic

ratio from a standard

$$\delta^i M_{\text{sample}} = \left(\frac{R_{\text{sample}}^{i/j}}{R_{\text{STD}}^{i/j}} - 1 \right) \times 1000 \quad (1.1)$$

where R is the ratio of specific isotopes i and j of element M , STD is a standard reference material, and the way for presenting this value is in “*per mil*” (‰). If we are going to discuss isotopic fractionation between two phases A and B, following equation 1.1, the fractionation factor (α_{A-B}) is defined as:

$$\alpha_{A-B} = \frac{R_A^{i/j}}{R_B^{i/j}} = \frac{1000 + \delta^i M_A}{1000 + \delta^i M_B} \quad (1.2)$$

Because α_{A-B} is normally very close to 1, and both $\delta^i M_A$ and $\delta^i M_B$ are much smaller than 10^3 . Therefore, the isotopic fractionation difference between two phases is expressed as:

$$\Delta_{A-B} \equiv \delta^i M_A - \delta^i M_B \approx 10^3 \ln \alpha_{A-B} \quad (1.3)$$

1.2.1 Mass independent variation

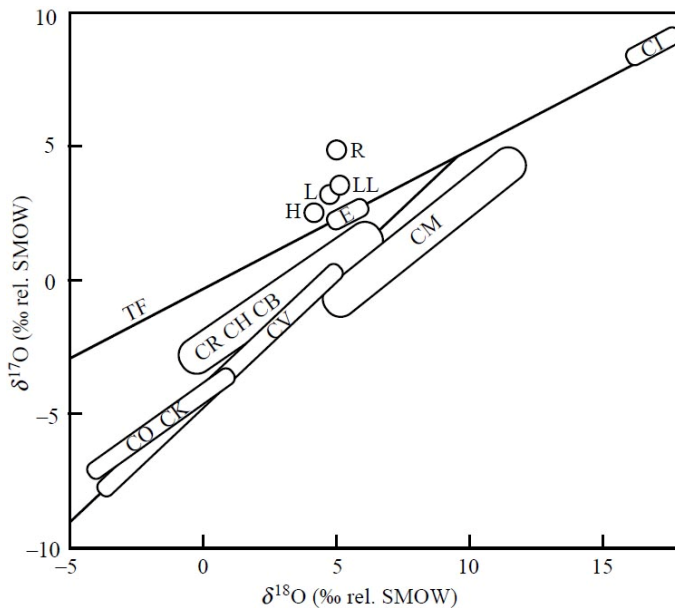


Figure 1.4 Whole-rock oxygen isotopic compositions of major chondrite classes. TF (terrestrial fractionation) line and CCAM (carbonaceous chondrite anhydrous mineral) line are shown for reference. (Clayton, 2003)

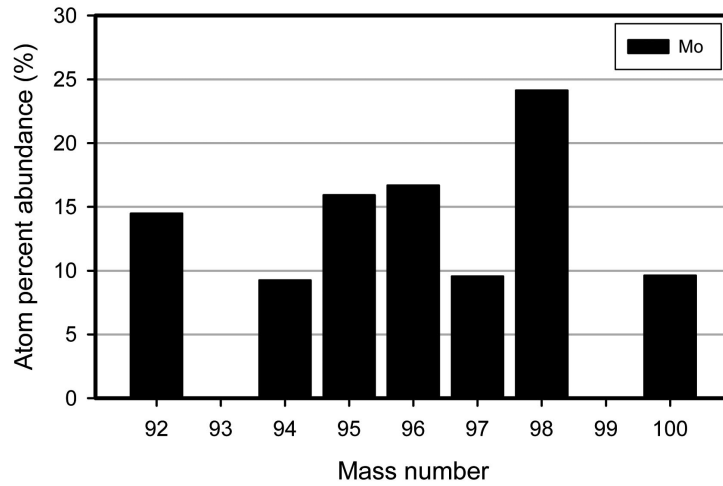


Figure 1.5 Histogram for illustrating relative abundances of Mo stable isotopes

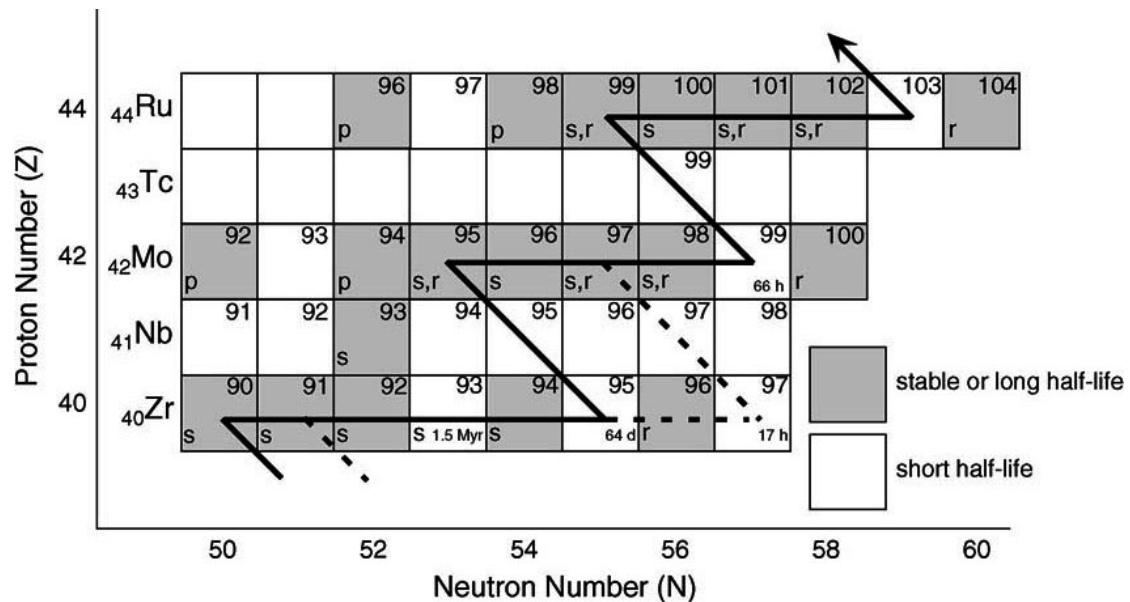


Figure 1.6 The chart of the nuclides in the mass region of Mo, whilst the s-process, p-process and r-process produced isotopes are as indicated (Wieser et al., 2007).

Apart from radiogenic or nucleogenic effects, mass independent isotopic effects are mainly known as a feature of inherited diverse nucleosynthetic components. However, mass independent isotopic variations were first observed in the oxygen isotope ratios in meteorites, and this is no longer thought to be nucleosynthetic in origin but the result of self shielding during irradiation in the early solar nebula (Clayton, 2003; Thieme, 2006). The oxygen isotopic composition becomes a powerful

fingerprint that allows it to be used to distinguish different parent bodies of meteorites as well as investigating the chemical and physical processes happening during Solar System evolution (Clayton, 2003). For example, the oxygen isotopic composition of enstatite chondrites overlaps that of the Earth (Figure 1.4) and has been used to argue that similar material built our planet (Javoy et al., 1986). The large ranges of oxygen isotopic compositions for various groups of meteorites (see below) also suggest they underwent varying degrees of low temperature aqueous alteration (Clayton, 2003).

Molybdenum is an ideal element for the investigation of nucleosynthetic processes due to its seven stable isotopes with similar abundances (Figure 1.5). Molybdenum isotopes are derived from three different nucleosynthetic processes corresponding to *r*-process (rapid neutron captures, occurs in core-collapse supernova), *s*-process (slow neutron capture-process, occurs at relatively low neutron density and intermediate temperature conditions in stars), and *p*-process (proton capture process, source of certain, naturally occurring, proton-rich isotopes) (Figure 1.6), and four of them are derived from single process only (Figure 1.6). For example, Nicolussi et al. (1998a) reported depletions of isotopes at masses 92 and 94 (*p*-process only) and 100 (*r*-process only) in presolar silicon carbide grains. The finding of *s*-process isotopic enrichments suggests the initial isotopic heterogeneity in the Solar System does exist and can be preserved (Nicolussi et al., 1998a).

1.2.2 Mass dependent fractionation

Many processes, including condensation and evaporation of dust grains, metal-silicate segregation, core crystallization, and aqueous alteration, could fractionate isotopes dependent on their mass. While discussing mass dependent isotopic fractionation occurs on an element has three or more isotopes, the fractionation can be defined by two or more isotopic ratios. In consequence, the fractionation of different isotopes will be a function of their relative mass differences. Assuming the fractionation happens for element E with three isotopes i, j , and k , and m_i, m_j , and m_k are their masses respectively. The isotopic fractionation of $R^{i/j}$ may be relevant to $R^{k/j}$ as (Johnson et al., 2004):

$$\alpha_{k/j} = (\alpha_{i/j})^z \quad (1.4)$$

where

$$z = \frac{m_i/m_k}{(m_k - m_j)/(m_i - m_j)} \quad (1.5)$$

If the isotopic composition is discussed over a small range, equation 1.4 can approximated to:

$$\delta^k M \approx \left(\frac{k-j}{i-j} \right) \delta^i M \quad (1.6)$$

(Johnson et al., 2004)

The variations between different isotopes of an element can be presented as three-isotope plot (e.g. figure 1.4). Therefore, when mass dependent fractionation happens, according to equation 1.6, $\delta^i M$ and $\delta^k M$ will produce a

“mass-dependent fractionation line” in their three-isotope plot (e.g. terrestrial fractionation line in figure 1.4). However, isotopes mass dependent fractionation could occur in two different ways, equilibrium fractionation or kinetic fractionation. Equilibrium fractionation happens at the quantum level, while kinetic fractionation is resulting from relative ease of motion of isotopes (Schauble, 2004). These two processes proceed with different fractionation rules, and the exact slope of the mass fractionation line for the equilibrium (β_{equi}) and kinetic (β_{kin}) fractionation are as follows:

$$\beta_{equi} = \frac{\left(\frac{1}{m_k} - \frac{1}{m_j}\right)}{\left(\frac{1}{m_k} - \frac{1}{m_i}\right)} \quad (1.7)$$

$$\beta_{kin} = \frac{\ln\left(\frac{m_k}{m_j}\right)}{\ln\left(\frac{m_k}{m_i}\right)} \quad (1.8)$$

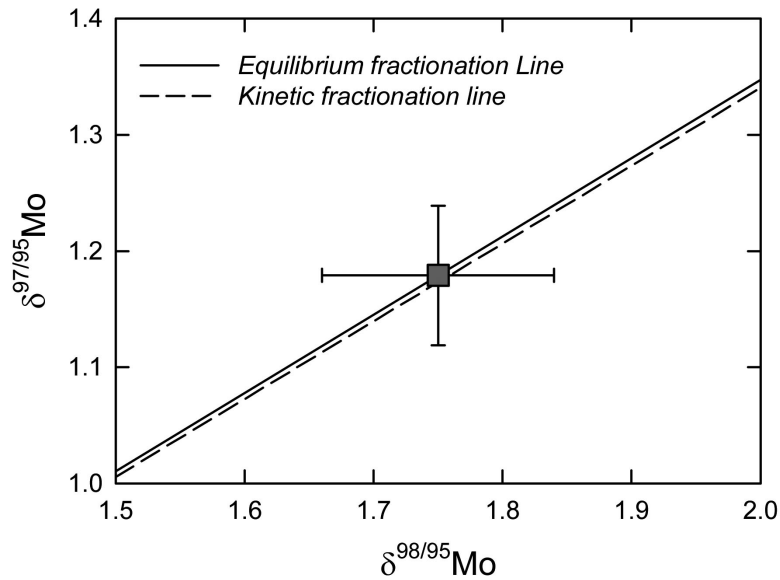


Figure 1.7 Equilibrium and kinetic mass-dependent fractionation line for Mo isotopic system. Plotted point with error bars shows external instrument reproducibility of our standard solution in this study.

These slopes seem to be helpful for identifying between the two fractionation types theoretically. However, when we apply $\delta^{98/95}\text{Mo}$ and $\delta^{97/95}\text{Mo}$ as our example, these exponents would become $\beta_{equi} = 0.6737$ and $\beta_{kin} = 0.6703$. The difference between them is too small for recognizing the type of fractionation processes in practice (Figure 1.7). Therefore, mass-dependent fractionation lines are normally used just for data quality control.

1.3 Molybdenum isotope geochemistry

1.3.1 General information of molybdenum

Molybdenum is moderately siderophile, refractory, and the 54th most abundant element in Earth's crust. The elemental abundance of Mo in crustal materials is generally around a few ppm, whereas its concentration in the mantle is around 50 ppb (McDonough and Sun, 1995). Molybdenum has an atomic number of 42 and possesses seven stable isotopes, spanning a mass range from 92 to 100. Isotopes of Mo are synthesized by two *p*-process-only isotopes (^{92}Mo and ^{94}Mo), one *s*-process-only (^{96}Mo), one *r*-process-only (^{100}Mo) and three of mixed *r*-process and *s*-process origin (^{95}Mo , ^{97}Mo , and ^{98}Mo) (Figure 1.6). Among these seven stable isotopes, ^{98}Mo is the most abundant isotope and comprises 24.13% of all molybdenum (Rosman and Taylor, 1998). The abundances of all the other Mo stable isotopes range from 9.25 to 16.68% (Rosman and Taylor, 1998) and so are readily

measurable. This isotope distribution makes Mo a useful element for mass spectrometric analysis for both nucleosynthetic and isotope fractionation effects.

1.3.2 Molybdenum behavior in surface processes

In the oceans, Mo is relatively abundant with a concentration of 10.3 µg/l (Collier, 1985). Molybdenum(VI) is the stable oxidation state in oxic seawater found as MoO_4^{2-} (molybdate), and it has a long residence time of ca. 800ka (e.g. Morford and Emerson, 1999). However, Helz et al. (1996) have noted the very large equilibrium constants for transformation of molybdate to thiomolybdate, and hypothesize that in the presence of HS^- , one sulphur replaces an oxygen on MoO_4^{2-} , creating a complex that is more particle reactive and can be scavenged bound to iron sulphides or humic-SH complexes in reducing conditions. Under euxinic conditions with free H_2S in the water column, Mo is scavenged as sulphide and scavenging becomes very effective (Erickson and Helz, 2000).

This redox sensitive behaviour of Mo has been used to infer redox-state changes in marine sedimentary environments (e.g. Colodner et al., 1995; Morford and Emerson, 1999). Molybdenum is relatively insoluble under the reducing conditions, which means the sediments that form in reducing conditions will potentially have sedimentary Mo enrichments. On the other hand, Mo is also adsorbed to Mn oxides, which may remove up to 70% of the Mo from the oceans, while the remaining

proportion is precipitated in reducing sediments (Morford and Emerson, 1999). Therefore, when Mo isotopes were fractionated simultaneously during these processes, the isotope signature for each sinks is thought to be distinct (Anbar, 2004).

The simplified idea behind Mo isotopes as a quantitative redox tracer in the marine environment is that Fe-Mn deposits fractionate Mo isotopes to light compositions leaving seawater heavy. In contrast, euxinic sediments incorporate the Mo isotope composition of seawater, due to very effective scavenging. With this basic setup, a reduction of oxygenated ocean floor would result in less light Mo being taken from the oceans, and therefore a lighter Mo isotope composition recorded in euxinic sediments. Various studies have used these principles for reconstructions of paleo-redox conditions in the oceans (e.g. Arnold et al., 2004; Pearce et al., 2008; Siebert et al., 2005; Wille et al., 2008).

It is apparent that the geochemical processing of Mo isotopes in surface processes is more complex than the system described above. A number of recent studies have therefore investigated source and sink processes. Siebert et al. (2006) presented molybdenum isotope data for four sediment profiles from continental margin settings and suggest that the Mo isotope signature of reducing sediments may serve as a tracer for the cycling of organic carbon in continental margin sediments. Recently, Goldberg et al. (2012) discussed their Mo isotopic data from modern anoxic marine sediments deposited beneath an oxic to suboxic water column and suggested Mo

isotope signatures are largely controlled by Mo adsorption and desorption to various geomedia. Those Mo isotopic variations reported in ancient sediments might actually relate to the prevailing molybdenophilic substrates rather than simply reflect changes in the global ocean redox conditions (Goldberg et al., 2012).

Another complication of the Mo system is crustal processes and the isotope composition of the riverine input and the processes that might cause variations over time. Molybdenum isotope compositions and concentrations in water samples from a variety of river catchment profiles were reported by Neubert et al. (2011). They provided evidence that the Mo isotopic composition of continental runoff depends on the relative weathered masses of magmatic and sedimentary rocks exposed in river catchments. But due to the imbalance of light and heavy Mo isotopes, they proposed improved models of the global Mo cycle, which is the recycling of pelagic sediments in subduction zones in addition to the continental runoff. In this case, they predicted arc magmas should to be isotopically lighter than non-arc magmas (Neubert et al., 2011). Similar isotopic composition of river water and in the Mo released from the basalt bedrock were found by Voegelin et al. (2012), and it is likely Mo isotope fractionation during incongruent weathering of basalt might be able to explain the observed isotopically heavy aquatic Mo signatures. Furthermore, they suggested that magmatic sulphides might be the key phases possessing the distinctly heavier Mo isotope signature, rather than the coexisting silicates (Voegelin et al.,

2012).

1.3.3 Molybdenum isotopes fractionation in high temperature processes

In high temperature processes, Mo behaves as an incompatible, refractory and moderately siderophile element. However, studies about Mo isotope behavior in high temperature processes are very limited. McManus et al. (2002) analyzed hydrothermal samples from submarine hydrothermal springs on Baby Bear in the Cascadia Basin. They demonstrated that the springs have not only greater Mo concentrations but that the hydrothermal endmember is isotopically lighter than seawater. Molybdenum isotope fractionation in molybdenites from ore deposits is reported by Hannah et al. (2007) and Mathur et al. (2010). The variation of Mo isotopic composition in the investigated ore deposits is surprisingly large, and the isotopic fractionation of Mo might be related to the different mineral phases during the ore-forming processes (Mathur et al., 2010). Data on Mo behaviour in magmatic processes exists only in abstract form, and the revealed variation seems limited (Burkhardt et al., 2013; Siebert et al., 2003; Voegelin et al., 2012).

As early as 1960s, mass dependent variations of Mo isotopes in some iron meteorites were discussed by Murthy (1962), and Wetherill (1964). However, analytical errors did not allow conclusive results. Mass-independent isotope fractionation of Mo in unprocessed presolar carbide and graphite grains carrying extreme molybdenum

isotopic signatures was shown by Nicolussi et al. (1998a) and Nicolussi et al. (1998b). Yin et al. (2002) and Dauphas et al. (2002a, b) also reported that molybdenum isotopic composition of bulk carbonaceous chondrites is distinctly different from the accepted average solar value. The presence of molybdenum isotope anomalies is thought to reflect a mixture of different nucleosynthetic components that have survived planetary-scale homogenization in the proto-solar nebula. This has led to the conclusion that this isotope heterogeneity provides evidence of a “cosmic chemical memory” inherited from the interstellar environment from which the Solar System was formed (Dauphas et al., 2002a). More studies have observed small molybdenum isotope anomalies in chondrites, CAIs, iron meteorites, mesosiderites, and pallasites (Becker and Walker, 2003; Dauphas et al., 2002a, b; Fujii et al., 2006), and these also provide evidence for isotope heterogeneity of the protosolar nebula.

More recently, Burkhardt et al. (2011) presented Mo isotopic data for a wide range of samples, including Ca–Al-rich inclusions, chondrites and differentiated meteorites, as well as martian and terrestrial samples drawing conclusions on Mo nucleosynthesis, solar nebula heterogeneity, and origin of Earth's parent body. Their results show that Mo isotopic anomalies in bulk meteorites correlate with those in ruthenium (Ru) reflecting a heterogeneous distribution of a common *s*-process carrier for Mo and Ru. Furthermore, all meteorites among their sample set seem more and less depleted in *s*-process Mo isotopes relative to the Earth. They argued this might indicate the Earth

on average accreted from material that is different from known types of meteorites, and further high precision isotopic data are still needed for comparing the isotopic composition of the Earth to chondrites (Burkhardt et al., 2011).

1.3 Targets of this study

For more than a century, chemical and isotopic compositions of stars, planets, asteroids, and comets have been used to study the evolution of the Solar System. Following the huge improvement of analytical technology, we are much closer to answer the question of the origin and evolution of the Solar System. There are so many processes that might have fractionated and Mo in the early Solar System that include condensation and evaporation of dust grains, metal–silicate segregation, core crystallization, and aqueous alteration. Mass dependent isotope fractionation between meteorites and planetary materials (e.g. peridotite) has been used before to assess processes that occurred during formation of the Earth that might have fractionated isotopes, and to give information about the formation of the Earth's core.

So far little is known about mass dependent isotope fractionation of Mo at high temperatures in the Earth, in particular during mantle processes. This is important to understand for the long term Mo cycle as well as for the use of Mo as a tracer for magmatic processes. For studying the mantle, ultramafic rocks are defiantly a sort of

important mantle derived samples. Furthermore, mantle derived basalts also must be considered, while ocean island basalts are thought to source from deeper parts of the mantle, mid-ocean ridge basalts are generally thought coming from upper parts of the mantle.

Firstly, I'll present Mo isotopic data of ocean island basalts (OIB), in order to systematically access Mo isotope fractionation during igneous processes. A series of mafic rocks from from variety of localities were analyzed, and the data shows a large variation in both Mo contents and isotope compositions. (Chapter 3)

Moreover, I'll present the results of mid-ocean ridge basalts (MORBs) and ultramafic rocks, and try to investigate the Mo isotopic signature of the mantle. Based on our first Mo isotopic measurements of ultramafic xenoliths, I will also try to determine a more reliable average value of both Mo absolute abundance and isotopic composition in bulk silicate Earth. (Chapter 4)

Furthermore, I have measured Mo isotopic compositions of primitive as well as differentiated meteorites and compare them to terrestrial samples. Bulk meteorites (e.g. ordinary chondrite, enstatite chondrites, carbonaceous chondrites, and iron meteorite) have been analyzed in order to further access how Mo isotopes fractionated in the Solar System, and how they behave during metal silicate separation and core formation. (Chapter 5)

CHAPTER TWO



Method

2.1 Introduction

Molybdenum has a variety of chemical characteristics that attract both geochemists and biochemists. Molybdenum has seven stable isotopes, which makes it ideal for the study of mass dependent stable isotope fractionation. Molybdenum isotope variations were analyzed by thermal ionization mass spectrometry (TIMS) since the 1960s. Molybdenum isotope compositions of some iron meteorites and terrestrial rocks were measured with TIMS and reported by Murthy (1962, 1963) and Wetherill (1964). Nowadays, although Mo isotopes are still analysed by TIMS (Dauphas et al., 2002a, b; Yin et al., 2002), multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has become the dominant method for the analysis of high precision Mo isotope data. This technique allows for rapid sample processing, and its ICP ion source has a high ionization efficiency for Mo.

The correction of analytical mass fractionation is one of the most crucial issues in MC-ICP-MS analysis. Calculation and correction of instrumental mass bias is based on one of these three methods: (1) sample-standard bracketing, (2) element doping, and (3) double spiking. If instrumental mass fractionation is very stable over time, sample-standard bracketing is a suitable method for correction. However, non-systematic drift in instrumental mass fractionation is a concern and could occur, e.g. due to a matrix effect between samples and standards. Sample-standard bracketing is difficult with TIMS measurement because the isotopic composition of

the analyte changes continuously during evaporation and analysis. While Murthy (1962, 1963) corrected instrumental mass bias of TIMS with sample-standard bracketing, he also acknowledged this problem. His data produced an apparent isotope enrichment due to inappropriate analytical mass bias correction, and were refuted by Wetherill (1964) subsequently.

There are many Mo isotopes available and the similar behaviour of Zr and Mo in the mass spectrometer, means that both element doping with Zr and isotopic double spike techniques have been used for analysis of Mo stable isotopes by most researchers using MC-ICPMS (e.g. Barling et al., 2001; Siebert et al., 2001). Element doping (Zr) was used to analyze Mo isotope fractionation in geological samples by Barling et al. (2001), and achieved a precision of $\pm 0.25\%$ on $\delta^{97/95}\text{Mo}$ (2s.d.). By using a double spike technique, Siebert et al. (2001) achieved a precision of $\pm 0.06\%$ on $\delta^{97/95}\text{Mo}$ ($\pm 0.1\%$ on $\delta^{98/95}\text{Mo}$; 2s.d.).

The double spike method adds two isotopes of the element to be analysed with a known ratio and quantity to the unknown sample. This allows the calculation of instrumental mass bias with the same element to be analysed within each run, thus eliminating problems of changes in mass bias over time and fractionation differences between different elements. In addition, the double spike can be added before chemical treatment of the sample facilitating correction for fractionation during chemistry procedures. Wetherill (1964) started to apply double spiked Mo isotope

analysis with TIMS, and Siebert et al. (2001) firstly used this technique with MC-ICP-MS.

In this thesis, I basically follow the analytical method developed by Siebert et al. (2001) along with the modification applied in Siebert et al. (2006). However, I modified the chemical procedures further for better results on extra-terrestrial samples. All of the details are given later in this chapter.

2.2 Sample digestion

Fresh rock specimens and iron meteorites were digested using wet digestion with quartz-distilled acids. Small amounts of Suprapur[®] hydrogen peroxide (produced by Merck[®]) are used during digestion. Any water used during entire chemical procedure is 18.2M Ω -grade purified by a MilliQ Element water polisher.

2.2.1 Mafic rocks

Most mafic rock samples were crushed into fine powder with a jaw-crusher and tungsten carbide ball mill. All mid-ocean ridge basalt (MORB) samples were handpicked under microscope, and these fresh pieces of glass were digested without crushing. A conventional hotplate digestion method is applied on all terrestrial samples, with a volume ratio of 3:1 concentrated HF-HNO₃ mixtures. Samples were placed in cleaned Savillex[®] teflon beakers and left on a hotplate at 130°C. After

approximately 72hs, these sample solution were evaporated on a hotplate, and residues were then dissolved in concentrated HNO_3 and left to dry. This procedure was repeated until all fluorides precipitation completely disappeared. Following this step, samples were re-dissolved into 5M HCl twice with evaporation in between to make sure they were fully digested, and then they were ready for ion exchange chromatography.

2.2.2 Chondrites and ultramafic rocks

Ultramafic rocks and chondrites contain more refractory minerals compared to basaltic terrestrial rocks, and complete dissolution of these samples is difficult using normal conventional hotplate digestion only. Therefore, a digestion method using pressurized Teflon bombs presented by Prytulak et al. (2011) was used. The maximum amount for each 7mL Teflon bomb is 100mg sample. If more was needed, a sample had to be dissolved as several aliquots and recombined after digestion. A concentrated HF- HNO_3 mixture in a volume ratio of 1:1 (1ml each acid) was loaded onto each sample. After the caps were tightly sealed, the bombs were placed in an oven at 130°C for 3 days, and then evaporated on a hotplate. Concentrated HF-HCl mixture in a volume ratio of 1:1 (1ml each acid) was then loaded into the bombs with the dried residue, and the sealed bombs were again put in an oven at 130°C for another 3 days. Both procedures were repeated until all the samples were fully digested. Following the digestion, samples were treated with HNO_3 as with “normal”

hot plate digestion in order to remove fluorides. If the samples were fully digested, there should be no visible particles left after fluorides were removed. Samples were then dried and re-dissolved in 5M HCl twice before ion exchange chromatography (see below).

2.2.3 Iron meteorites

Iron meteorite samples were polished with SiC sandpaper and then cleaned with MilliQ water, followed by a leaching step using cold 6M HCl for 30 minutes which was repeated at least 3 times. After this step, all iron meteorite samples had more than 90% material left. Cleaned iron meteorites were then placed in Savillex® teflon beakers and dissolved in 6M HCl on a hotplate at 120°C overnight. In order to attack possible organic matter, all samples were dried down and re-dissolved in HNO₃ for several times until no further visible organic matter remained. And then all the iron meteorites were dried and re-dissolved in 5M HCl before ion exchange chromatography.

2.3 Ion exchange chromatography

In order to obtain high precision isotope measurements by MC-ICP-MS, Mo has to be separated from its rock matrix. Sample impurity can cause isobaric interferences and matrix effects, the latter possibly affecting ionization, signal stability, sensitivity and peak resolution. Therefore, a two step ion exchange chromatography was employed

to separate Mo from the rock matrix of the samples.

Following the chemistry procedure presented by Siebert et al. (2001) along with the modification applied in Siebert et al. (2006), a two step ion exchange chemistry was used in this study, which employs both anion and cation exchange resins. The first step uses BioRad AG1-X8 (200-400 mesh, chloride form) anion exchange resin to remove most of the major matrix elements (e.g. Na, Mg, Al, Si, K, Ca, Ti, Mn, Ni) and elements with possible isobars (e.g. Zr), and this separation is performed in HCl solution. The distribution coefficient of Mo reaches a minimum value of ~ 20 in 0.5M acid and augments increases with acidity to reach a maximum near 5M HCl (Korkisch, 1989). At higher acidities (up to 12M HCl), the adsorption of Mo decreases again but distribution coefficients are never lower than 10^2 (Korkisch, 1989).

Table 2.1 Anion column (BioRad AG1-X8, 200-400 mesh, chloride form) procedure for separating Mo from a geological matrix.

	Solution	Volume
Pre-cleaning	1M HCl	40 ml
Pre-conditioning	5M HCl	2 x 3ml
Sample loading	5M HCl	3 ml
Rinse	5M HCl	40 ml
Elution	1M HCl	30 ml

Table 2.2 Cation column (BioRad AG50W-X8, 200-400 mesh, hydrogen form) procedure for Mo separation.

	Solution	Volume
Pre-cleaning	MilliQ water	10 ml
Pre-conditioning	0.5M HCl	2 x 3ml
Sample loading	0.5M HCl	3 ml
Elution	0.5M HCl	30 ml

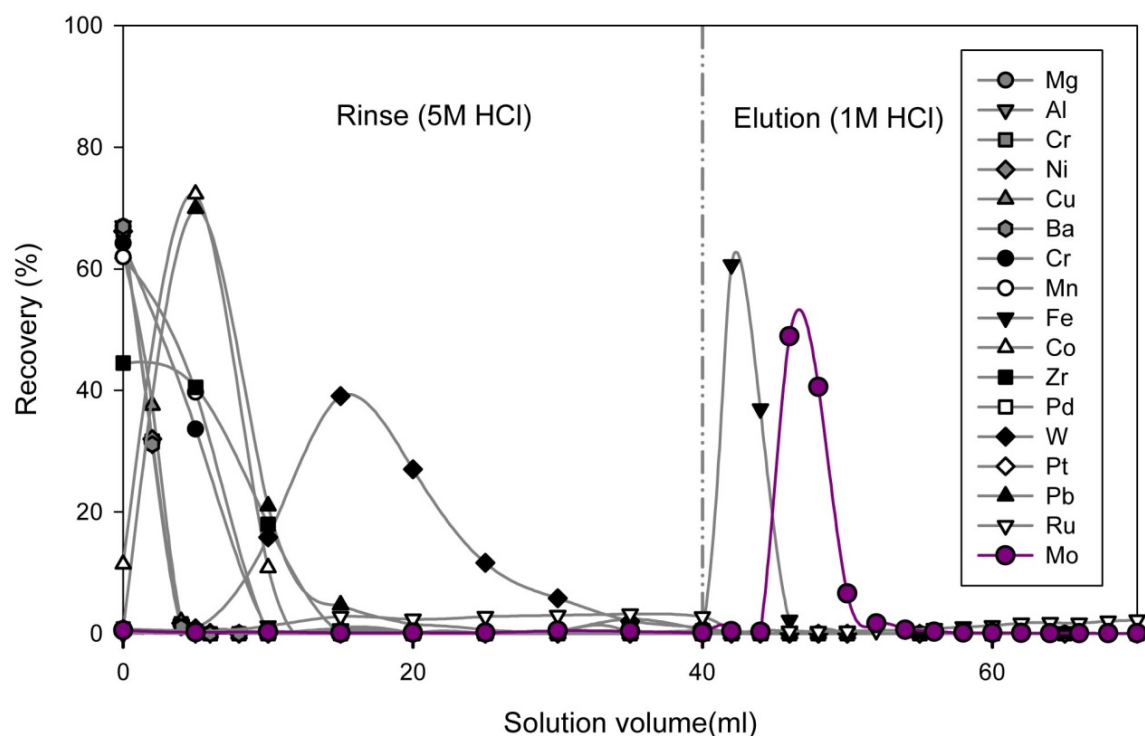


Figure 2.1 Elution curves for BioRad AG1-X8 (200-400 mesh, chloride form) resin.

The resin was pre-cleaned in a container with MilliQ water and then repeated washes of 1M HCl for several days. Two ml bed volume of resin is loaded into a standard BioRad Poly-Prep® column. The anion column recipe and elution curves are given in Table 2.1 and Figure 2.1 respectively.

As shown in Figure 2.1, Mo cannot be separated from Fe with this single anion column chemistry. Therefore, BioRad AG50W-X8 (200-400 mesh, chloride form) cation exchange resin is applied as the second chemistry step. In HCl solutions with acidities ranging from 0.1 to 4M, Mo distribution coefficients on this cation exchange resin are low, ranging between ~ 10 to <1 . On the other hand, Fe is strongly adsorbed in diluted HCl with the same resin. Therefore, Mo and Fe can be separated efficiently by the described cation exchange step (Table 2.2). The resin was pre-cleaned similar

to the anion resin before use (MilliQ water and 0.5M HCl). Again, two ml bed volume of resin was loaded into a standard BioRad Poly-Prep® column. For samples with high Fe content, this separation step was repeated up to three times to remove all Fe.

Table 2.3 Eichrom® TRU resin column procedure for separating Mo from Ru.

	Solution	Volume
Pre-cleaning	MilliQ water	10 ml
Pre-conditioning	7M HNO ₃	2 x 3ml
Sample loading	7M HNO ₃	1 ml
Rinse	7M HNO ₃	6 ml
Elution	0.1M HNO ₃	13 ml

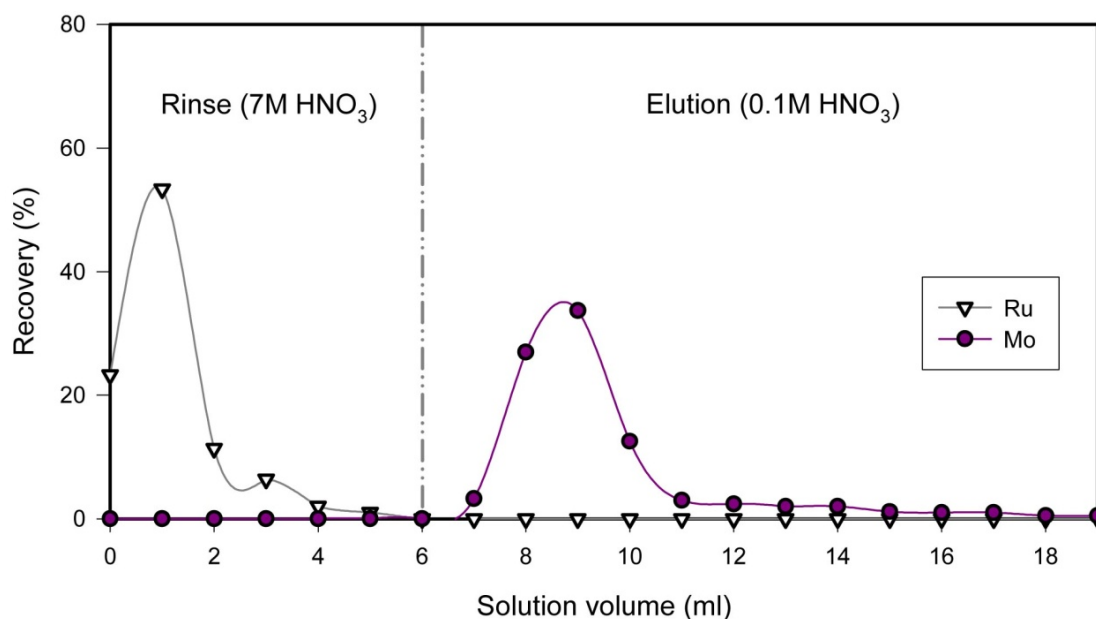


Figure 2.2 Elution curves for Mo and Ru in Eichrom TRU resin.

However, the first two separation steps can only remove 90% of Ru, which has three isobaric interferences on Mo masses. This is not a major issue for terrestrial samples because Ru is hardly found in most of them. In average continental crust, the Mo/Ru ratio are approximately 1500 (Rudnick and Gao, 2003), and this ratio is even higher in mafic rocks. For example, in several most common USGS basaltic rock standards (e.g.

BHVO-2 and BIR-1), the absolute Ru abundance is lower than 0.2 ppb (Meisel and Moser, 2004). However, it is a crucial problem in meteorite samples with higher contents of Ru (Mo/Ru of up to 1). Therefore, I applied an additional separation step to remove Ru from samples with detectable Ru contents. Based on the chemistry procedure presented by Burkhardt et al. (2011), Eichrom® TRU resin was used for removing Ru (Table 2.3). The resin was pre-cleaned in a Teflon container with MilliQ water repeatedly. Then one ml bed volume of resin is loaded into a standard BioRad Poly-Prep® column. The elution curves are given in Figure 2.2.

2.4 Mass spectrometry

All measurements in this study were performed with a Nu Plasma High Resolution Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS, Nu Instruments, Wrexham, UK) at the Department of Earth Sciences, University of Oxford. In this section I summarize some important background and protocols for Mo isotope measurements on this instrument.

2.4.1 Principles of MC-ICPMS

This section is some description of the principles of mass spectrometry (Becker, 2007; Herbert, 2003; Hoffmann, 2007), and parts of them are focus on analysing Mo isotopes.

2.4.1.1 Introduction system

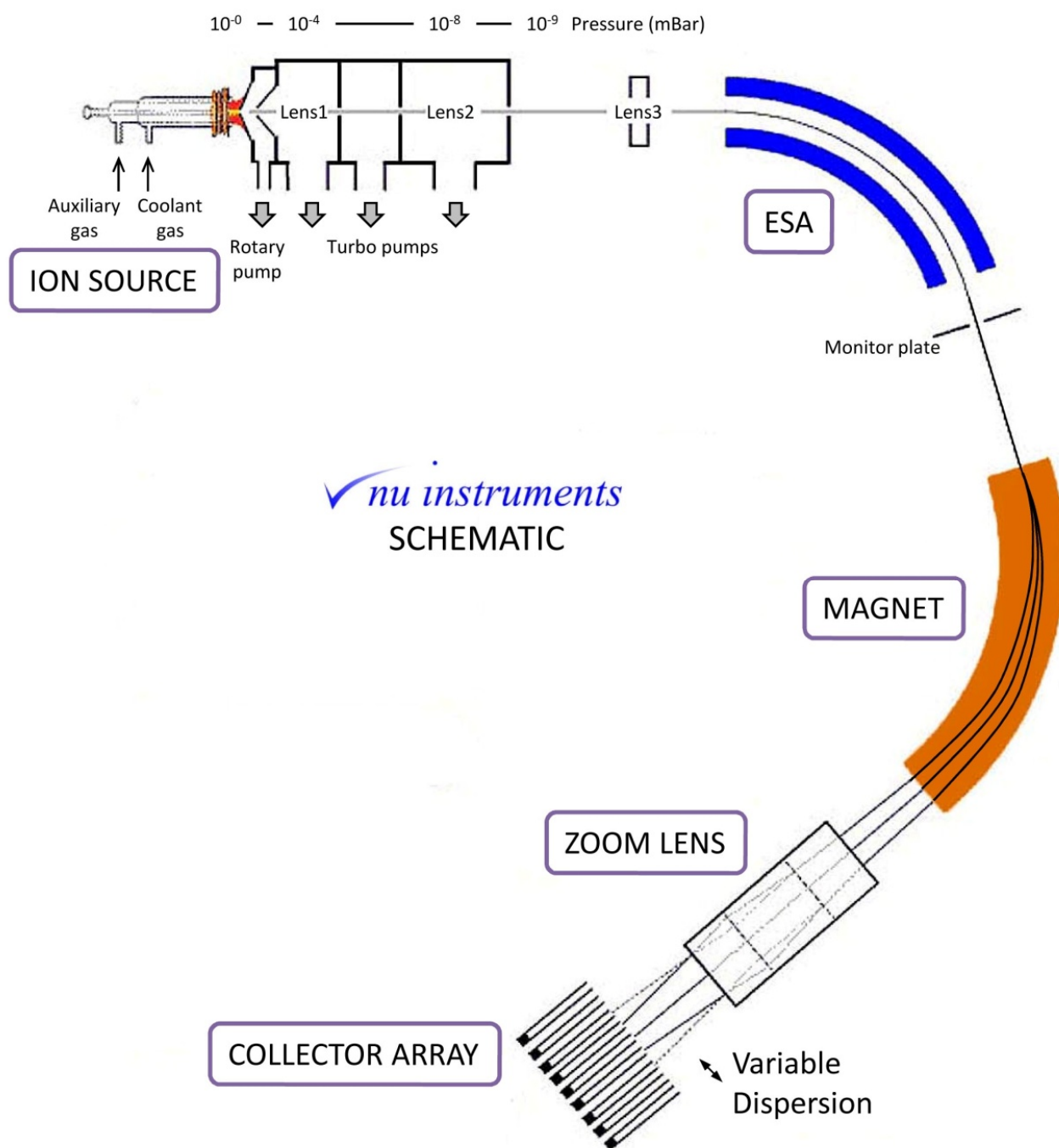


Figure 2.3 Schematic of the Nu Plasma MC-ICP-MS (Nu Instruments), after Becker (2007).

The MC-ICPMS measurements in this thesis were performed using two sample introduction systems. One of them is a “wet plasma,” where a liquid aerosol is

introduced into the plasma (ionization source). In detail, the sample solution is taken up by a concentric micro-flow PFA nebuliser, and the resulting aerosol is then sprayed into a cooled cyclonic spray chamber to remove larger droplets. Small aerosol particles will be transferred into the plasma for ionization, while the rest of the solution will condense and be drained out. In this study, standard and spike calibration measurements were performed using a wet plasma technique in order to produce a very stable signal without possible mass fractionation effects. However, because of the low sensitivity of this introduction method, it is not suitable for samples with low Mo content.

For our unknown sample measurements, a DSN-100 Desolvating Nebuliser System (Nu Instruments) is used for sample introduction. After the sample solution is taken up by a concentric micro-flow PFA nebuliser, the aerosol sprays into a heated Teflon spray chamber, where the sample solution is transferred into a heated Teflon membrane in order to dry the aerosol and extract the solvent. These heated droplets are reduced in size and then transferred into the ionization system by a flow of Ar gas. This “dry plasma” is more efficient and increases sensitivity. It also reduces the possible molecular interferences due to formation of oxides, hydrides, and nitrides from solvent molecules. However, the Desolvating Nebuliser System is thought to introduce greater and more variable fractionation, and may not be ideal for precise standard and spike calibration.

2.4.1.2 Ion source

The ion source for this mass spectrometer is an inductively coupled plasma. The argon (Ar) plasma is sustained in a “torch”, the end of which is placed in an electrical coil applying a radio frequency (RF) electromagnetic field. The torch is composed of three concentric quartz tubes. Argon gas flows through between the two outermost tubes at a flow rate of ~ 15 L/min (“coolant gas”, which is the main plasma supporting gas, figure 2.3) and also through the next inward layer at a flow rate of ~ 1 L/min (auxiliary gas, which keeps the position of the plasma within the torch, figure 2.3). The RF field changes at high frequency (27MHz) and is operated by the RF generator with a power of ~ 1300 W. In the beginning, an electric spark is used for introducing free electrons into the Ar flow, and these electrons are accelerated by the RF field and collide with Ar atoms. The collisions produce additional electrons causing a chain reaction that sustains the plasma where the release of electrons is balanced by the recombination of electrons with Ar^+ . The plasma will reach temperatures of $\sim 5,000$ - $10,000$ K eventually. Its high energy facilitates ionisation of most of the elements in the periodic table.

The sample aerosol is carried by the Ar gas stream from the introduction system into the injector, and then flows through the centre tube of the torch directly into the plasma. Samples are ionized at atmospheric pressure and high temperature. Therefore, they must be transferred via an interface into the high vacuum region of

the mass spectrometer. Two nickel cones (so called sampler and skimmer cone) with small holes are placed at the end of the plasma flame. The chamber between the cones has an initial vacuum of 10^0 mbar, and the remaining particles that are not cations are removed here. The pressure behind the skimmer cone will be pumped down to 10^{-4} mbar, and the mass analyser will finally be around 10^{-9} mbar. Cations are accelerated through the system by decreasing the potential starting at the plasma interface. The initial accelerating potential provided by the cones is 6 kV. The ion beam is focused by sets of lenses. Before this aligned ion beam enters the mass-analyser, around 99% of the material will have been lost. Most of this is thought to occur at the interface between sample and skimmer cones.

2.4.1.3 Mass analyser

When ions reach the mass analyser, they will be separated according to their mass-to-charge ratio (m/z). The Nu Plasma-HR is a double-focussing instrument employing an electromagnet and an electro-static analyser (ESA). The principle is when moving ions travel through a constant magnetic field, they will be deflected. The magnitude of the deflection relies on their mass to charge ratios (m/z) and their kinetic energy. If the kinetic energy of these ions experiencing the magnet field is the same, the lighter ions will be deflected more than the heavier ones because they have less momentum.

However, the plasma source produces ionised particles with a wide spread of energies, and this makes a momentum analyser not equal to a mass analyser. Therefore, the ESA is employed to account for the energy spread of the ion beam inherited from the plasma source. The electro-static analyser works as two curved electrically charged plates in the inner and outer side of the flying tube. When they are charged negatively and positively at each side respectively, it will become a radial electrostatic field. Given an intensity of the electrical field (E), radius of flight tube (r), and the number of charges on the ion (z), the electrostatic force in a radial electrostatic field should be equal to centrifugal force,

$$zE = \frac{mv^2}{r} \quad (2.1)$$

and the kinetic energy (E_{kin}) of the ion is related to its mass(m) and velocity(v),

$$E_{kin} = \frac{1}{2}mv^2 \quad (2.2)$$

thus the ESA is focusing ions with their kinetic energies:

$$r = \frac{mv^2}{zE} = \frac{2E_{kin}}{zE} \quad (2.3)$$

In Nu plasma HR, the ions will enter the ESA and be focused according to their kinetic energy before arriving at the electromagnet (figure 2.3), where they are going to be separated due to their mass-to-charge ratio.

2.4.1.4 Detectors

The Nu Plasma is equipped with 12 fixed Faraday cups and 3 secondary electron multipliers with ion counters (IC). Although Faraday cups have intrinsic background

noise and are not ideal for the detection of very small ion beams, they are very stable and precise for higher signals. A Nu Plasma Faraday detector normally has a $10^{11}\Omega$ resistor. Therefore, a 10^{-11}A electrical current will produce a 1V signal measured by a digital voltmeter. The maximum measurable current for a standard Nu Plasma Faraday cup is 10^{-10}A . These 12 Faraday cups are arranged as a fixed detector array.

For Mo isotope measurements, we measure all Mo isotopes and monitor one Ru isotope (^{99}Ru , for interference control) simultaneously in static collection mode as shown in Table 2.4. Zirconium isotopes were not monitored simultaneously because ^{92}Mo , ^{94}Mo , and ^{96}Mo have been avoided using in the calculation due to possible Zr isobaric interferences (see below section 2.5).

Table 2.4 Configuration of the Faraday collectors for the Mo data acquisition.

Element	collectors											
	L5	L4	L3	L2	L1	AX	H1	H2	H3	H4	H5	H6
Mo isotope	92		94	95		96		97		98		100
Ru isotope											99	

2.4.2 Instrument resolution

The plasma ion source has a high ionisation potential, but in turn more polyatomic interferences might also be produced. In order to resolve analyte and polyatomic interference beams, increased resolution of mass spectrometry is an useful solution. The Nu plasma is equipped with a source slit with adjustable aperture, which allows the instrument to be operated at three different resolution modes. When the slit is

fully open, which is in the lowest resolution, the instrument will have a resolving power ($m/\Delta m$, where Δm is between 5% and 95% of the peak height and m is the mean of the two masses) of ~ 400 . In medium and high mass resolution it can achieve a resolving power of up to $\sim 3,500$ and $\sim 8,000$ respectively. However, in order to reach better resolution, the aperture width on the source slit needs to be reduced and an intermediate value for the alpha slit should be chosen. The sides of the ion beam will be cut simultaneously. In the case of in high resolution mode, transmission can be reduced to 5%.

For Mo isotopic measurement, the most critical isobaric interference comes from Zr and Ru. However, isobaric interferences in Mo isotopic measurement cannot be resolved instrumentally while fully resolving ^{96}Ru from ^{96}Mo needs a resolving power of > 32000 . Other molecular interferences, such as $^{56}\text{Fe}^{40}\text{Ar}$, need a resolving power of > 13000 to totally resolve $^{56}\text{Fe}^{40}\text{Ar}$ from ^{96}Mo . Due to these limits of the instrument technique, it is necessary to remove interferences by purifying Mo in the sample with ion exchange chromatography. Thus samples can be analysed in low resolution mode with better transmission.

2.5 Isotopic double spike

In order to determine the natural isotope fractionation of an element precisely, it is necessary to identify the degree of analytical mass fractionation and then correct it

properly. These analytical mass fractionations might appear during chemical procedures and/or isotopic measurement with the instrument. The fractionation during chemical processing most likely happens in the step of chemical separation. While chemical fractionation is most often prevented by a full recovery of the element of interest, instrumental fractionation is not preventable. Instrumental fractionation factor (f) is commonly used for correcting instrumental mass bias, and it is usually calculated using an exponential law,

$$\frac{R_{real}}{R_{measure}} = \left(\frac{m_i}{m_j}\right)^f \quad (2.4)$$

or power law,

$$\frac{R_{real}}{R_{measure}} = (1 + f)^{\Delta m} \quad (2.5)$$

where m_i and m_j are the mass of two isotopes i and j respectively, R_{real} is the real ratio while $R_{measure}$ is the measured ratio of two isotopes, and Δm is their mass difference. Generally, the exponential fractionation law is thought to be more realistic at high resolution (Russell et al., 1978), so it is used for the calculation in Mo double spike technique.

Molybdenum isotope measurements in this study were corrected using the double spike technique. As mentioned earlier, it also allows us to correct for both the chemical and instrumental fractionation simultaneously as we dope our sample with spike right after sample digestion. Fractionation during separation chemistry is dependent on the yield achieved. The double spike technique is a particular

advantage with samples with varying matrices because the difficulty of adjusting the chemistry for these matrices, often results in lower yields.

Molybdenum isotopes ^{97}Mo and ^{100}Mo were chosen as spike isotopes because they allow for a precise correction of instrumental mass bias, and they are relative low in abundance and free from isobaric interferences (Rudge et al., 2009; Siebert et al., 2001). Although ^{100}Ru is a potential interference for ^{100}Mo , ruthenium is rare in most of the terrestrial samples and will be monitored during Mo measurements.

For spike calibration, small aliquots of pure spike and pure standard solution were doped with a pure Pd standard solution for correction of instrumental mass bias during spike calibration. The $^{104}\text{Pd}/^{102}\text{Pd}$ ratio of 10.922 was used (Parrington, 1996). In order to use the spike for high precision measurements, ratios of all isotopes in the spike and reference standard (Alfa Aesar Mo plasma standard solution, Specpure® #38791, lot no. 011895D) must be calibrated. Due to the fixed collector array of the Nu Plasma instrument, masses from 96 to 104 were measured and the $^{100}\text{Mo}/^{97}\text{Mo}$ ratios for both solutions were precisely defined. In a second calibration step, this ratio was used to correct for mass bias during measurements of masses 100 to 92 internally. Then a number of pure spike / standard solution with varying spike / standard ratios were analysed to test the reliability of the calibration. The measurement results of Alfa Aesar standard with different spike / sample ratios (expressed by $^{97}\text{Mo}/^{98}\text{Mo}$ ratio) are demonstrated in Figure 2.4. All these

measurements are perfectly aligned, which indicate within this range ($^{97}\text{Mo}/^{98}\text{Mo}$ ratio between 1.4 and 5.4), the spike / samples ratio is insignificant for the accuracy of measurements. But no larger range has been tested. In this research, I always attempt keeping spike / samples mixture having $^{97}\text{Mo}/^{98}\text{Mo}$ ratio around 3. If the results show spike / samples mixture having $^{97}\text{Mo}/^{98}\text{Mo}$ ratio smaller than 1.4 or larger than 5.4, these data will be excluded. In this case, a new aliquot of the same sample will be taken and processed through the entire chemistry procedure before re-analyzed.

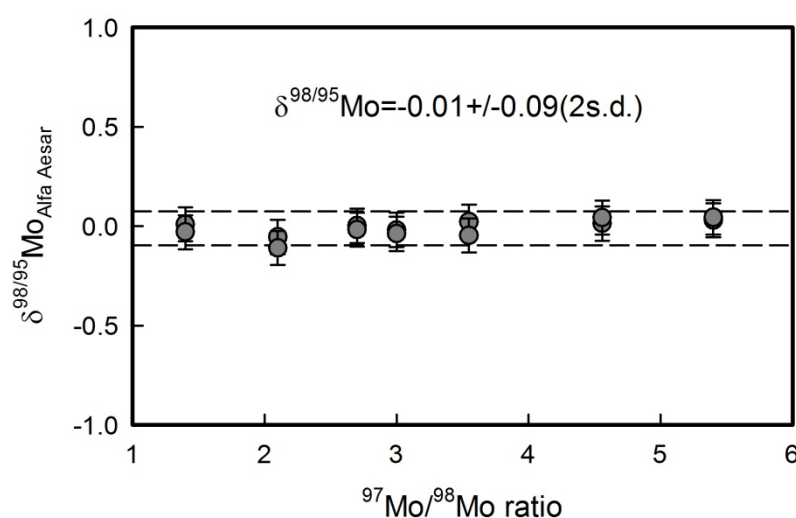


Figure 2.4 Plot of $\delta^{98/95}\text{Mo}$ value of Alfa Aesar standard versus spike / sample ratio (expressed by the $^{97}\text{Mo}/^{98}\text{Mo}$ ratio).

While molybdenum has 7 isotopes, we have many choices of how to present its mass dependent fractionation. However, as the double spike calculation need 4 precisely measured isotopes at least, ^{92}Mo , ^{94}Mo , and ^{96}Mo are usually not preferable due to possible Zr isobaric interferences. While ^{97}Mo and ^{100}Mo were chosen as spike isotopes, ^{95}Mo , and ^{98}Mo are used to represent non-spike isotopes.

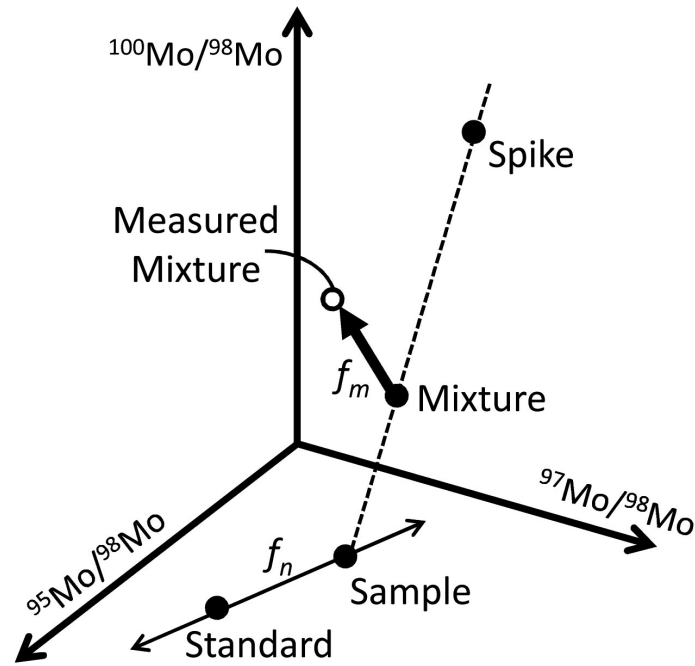


Figure 2.5 Geometrical sketch representation for demonstrating the relationships between spike, sample, sample-spike mixture, and standard isotopic compositions (after Siebert et al. (2001)). The thin double headed arrow and thick arrow illustrate the nature and instrumental fractionation directions respectively. Open circle represents the measured isotopic composition of mixture affected by instrumental mass fractionation.

A geometrical sketch illustrating the principal of double spiking is shown in Figure 2.5.

More details are presented in Galer (1999), Siebert et al. (2001), and Rudge et al.

(2009), and I simply describe how it works mathematically. For solving the double

spike equation geometrically, we have true values of three points (spike, standard,

and measured mixture), and we need to assume the initial values of f_n and f_m (figure

2.5). Using the equations described in Siebert et al. (2001), this assumed f_n and f_m are

used to calculate a “first” presumed value of the unfractionated spike sample

mixture, and therefore a “first” sample value. The interception of the line between

“Measured Mixture,” “Mixture,” (figure 2.5) and the plane defined by standard, spike,

and first presumed sample value will give us the “second” mixture value and the “second” f_m . The next step then uses the line through standard and the first presumed sample value, and the plane newly defined by spike, measured mixture, and “second” mixture values to calculate the interception to define the “second” sample value and therefore the “second” f_n . These steps are iterated until the values for f_n and f_m converge, i.e. do not change any more. Using the fractionation factor for 98/95ratio, the other Mo isotope ratios would be corrected for mass bias.

In this study, the Mo isotope composition is presented using $\delta^{98/95}\text{Mo}$, which is defined as,

$$\delta^{98/95}\text{Mo} = \left(\frac{(^{98}\text{Mo}/^{95}\text{Mo})_{\text{sample}}}{(^{98}\text{Mo}/^{95}\text{Mo})_{\text{standard}}} - 1 \right) \times 1000 \quad (2.6)$$

2.6 Analytical protocol

Except spike and reference standard calibration, generally all of the measurements applied the same analytical protocol as in the following description. After the chemical purification, samples were evaporated and re-dissolved in 0.1M HNO_3 . Normally sample solutions were diluted to concentrations of 30-50 ppb before analysis. Samples with low Mo contents were run at a minimum concentration of 15ppb to avoid blank issues. Each molybdenum isotopic measurement consists of a sequence of 40 cycles with an integration time of 10s, and the background noise is measured for 20s before each sequence. Total procedure blanks for the technique

described in this chapter were below 3ng Mo, and the operating setting and condition of Nu Plasma-HR for Mo isotopic analysis are given in table 2.5.

Table 2.5 *Instrument operating setting and condition*

<i>Parameter</i>	
RF power	1300 W
Initial accelerator potential	6 kV
Sampler cone	Nickel, Type B
Skimmer cone	Nickel, Type B
Coolant gas flow rate	13 L/min
Auxiliary gas flow rate	1 L/min
Nebuliser gas pressure (DSN)	20-30 psi
Hot gas pressure (DSN)	0.1-0.2 psi
Membrane gas pressure (DSN)	2.5-3.2 psi
Sample uptake rate	50-75 μ l/min
Resolving power	~400
Mo sample running concentration	15-50 ppb
Sensitivity on Mo	80-130 V/ppm

Although I used an Alfa Aesar Mo plasma standard solution (Specpure® #38791, lot 011895D) as laboratory and measurement standard in this research, for interlaboratory comparison all data reported in this thesis have been normalized to the NIST SRM3134 value (Greber et al., 2012). The offset of the Mo isotope value between the Alfa Aesar standard solution used in this study and NIST 3134 was determined by analyzing both standard materials on the Oxford Nu Plasma instrument (Greber et al., 2012). Our Alfa Aesar standard solution has a $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ value of $-0.12 \pm 0.06\text{‰}$ (Greber et al., 2012), and the $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ values of different Mo reference materials are listed in table 2.6.

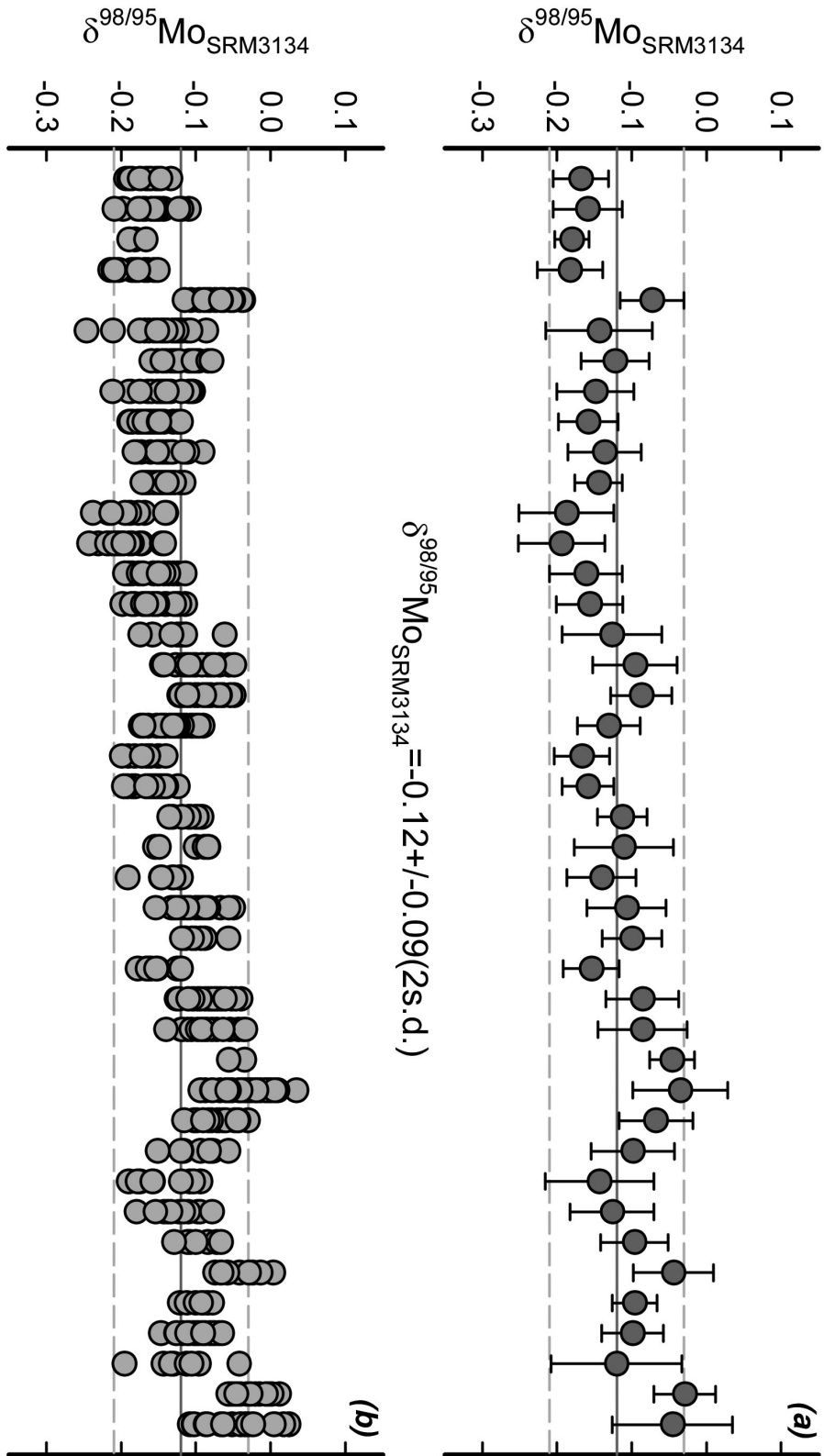
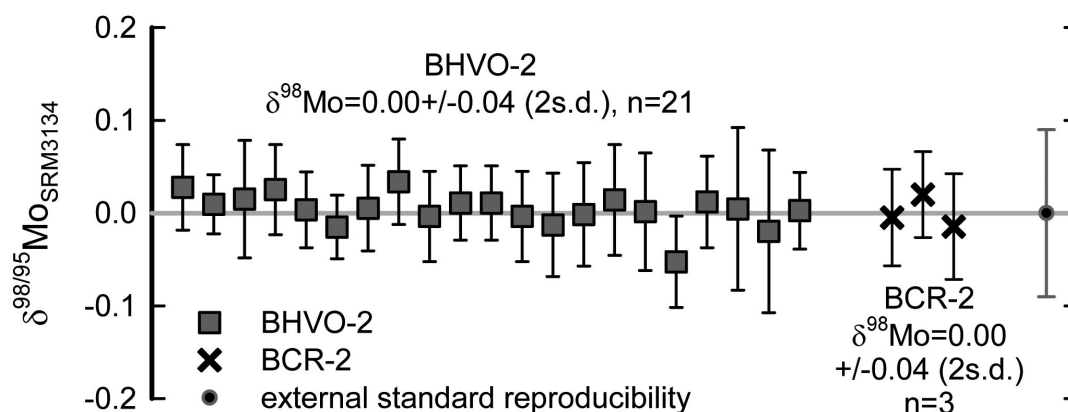


Figure 2.6 Long term reproducibility of Mo isotopic measurement on Nu plasma HR MC-ICPMS over the time period of sample analysis (August 2011–November 2012), tested with Alfa Aesar Mo plasma standard solution. (a) Plot of the average compositions for Alfa Aesar standard solution per analytic session, and **errors given are 2 s.d. of each session (2–4 days)** (b) Plot of every individual $\delta^{98/95}\text{Mo}$ measurement of Alfa Aesar standard solution corresponding to each analytic session.

Table 2.6 $\delta^{98/95}\text{Mo}$ for reference materials (all relative to NIST SRM 3134) (Greber *et al.*, 2012).

Reference materials	N	$\delta^{98/95}\text{Mo}$ (‰)	2 s. d.
Alfa Aesar Oxford	15	-0.12	0.06
NIST SRM 610	12	0.06	0.09
NIST SRM 612	12	0.04	0.10
JMC Bern ^a	28	-0.25	0.08
MOMo ^b	5	2.09	0.07

^a Johnson Matthey ICP standard solution, lot 602332B^b mean open ocean water Mo**Figure 2.7** Long term reproducibility and mean $\delta^{98/95}\text{Mo}$ values of USGS rock standards, BHVO-2 and BCR-2. The time period of sample analysis is from August 2011 to November 2012. Errors given individually are 2 s.d. of standard measurements in each measuring session.

The long-term external instrument reproducibility of our Alfa Aesar standard solution over the time period of sample analysis (16 months) on the $^{98}\text{Mo}/^{95}\text{Mo}$ ratio was $\pm 0.09\text{‰}$ (2s.d. Figure 2.6). In addition, at least one USGS rock standard was processed through the entire chemistry procedure and analyzed with each batch of samples. Due to mainly mafic or ultramafic nature of our sample material, BHVO-2 was analyzed with each measurement session and occasionally BCR-2. The long term rock standard reproducibility on $^{98}\text{Mo}/^{95}\text{Mo}$ for both BCR-2 and BHVO-2 are $\pm 0.04\text{‰}$, and their average $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ values are both around 0 (Figure 2.7). The

reason that the long term rock standard reproducibility ($\pm 0.04\%$) seems better than external instrument reproducibility of standard solution ($\pm 0.09\%$) is the rock standard results have been normalized to standard solution, which would also calibrate the data from instrument insatiability.

CHAPTER THREE



Molybdenum isotope fractionation in ocean island basalts

3.1 Introduction

Molybdenum has been widely discussed because it is an essential trace metal in many biological and geochemical processes. Biochemically, molybdenum-containing enzymes are essential catalysts for life in nearly all organisms resulting from its consequence to nitrogen fixation, nitrate reduction and sulphite oxidation. Geochemically, molybdenum has become a proxy for redox-related processes due to its highly redox-sensitive behavior. Molybdenum speciation in natural waters under oxic conditions is believed to be dominated by the chemically inert molybdate ion MoO_4^{2-} . In the ocean, its concentration is about 10.3 $\mu\text{g/l}$ (Collier, 1985) with a residence time of ~800ka (e.g. Morford and Emerson, 1999).

The molybdenum ocean budget is thought to be strongly depending on the input of Mo from continental weathering processes and subsequent river transport (McManus et al., 2002; Morford and Emerson, 1999). Molybdenum is removed from the ocean by scavenging in anoxic sediments and adsorption to Mn-oxides (Barling and Anbar, 2004; Morford and Emerson, 1999). The first natural Mo isotope variations were reported by Barling et al. (2001). Subsequent studies concentrated on reservoirs, and the sinks and sources of the oceanic Mo cycle, including igneous rocks, ferromanganese oxides, sediments, and seawater (Arnold et al., 2004; Goldberg et al., 2012; McManus et al., 2002; Neubert et al., 2011; Siebert et al., 2003; Voegelin et al., 2012).

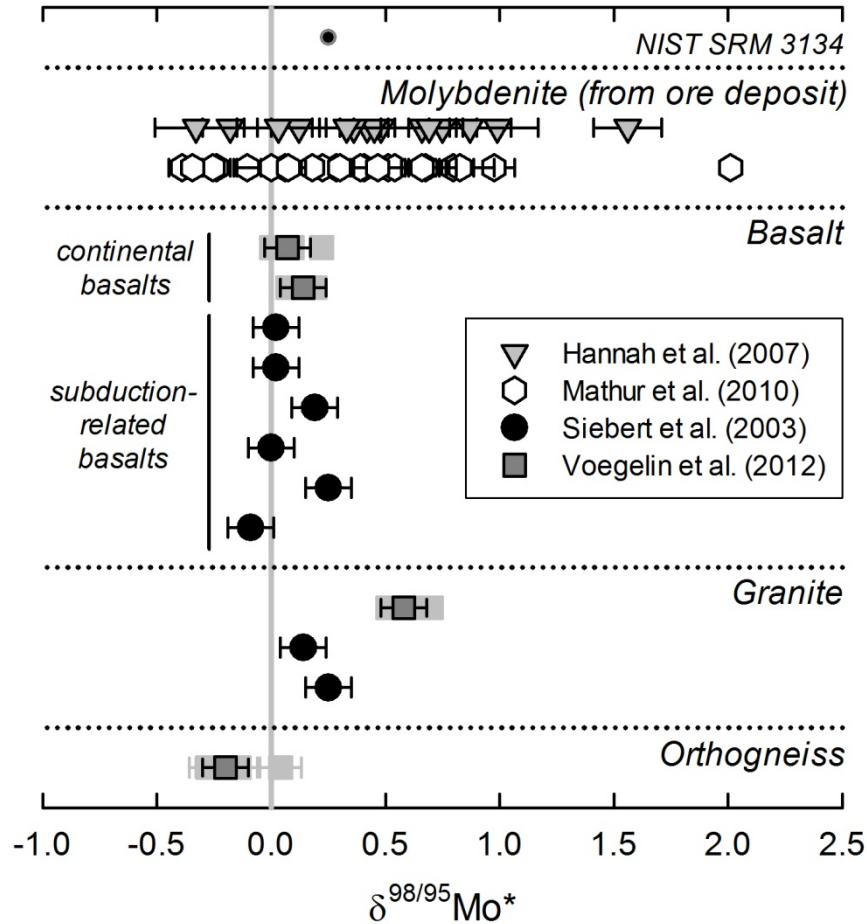


Figure 3.1 Summary of Mo isotope fractionation data for high temperature processes from published studies. Duplicates of same samples are shown as grey squares in background. * $\delta^{98/95}\text{Mo}$ value presented here are relative to their Johnson Matthey ICP standard.

According to published data, the Mo isotope variation between igneous rocks seems smaller than in other reservoirs. Siebert et al. (2003) firstly presented Mo isotope data for subduction volcanics and granites, and their $\delta^{98/95}\text{Mo}$ values range between -0.09 and 0.25‰ (relative to their Johnson Matthey ICP standard, while $\delta^{98/95}\text{Mo}$ values of NIST SRM3134 relative to Johnson Matthey ICP standard is 0.25‰ (Greber et al. 2012)). Voegelin et al. (2012) recently report data for orthogneiss, granite, and basalts, and reveal slightly more variation (figure 3.1). However, research on Mo

isotopic fractionation in igneous rocks is still very limited, and only few high temperature data have been published. McManus et al. (2002) analyzed warm hydrothermal samples from submarine hydrothermal springs, and these springs have higher Mo concentrations, and are isotopically lighter than seawater. Molybdenum isotope fractionation in molybdenites from high-temperature geologic environments (ore deposits) is reported by Hannah et al. (2007) and Mathur et al. (2010), and these variations might be related to the fractionation in different mineral phases during the ore-forming processes (Mathur et al., 2010).

Ocean island basalts are widespread in oceanic and continental settings and represents parts of intraplate magmatism. Ocean island basalt and mid ocean ridge basalt are frequently cited as two basalt types originate in different parts of the mantle, while OIBs were thought to be the products of convective plumes originating in the lower mantle. In contrast to MORBs, OIBs are less depleted in incompatible elements, and the source of OIBs is generally thought to have been melted to a smaller degree than the mantle under MORBs. The formation of OIBs is believed to be related to mantle plumes, and the long-term cycling of mantle material (Galer and O'Nions, 1986). Additionally, subducted oceanic crust (Hofmann and White, 1982) can be added to the magma source. Radiogenic Sr, Nd and Pb isotope ratios are commonly used to identify different extreme types of OIBs, e.g. HIMU, EM1 and EM2, which are thought to represent different source reservoirs (Hofmann, 2007). Most of

the oceanic basalts can be explained by mixing between these end members and the depleted mantle. Therefore, studying the Mo isotope fractionation in OIBs will allow us to discover the Mo isotope behavior in a relatively smaller degree of mantle partial melting. Based on the results, we could even have further discussion about Mo isotope fractionation under the effect of degree of partial melting, different source reservoirs, fractional crystallization, etc. during mantle melting.

Using the double spike technique and MC-ICPMS, I attempted to measure small Mo variations in high-T processes with high precision. In this chapter data are reported for OIBs and continental intraplate basalts from various localities to determine the association between Mo isotopic fractionation and partial melting.

3.2 Geological background and samples

Thirty-two well characterized mafic samples were selected from a variety of localities including 2 USGS standards, BCR-2 and BHVO-2. Most of the samples are ocean island basalts (OIB). Samples from the Atlantic Ocean include the Azores, the Cameroon Line, Madeira, and Trinidad, which have been studied for their major, trace element and radiogenic isotopic compositions (Halliday et al., 1990; Halliday et al., 1992; Halliday et al., 1995; Yi et al., 1995). Four samples from the Pacific Ocean are from Galapagos and Loihi seamount. These samples are submarine lavas and also characterized for major and trace elements (Yi et al., 2000).

The Azores archipelago are located in the region of the triple junction of the African, Eurasian, and North American plates, which is between the latitudes 37°N and 40°N and the longitudes 25°W and 31°W. The archipelago is composed dominantly of alkali basalt and its differentiation products, and its trace element and radiogenic isotopic compositions have been well discussed by many previous studies (Beier et al., 2007; Elliott et al., 2007; Halliday et al., 1990; Halliday et al., 1992). Large trace element and radiogenic isotopic variability has been found in Azores archipelago, and its enrich component has been suggested originating from ancient recycled oceanic crust (Beier et al., 2007) or under-plated basalt which intruded into oceanic mantle lithosphere (Elliott et al., 2007).

Among OIBs, the Cameroon line is thought to provide a link between ocean-island and continental intraplate alkaline magmatism. The Cameroon line is a 1600 km long chain that is well known as a Y-shaped intra-plate alkaline volcanic province, extending from the Atlantic island of Pagalu to the interior of the African continent. This chain comprises both oceanic and continental volcanoes with given ages ranging from Tertiary to recent, which means it has been active for at least 65 Myr (Fitton and Dunlop, 1985). Some small intrusive plutonic complexes in the continental sector express the earlier igneous activity on the Cameroon line between 65 and 30 Myr. The younger volcanic activities are represented by 12 main extrusive centres with the oldest dated oceanic rocks (Principe) at 31 Ma (Fitton and Dunlop, 1985), and one of

them, Mount Cameroon, is even still active recently. Based on isotope dating results, it seems there has been no systematic change in the focus of magmatism within the entire igneous activity period. This indicates that the Cameroon line volcanic chain cannot be simply explained by a traditional plume model as for the Hawaiian hotspot trail.

It has been shown that the young basalts from both continental and oceanic sectors in the Cameroon line are compositionally identical, which might mean the lavas were derived from sublithospheric depths (Fitton and Dunlop, 1985). However, this has been revised by isotope studies. Halliday et al. (1988) reported the lavas from continent/ocean boundary (c.o.b.) region have relatively radiogenic Pb. A systematic decrease was found in $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ from the continent/ocean boundary to both ends of the volcanic chain (Halliday et al., 1990). This high $^{206}\text{Pb}/^{204}\text{Pb}$ value, which is a characteristic of a “HIMU” mantle endmember, has been explained as remelting of an enriched fossil plume head underneath the site of south Atlantic opening in the present Gulf of Guinea (Halliday et al., 1990). Thirteen samples from the continent/ocean boundary region of the Cameroon line have been analyzed in this study to investigate the Mo isotopic fractionation under relatively small degrees of partial melting of the mantle and the possible associated source effects.

The Galapagos Islands are located in the Central East Pacific Ocean. To the north of

the archipelago is an active mid-oceanic ridge, the Galapagos Spreading Center (GSC), which separates the Cocos plate from the Nazca plate. The Galapagos Islands are believed being formed through the interaction of hotspot with ridge, therefore, the trace element and isotopic compositions show anomalous features (Fitton, 2007). The geochemical studies on the basalt from the Galapagos Islands indicate there is an involvement of depleted upper mantle in the formation (Geist et al., 1988; White et al., 1993). The wide scatter extending variations in radiogenic Sr-Nd-Pb isotopic composition could be explained by mixing between two end-member components, which are the Galapagos plume and ambient upper mantle (N-MORB) represented by the East Pacific Rise data (Fitton, 2007; Geist et al., 1988; White et al., 1993).

Iceland is thought to represent the surface expression of a mantle plume intersecting a mid-ocean ridge and offers an unusual opportunity to investigate large-degree partial melting (Schilling et al., 1982). The Mid-Atlantic Ridge on Iceland is represented by a southwest to north striking zone of late Quaternary volcanism (less than 0.7 Ma). These neovolcanic zones are enclosed by Pliocene–Pleistocene formations to the east and Tertiary lava piles to the west (Hardarson and Fitton, 1997). In order to compare volcanic rocks of different ages, we chose two Quaternary samples from Snaefellsnes, which is an area related to isolated off-axis volcanism, and also analyzed three Tertiary basalts (between 12.4 to 5.3Ma) sampled from eastern and northern Iceland (Hardarson and Fitton, 1997). While Tertiary and

Pliocene–Pleistocene basalt lavas are remarkably uniform in chemical and isotopic composition (Schilling et al., 1982), Hardarson and Fitton (1997) have shown that large flows that originated within the axial zone and spread far enough to become preserved in the accessible part of the future offaxis lava pile are very homogeneous in composition and comparable to those forming the Tertiary lava successions.

Loihi Seamount is the southernmost and the most recent active volcano in the Hawaiian-Emperor volcanic chain. This submarine Hawaiian shield volcano has a cratered summit at approximately 1000 m below sea level, and it is situated on the southern flank of Mauna Loa volcano on the island of Hawaii. Loihi glasses have been well studied for major elements (Moore et al., 1982), trace elements (Kent et al., 1999; Yi et al., 2000), radiogenic isotopes (Lanphere, 1983; Staudigel et al., 1984), and volatiles (Moore et al., 1982; Kent et al., 1999). Based on the previous studies of its alkali basaltic lavas, Loihi seamount is considered representative of the early phase of Hawaiian volcanism (Moore et al., 1982).

The Madeira archipelago is an about 700 km long by approximately 200 km wide chain of volcanoes situated in the Atlantic ocean close to the NW corner of Africa. It has been proposed that this belt of volcanoes could represent a hotspot track located on a 140 Ma old oceanic crust (Morgan, 1981). With a progression of increasing ages (1-70Ma, White, 2010) from southwest to northeast, this archipelago represents the present location of a >70 Ma old hotspot. Madeira is the major island

of this archipelago, and it is dominated by alkaline olivine basalts and their differentiates which have been dated between 0 and 5Ma (Geldmacher et al., 2000). However, due to the Madeira volcanic rocks show the MORB-like Sr- and Nd-radiogenic isotopic compositions but low $^{207}\text{Pb}/^{204}\text{Pb}$ ratios, Halliday et al. (1992) and Halliday et al. (1995) proposed a “near-surface fractionation” metasomatism of the oceanic lithosphere here shortly after its formation, which results high U/Pb ratios and low $^{207}\text{Pb}/^{204}\text{Pb}$ ratios over the life span of the lithosphere.

The Trindade Island is located in the southern Atlantic Ocean and lies 1140 km east of the Brazilian coast at approximately 20°30'S, 29°20'W. This island rises about 5000 m above the ocean floor and lies on a continuation of Vitória–Trindade Ridge that extends from the Brazilian mainland. The W–E trend of this ridge is believed to represent the volcanic track left by the Trindade mantle plume on the overriding South American Plate (O'Connor and Duncan, 1990). There are five periods of volcanic activities have been recognized on Trindade Island, which are mostly dominated by rocks undersaturated in silica and are all dated at < 4Ma (Mitchell-Thomé, 1970). They are basically in the form of pyroclastics deposits intruded by compositionally diverse dykes and domes, together with some lava flows which include nephelinite, phonolite, and ankaratrite (Weaver, 1990). Some previous studies of Trindade volcanics are focus on trace elements and radiogenic isotopes and provide hypotheses concerning the origin of these magmatic rocks (Halliday et al., 1992;

Halliday et al., 1995; Yi et al., 1995), which might have resided in the upper mantle since the oceanic lithosphere was formed.

3.3 Analytical methods

The analytical methods in this study principally follow the techniques described in Siebert et al. (2001) and chapter 2. In order to correct the chemical and instrumental mass fractionation, all samples were spiked with a double isotope tracer (^{100}Mo , ^{97}Mo) before digestion. All samples were crushed with a jaw-crusher and a tungsten carbide ball mill, and then dissolved with a mixture of HF and HNO_3 in sealed Teflon vials on a hotplate at 140°C for at least 3 days. For Mo purification, techniques presented by Siebert et al. (2001) were used along with the modification applied in Siebert et al. (2006) (details are described in chapter 2).

Trace element concentrations were measured on Thermo Scientific® ELEMENT® ICP-MS, and Mo isotopic composition measurements were made on a Nu instruments® MC-ICPMS at the Department of Earth Sciences, University of Oxford. An Alfa Aesar Mo plasma standard solution, Specpure® #38791 (lot no. 011895D) was used as laboratory and measurement standard. All Mo isotopic variations are represented by the delta notation as the deviation in per mil (‰):

$$\delta^{98/95}\text{Mo} = \left(\frac{(^{98}\text{Mo}/^{95}\text{Mo})_{\text{sample}}}{(^{98}\text{Mo}/^{95}\text{Mo})_{\text{standard}}} - 1 \right) \times 1000 \quad (3.1)$$

The external standard reproducibility of $^{98}\text{Mo}/^{95}\text{Mo}$ ratio in the Alfa Aesar Mo plasma

standard solution over the time period of sample analysis is $\pm 0.09\text{‰}$ (2s.d.).

Recently, Greber et al. (2012) published $\delta^{98/95}\text{Mo}$ values for several NIST reference materials and suggest SRM 3134 as an international reference standard for δMo . The Mo isotope value of the Alfa Aesar standard solution used in this study is offset from NIST 3134 by a $\delta^{98/95}\text{Mo}_{\text{SRM 3134}}$ value of $-0.12 \pm 0.06\text{‰}$ (Greber et al., 2012). Therefore, all data reported here have been re-normalized to the NIST SRM3134 value to make interlaboratory comparisons possible.

3.4 Results

The Mo mass dependent fractionation for all samples is shown in Table 3.1 with 2 standard deviations of all replicates of each sample, and each duplicate analysis always consisted of a repeat of the entire procedure in a different day from the same crushed rock sample. Figure 3.2 shows the degree of replication achieved for each sample. One or two aliquots of basaltic USGS standard BHVO-2 and BCR-2 were processed with each batch of samples. The reproducibility on $^{98}\text{Mo}/^{95}\text{Mo}$ for BCR-2 and BHVO-2 are ± 0.04 and $\pm 0.03\text{‰}$ (2s.d.) respectively during the time period of measurement with an average $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ value of 0.00‰ (Table 3.1, Figure 3.2). The results of trace element contents are listed in Table 3.2, and the accuracy of all the ICP-MS concentration measurements are better than $\pm 10\%$.

Table 3.1. Molybdenum concentration and isotope compositions of ocean island basalts (OIB) and continental intraplate basalts.

Sample	n ^a	Mo (ppm)	$\delta^{98/95}\text{Mo}_{\text{SRM3134}}$		
			replicates	average	2 s. d. ^b
USGS standards					
Columbia River, Oregon					
BCR-2	3	236	0.00, 0.02, -0.01	0.00	0.04
Halemaumau, Hawaii					
BHVO-2	12	3.48	0.03, 0.03, 0.00, -0.01, 0.01, 0.03 0.00, 0.01, 0.01, 0.00, -0.01, 0.00	0.01	0.03
Azores					
AZF1	3	2.76	-0.16, -0.16, -0.17	-0.16	0.01
AZFY3	1	2.18	-0.02	-0.02	0.04 *
AZP5	3	1.14	0.04, 0.08, -0.01	0.04	0.09
AZP6	3	3.10	0.08, 0.09, 0.08	0.08	0.01
Cameroon Line					
Bioko					
FP23	3	1.81	-0.08, -0.04, -0.14	-0.09	0.10
Etinde					
C20	3	1.65	-0.57, -0.56, -0.56	-0.56	0.01
C22	3	4.12	-0.16, -0.10, -0.10	-0.12	0.07
C128	3	4.17	-0.13, -0.19, -0.20	-0.18	0.08
C150	3	2.57	-0.39, -0.37, -0.45	-0.40	0.08
C152	3	16.1	-0.10, -0.09, -0.08	-0.09	0.02
C154	3	3.91	-0.03, -0.06, -0.03	-0.04	0.04
Manengouba					
C51	3	2.10	-0.17, -0.15, -0.19	-0.17	0.04
C72	3	2.03	-0.10, -0.09, -0.10	-0.09	0.01
Mt Cameroon					
C1	3	3.52	-0.16, -0.16, -0.12	-0.14	0.05
C25	3	3.39	-0.09, -0.12, -0.11	-0.11	0.02
C30	3	2.07	-0.13, -0.11, -0.08	-0.11	0.05

Table 3.1. (continued)

Sample	n ^a	Mo (ppm)	$\delta_{98/95} \text{Mo}_{\text{SRM3134}}$		
			replicates	average	2 s. d. ^b
C192	3	2.86	-0.03, -0.05, -0.04	-0.04	0.02
Galapagos					
PL02 25-1	3	1.28	-0.05, -0.05, -0.06	-0.06	0.01
PL02 30-1	3	0.69	0.05, 0.06, 0.02	0.04	0.04
Iceland					
CX19	2	0.56	-0.10, -0.11	-0.11	0.02
GS18	3	0.25	-0.31, -0.30, -0.33	-0.31	0.03
SNB19	2	1.19	-0.15, -0.15	-0.15	0.01
SNB40	2	1.09	-0.22, -0.15	-0.19	0.09
ST38	3	0.48	-0.34, -0.42, -0.40	-0.38	0.09
Loihi					
D4-6	2	0.83	0.00, -0.08	-0.04	0.12
D5-1	2	0.91	0.03, -0.03	0.00	0.09
Madeira					
M40	2	1.27	-0.18, -0.09	-0.14	0.12
Trinidad					
TD2	2	0.91	0.12, 0.13	0.13	0.01
TD4	2	3.82	-0.24, -0.16	-0.20	0.11
TD5	2	3.19	-0.34, -0.32	-0.33	0.03

^a Number of duplicates for the same sample.

^b The errors are 2 standard deviations of all duplicates of each sample.

* Only one aliquot successfully analysed for these samples, so the errors are given as 2 standard deviation of standard measurements in each measuring session.

Table 3.2 Major and trace element compositions of ocean island basalts (OIB) and continental intraplate basalts (abundances in ppm).

	Mg#	Rb	Sr	Y	Zr	Nb	Ba	La	Ce
USGS standards									
<i>Columbia River, Oregon</i>									
BCR-2	0.34	48	346	37	188	10.4	683	25	53
<i>Halemaumau, Hawaii</i>									
BHVO-2	0.54	9.8	389	26	172	18	130	15	38
Azores									
AZF1		44.2	755	26.9	230	68.0	812	58.3	114.9
AZFY3	0.61	28.4	657	21.2	232	37.3	360	32.9	71.8
AZP5	0.73	2.9	418	14.6	132	19.1	190	15.5	33.6
AZP6	0.49	27.0	785	26.7	302	37.6	326	38.4	87.7
Cameroon Line									
<i>Bioko</i>									
FP23	0.58	26.3	698	23.5	285	41.0	406	52.1	107
<i>Etinde</i>									
C20	0.44	85.2	3162	53.6	708	322	1423	263	504
C22	0.46	89.2	2125	48.2	660	252	942	223	448
C128	0.41	95.9	3123	48.0	731	309	1147	226	425
C150	0.53	89.1	1098	24.3	366	81.6	788	87.8	188
C152	0.43	114.4	2105	44.3	626	318	1006	212	377
C154	0.26	201.2	5103	37.3	914	334	3424	141	167
<i>Manengouba</i>									
C51	0.52	36.8	776	24.0	308	40.1	439	44.9	92.8
C72	0.53	42.7	964	25.7	334	56.5	526	58.1	118
<i>Mt Cameroon</i>									
C1	0.48	42.2	1000	36.7	400	117	530	72.3	147
C25	0.61	35.0	1002	31.5	352	107	437	77.4	156
C30	0.66	22.2	698	22.9	240	62.1	292	51.3	104
C192	0.47	30.8	924	32.0	312	86.9	378	61.4	125
Galapagos									
PL02 25-1	0.43	9.6	544	26.0	205	16.4	182	22.4	52.4
PL02 30-1	0.61	7.1	214	21.5	94.3	7.73	100	9.6	21.1
Iceland									
CX19	0.51	5.5	269	24.1	126	8.18	61	9.2	24.1
GS18	0.54	3.4	219	18.9	78.1	4.70	33	5.6	13.7
SNB19	0.66	13.1	449	23.3	148	36.1	322	24.7	52.4
SNB40		14.9	449	19.3	145	27.2	231	23.4	52.1
ST38	0.54	7.3	252	23.6	130	6.66	199	12.7	29.9
Loihi									
D4-6	0.49	8.4	431	23.7	158	9.63	118	14.1	34.7
D5-1	0.43	12.5	465	22.1	159	12.6	170	16.9	40.3
Madeira									
M40	0.62	14.0	567	19.6	183	24.7	217	26.3	57.0
Trinidad									
TD2		40.3	2724	53.6	748	99.9	1157	189	381
TD4	0.40	60.4	2374	53.2	626	103	1006	168	303
TD5	0.43	14.9	1510	46.7	515	84.8	819	115	253

Data in italic are adopted from references as listed. (a) United States Geological Survey, Certificate of Analysis, Basalt, Columbia River, BCR-2. (b) United States Geological Survey,

Table 3.2 (continued).

	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er
USGS standards									
<i>Columbia River, Oregon</i>									
BCR-2	6.8	28	6.7	2	6.8	1.07	6.43	1.33	3.64
<i>Halemaumau, Hawaii</i>									
BHVO-2	5.09	25	6.2	2.02	6.3	0.9	5.15	1.04	2.51
Azores									
AZF1	12.6	43.1	8.74	2.80	7.17	1.02	5.45	1.04	2.60
AZFY3	8.06	29.9	6.92	2.07	5.78	0.84	4.84	0.88	2.12
AZP5	4.16	16.9	4.30	1.47	3.92	0.59	3.39	0.59	1.49
AZP6	10.3	38.4	8.85	2.68	7.54	1.06	5.89	1.08	2.49
Cameroon Line									
<i>Bioko</i>									
FP23	11.7	43.3	9.48	2.71	7.56	1.02	5.40	0.94	2.21
<i>Etinde</i>									
C20	54.9	194	27.8	7.55	18.1	2.39	11.7	2.01	5.30
C22	49.8	190	26.8	7.24	17.6	2.31	11.0	1.89	4.83
C128	46.3	164	22.9	6.09	14.5	1.93	9.22	1.63	4.16
C150	21.5	72.5	12.8	3.30	8.42	1.08	5.22	0.93	2.22
C152	38.8	138	18.8	5.17	12.3	1.65	8.29	1.53	3.91
C154	13.7	42.8	5.87	1.82	5.00	0.80	4.81	1.05	3.08
<i>Manengouba</i>									
C51	10.5	38.3	8.88	2.69	7.24	1.02	5.35	0.91	2.11
C72	12.7	45.3	9.74	2.86	8.08	1.07	5.66	0.92	2.32
<i>Mt Cameroon</i>									
C1	16.9	67.1	12.0	3.45	9.13	1.25	6.49	1.09	2.90
C25	18.8	73.0	12.2	3.68	9.60	1.28	6.63	1.15	2.87
C30	12.9	48.4	8.92	2.69	7.35	0.98	5.09	0.90	2.21
C192	15.2	59.4	11.0	3.33	8.97	1.25	6.77	1.12	2.82
Galapagos									
PL02 25-1	6.69	26.4	6.80	2.12	6.30	0.93	5.23	0.97	2.42
PL02 30-1	2.83	11.3	3.49	1.12	3.63	0.61	3.96	0.84	2.21
Iceland									
CX19	3.24	14.5	4.44	1.49	4.91	0.79	4.60	0.95	2.39
GS18	1.94	8.65	2.83	0.98	3.27	0.56	3.59	0.72	1.90
SNB19	6.62	28.3	5.72	1.97	5.31	0.80	4.28	0.82	2.12
SNB40	6.23	24.3	5.51	1.80	4.85	0.70	4.08	0.77	1.96
ST38	3.84	15.9	4.60	1.47	4.83	0.80	4.47	0.91	2.32
Loihi									
D4-6	4.68	19.2	5.71	1.85	5.70	0.87	4.97	0.90	2.25
D5-1	4.73	19.1	5.23	1.68	5.19	0.79	4.44	0.82	2.14
Madeira									
M40	6.64	26.5	6.23	1.92	5.59	0.79	4.24	0.77	1.99
Trinidad									
TD2	40.4	132	24.3	6.31	16.9	2.23	11.0	1.82	4.47
TD4	38.4	140	27.1	7.35	20.2	2.55	13.1	2.06	4.65
TD5	31.3	115	23.4	6.24	17.5	2.21	10.9	1.80	4.05

Certificate of Analysis, Basalt, Hawaiian Volcanic Observatory, BHVO-2. (c) Halliday et al. (1995). (d) Fitton (2007). (e) Unpublished data from J. G. Fitton, Department of Geology and

Table 3.2 (continued).

	Tm	Yb	Lu	Hf	Ta	Pb	Th	U	Ref.
USGS standards									
<i>Columbia River, Oregon</i>									
BCR-2	0.54	3.5	0.51	4.8	0.51	11	6.2	1.69	a
<i>Halemaumau, Hawaii</i>									
BHVO-2	0.32	2	0.28	4.1	1.4	1.39	1.2	0.38	b
Azores									
AZF1	0.38	2.39	0.33			2.59	6.05	1.75	c
AZFY3	0.29	1.85	0.26			6.09	3.06	0.90	d
AZP5	0.22	1.28	0.17			1.06	1.29	0.29	d
AZP6	0.36	2.24	0.30			2.62	3.18	1.10	d
Cameroon Line									
<i>Bioko</i>									
FP23	0.30	1.87	0.25			2.41	4.45	1.29	d
<i>Etinde</i>									
C20	0.73	4.30	0.59	12.6	14.9	6.48	25.9	4.45	e
C22	0.63	3.79	0.49	13.9	13.5	8.14	22.9	5.83	e
C128	0.57	3.40	0.48	10.1	8.6	9.18	26.9	4.47	e
C150	0.29	1.71	0.24			3.46	7.75	2.12	d
C152	0.51	3.12	0.41	8.28	6.56	12.3	20.2	6.3	e
C154	0.50	3.61	0.54	9.98	4.66	17.5	7.3	10.5	e
<i>Manengouba</i>									
C51	0.27	1.81	0.22			2.44	4.34	1.27	d
C72	0.31	1.92	0.26			2.63	4.71	1.23	d
<i>Mt Cameroon</i>									
C1	0.37	2.35	0.30	7.61	3.26	4.56	8.77	2.38	e
C25	0.38	2.34	0.31	8.29	4.81	4.84	9.02	2.51	e
C30	0.31	1.71	0.25	6.27	1.68	3.00	5.38	1.42	e
C192	0.38	2.08	0.31	7.20	4.23	3.85	6.50	1.98	e
Galapagos									
PL02 25-1	0.34	2.25	0.31	4.94	2.11	1.58	1.62	0.56	f
PL02 30-1	0.33	2.28	0.35	2.19	0.88	0.77	1.06	0.27	f
Iceland									
CX19	0.35	2.17	0.30			0.75	0.66	0.20	g
GS18	0.29	1.94	0.26			0.51	0.38	0.10	g
SNB19	0.32	1.91	0.31	3.33	2.36	1.33	1.57	0.47	h
SNB40	0.30	1.85	0.27			1.17	1.65	0.40	
ST38	0.33	2.20	0.31			0.82	0.89	0.22	g
Loihi									
D4-6	0.30	1.93	0.25			1.24	0.93	0.31	f
D5-1	0.28	1.78	0.26	3.44	1.13	1.58	1.06	0.33	f
Madeira									
M40	0.25	1.63	0.21	4.02	2.30	1.50	2.25	0.63	d
Trinidad									
TD2	0.60	3.61	0.44			5.38	11.0	9.98	
TD4	0.57	3.41	0.43			3.83	10.1	3.39	d
TD5	0.49	2.89	0.37			4.37	8.80	2.81	d

Geophysics, University of Edinburgh, Edinburgh. (f) Yi et al. (2000). (g) Hardarson and Fitton (1997). (h) Kempton et al. (2000).

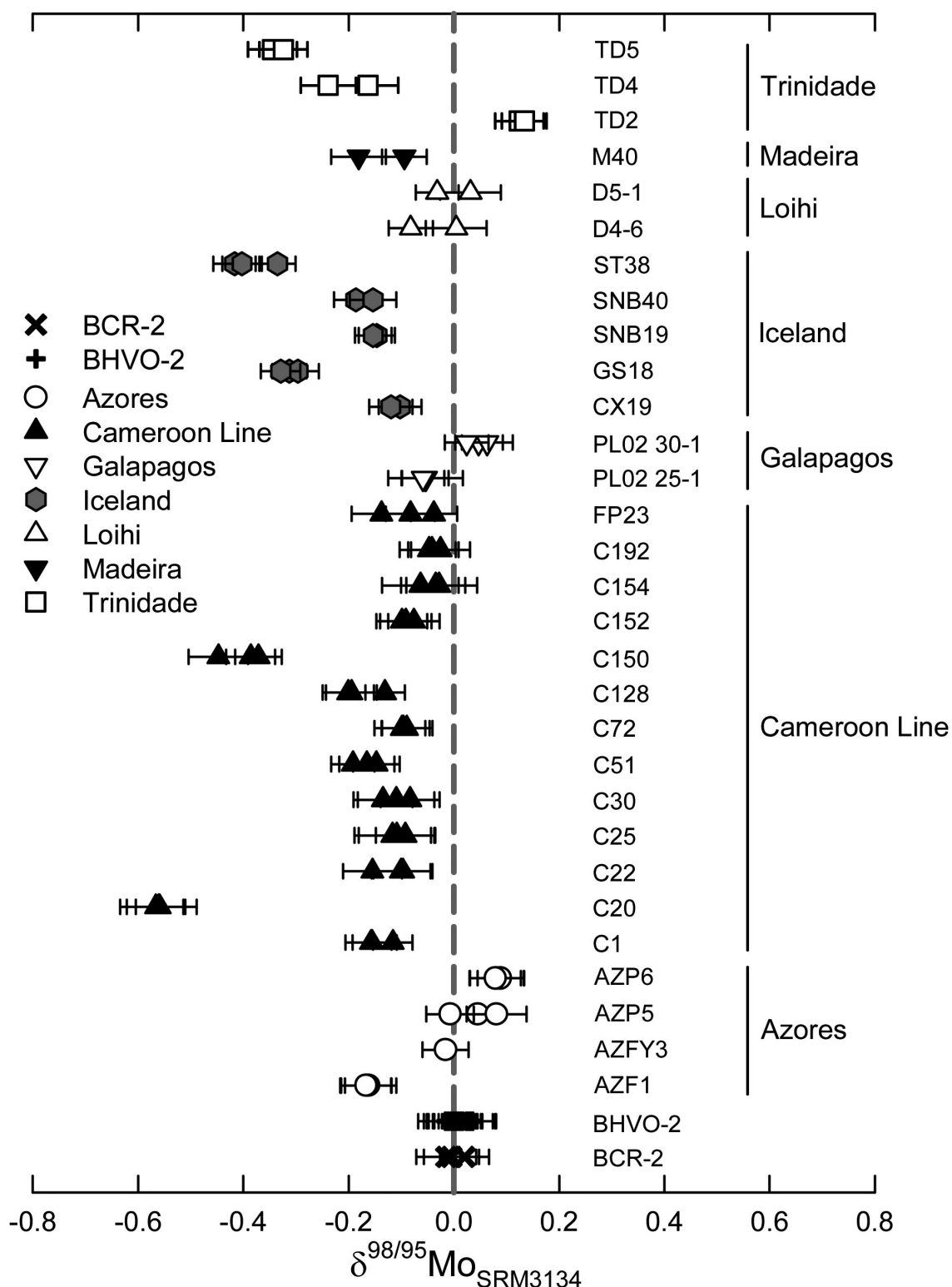


Figure 3.2. The Mo isotope compositions of ocean island basalts (OIB) and continental intraplate basalts, showing the degree of replication achieved for each sample. Errors given are 2 standard deviations of standard measurements in each measuring session. The long term external standard reproducibility of $^{98}\text{Mo}/^{95}\text{Mo}$ is $\pm 0.09\%$.

Molybdenum concentrations in our OIBs are generally similar to the values of mafic rocks reported in the literature which are between 0.25 and 4.17 ppm, except one hauyne nephelinite (C152) that has up to 16.1 ppm Mo content. In contrast, the Mo isotope compositions of our OIB samples show remarkable differences between each other and seem more scattered than the sparse literature values of mafic rocks. The distribution of $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ values in our sample set is ranging from -0.56 to 0.13 ‰ (Table 3.1, Figure 3.2).

3.5 Discussion

In contrast to previous studies (Siebert et al., 2003; Voegelin et al., 2012), the Mo isotopic compositions for our mafic samples vary significantly. Surprisingly, some OIBs have very distinct light $\delta^{98/95}\text{Mo}$ values. OIBs are believed to originate from partial melting of plumes from the lower mantle (Allegre, 1982; Hofmann and White, 1982; Storey et al., 1988) and/or relatively enriched components in the heterogeneous upper mantle (Fitton and Dunlop, 1985; Morris and Hart, 1983; Sleep, 1984; Zindler et al., 1984). Therefore, it is possible that the differences within OIB reflect a source difference. However, this seems an unlikely explanation of the observed signatures, because there are large $\delta^{98/95}\text{Mo}$ variations between OIB samples from the same location, and even the same volcano (e.g. Etinde of Cameroon Line). Radiogenic Sr, Nd and Pb isotope ratios are commonly used to identify different source reservoirs. Twenty of the OIB samples have published Pb, Sr,

and Nd isotope data, but no correlation between any of these parameters and Mo isotopes can be observed (Figure 3.3). Therefore, it seems likely that source effects are minor and the isotopic variations reflect magmatic processes associated with OIB production and differentiation.

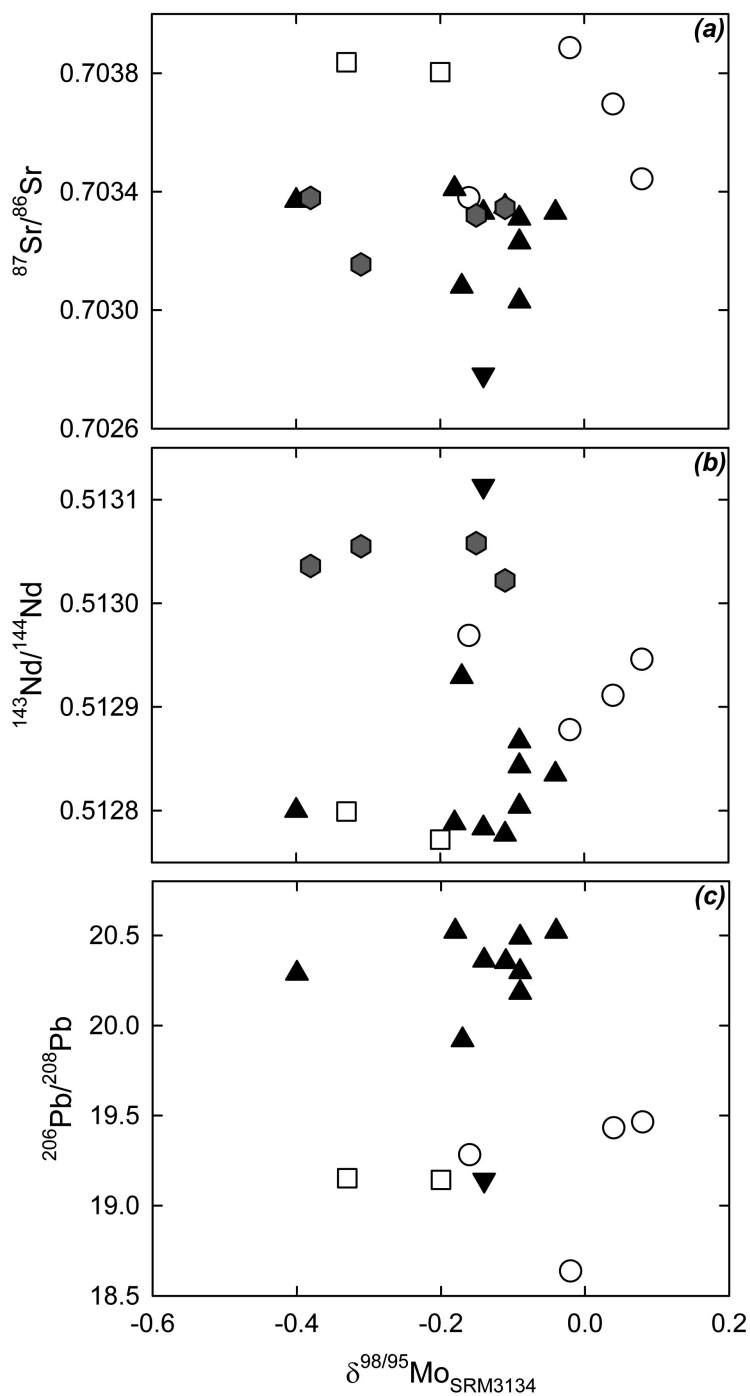


Figure 3.3. Radiogenic (a) Sr, (b) Nd, and (c) Pb isotope compositions plotted against $\delta^{98/95}\text{Mo}$ values for OIBs. Symbols as in Figure 3.2. Data from Table 3.1 and Halliday et al. (1990); Halliday et al. (1992); Halliday et al. (1988); Hardarson and Fitton (1997); Kempton et al. (2000).

Ocean island basalts are thought to be generated under relatively small degrees of partial melting of the mantle, therefore, another possibility for fractionating of Mo isotopes might be the degree of partial melting. Some of our samples from the Cameroon Line and Trinidad are nephelinites, which are silica-undersaturated igneous rocks believed to be produced by a low degree of melting of the mantle. This interpretation is supported by high La/Yb values (up to 68) observed within our nephelinite samples (Figure 3.4b). However, again there is no correlation between $\delta^{98/95}\text{Mo}$ and Mg# or La/Yb in all analyzed samples (Figure 3.4), which makes it unlikely that the Mo isotope fractionation is simply controlled by degree of partial melting or fractional crystallization.

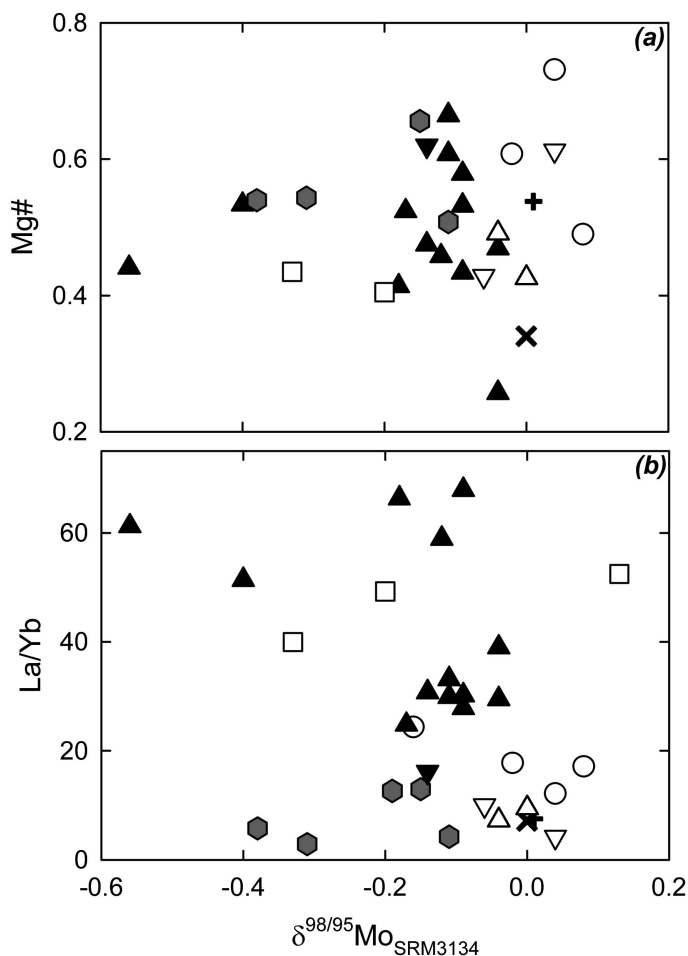


Figure 3.4. Plots of (a) Mg# and (b) La/Yb versus $\delta^{98/95}\text{Mo}$ values for OIBs. Data from Table 3.1 and 3.2. Symbols as in Figure 3.2.

Therefore, other causes that can produce the observed isotope fractionation must be considered. In order to investigate this in more detail, I have plotted incompatible trace elements ratios against their $\delta^{98/95}\text{Mo}$ values in Figure 3.5. Generally, some trace-element ratios, e.g. Nb/U, Ce/Pb, and Mo/Pr, are uniform in both MORBs and normal OIBs (Hofmann et al., 1986; Newsom et al., 1986). However, Mo may be slightly more incompatible than Pr (Newsom et al., 1986). Although Mo is thought to be less incompatible than Ce in mantle melting, the Mo/Ce values in MORBs seem to be uniform and were previously used to estimate the Mo abundance in the primitive mantle (Sims et al., 1990).

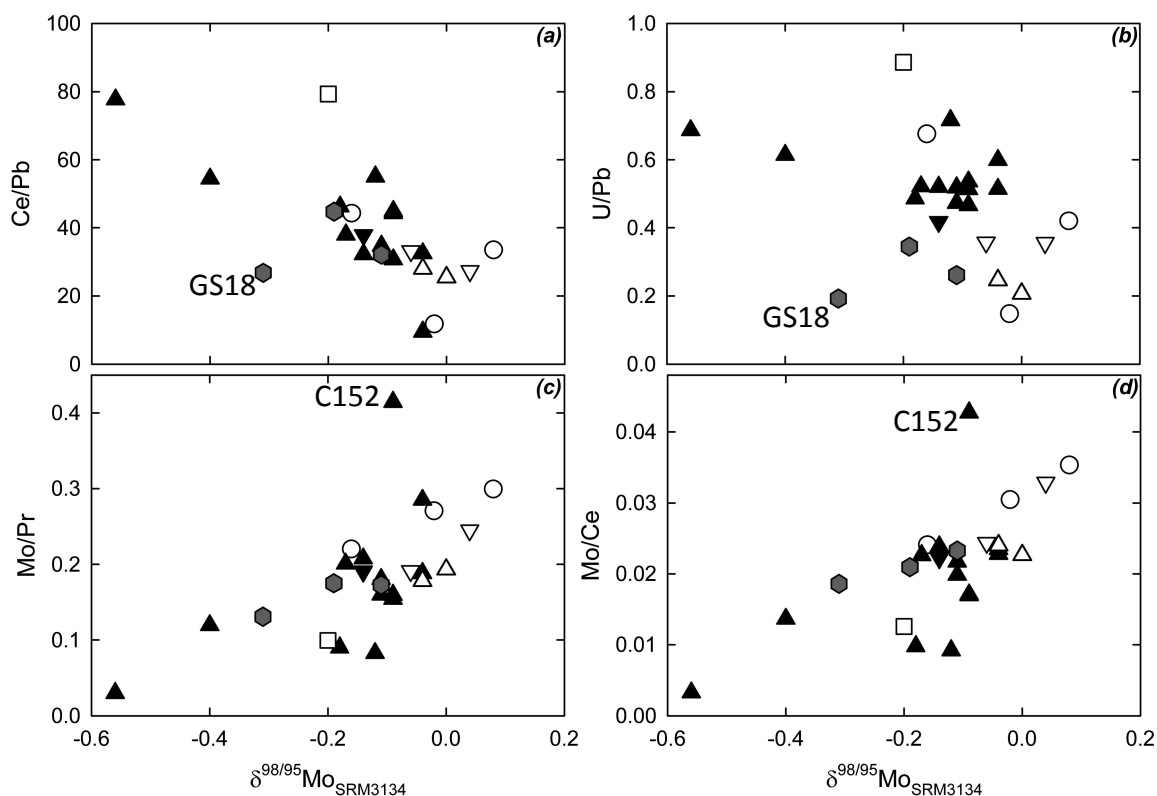


Figure 3.5. Plots of (a) Ce/Pb, (b) U/Pb, (c) Mo/Pr, and (d) Mo/Ce against $\delta^{98/95}\text{Mo}$ values for OIBs. Data from Table 3.1 and 3.2. Symbols as in Figure 3.2.

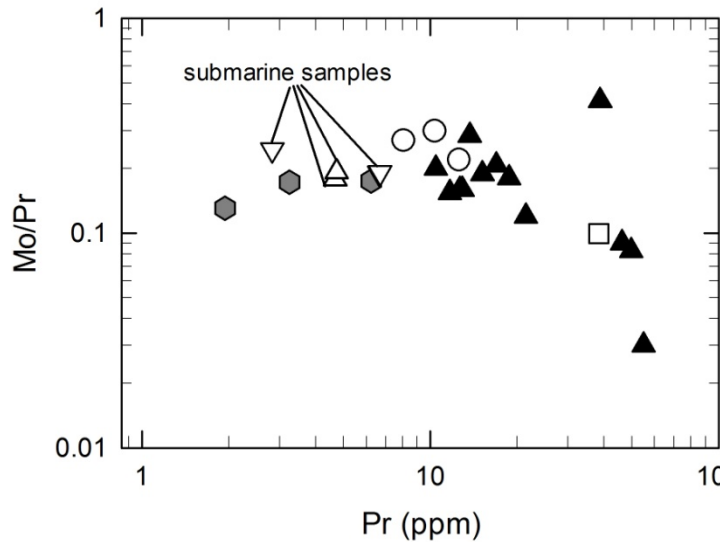


Figure 3.6. *Mo/Pr plotted against Pr content for OIBs. Data from Table 3.1 and 3.2. Symbols as in Figure 3.2.*

Uranium is well known to be more incompatible than Pb during mantle melting (Newsom et al., 1986), and Halliday et al. (1995) found fractionation in Ce/Pb and a positive correlation with U/Pb in highly enriched magmas such as nephelinites. This observation was explained by small degree partial melting in the presence of residual sulphide (Halliday et al., 1995). The more enriched intraplate magmas studied here are from the same sample suite from Cameroon Line and Trinidad (Halliday et al., 1992; Halliday et al., 1995). Note that although all samples are petrographically fresh, samples with Ba/Rb smaller than 5 or larger than 20 have been excluded, because this ratio has been shown to be especially sensitive to secondary alteration (Hofmann and White, 1983) which might affect Pb contents in particular. Meanwhile, BCR-2 and BHVO-2 were also excluded due to likely crustal contamination and various Mo contents in different batches, respectively. It can be seen in Figure 3.5a and 3.5b that $\delta^{98/95}\text{Mo}$ correlates with both Ce/Pb and U/Pb ($R^2 = 0.5$ and 0.3 respectively, exclude GS18), providing evidence of fractionation by a similar process. The only sample

plotting off the correlation is GS18, which is our most depleted sample. The La abundance of GS18 is less than 10 times primitive mantle and similar to MORBs. A correlation is also found between Mo/Pr, Mo/Ce and $\delta^{98/95}\text{Mo}$ (Figure 3.5c, 3.5d), and GS18 fits the correlation here. The only exceptional sample in Figure 3.5c is C152 from the Cameroon Line, which has a high Mo abundance. Note that the correlation between $\delta^{98/95}\text{Mo}$ and Mo/Pr or Mo/Ce is positive (Figure 3.5c, 3.5d) but there is no correlation between $\delta^{98/95}\text{Mo}$ and La/Yb (Figure. 3.4b).

If Mo is preferentially transported relative to REEs such as Pr in high temperature fluids, fumaroles and volcanic aerosols, then the correlation between Mo isotopes and Mo/Pr might reflect loss of Mo by volcanic degassing as is found for Te and Re (which are also chalcophile elements) in subaerial basalts (Yi et al., 2000). More recent studies also demonstrated that Mo could be found in volcanic aerosol/emissions, but the amount of Mo losing by volcanic degassing is limited (Henley and Berger, 2013; Mather et al., 2012; Zelenski et al., 2013). In order to test this hypothesis, the Mo/Pr ratios of all OIBs are plotted against their Pr content in Figure 3.6. There is no systematic difference between subaerial (Azores, Cameroon Line, Madeira, and Iceland samples) and submarine samples (Galapagos and Loihi). Thus the relatively low Mo/Pr ratios of the Trinidad and Cameroon Line samples must be related to these being enriched nephelinites rather than being subaerial volcanic rocks. In particular, the Mo/Pr ratio of nephelinite C20 is much lower than all

other samples and has the most negative $\delta^{98/95}\text{Mo}$ (Figure 3.2 and 3.5).

Chalcophile elements are those elements with an affinity for sulphide liquid phases during core formation and include Pb and Mo, whereas U, Ce and Pr are normally strongly lithophile. Meijer et al (1990) proposed that sulphide is likely to fractionate both U/Pb and Ce/Pb in ultramafic xenoliths. According to their calculation, even if all of Pb in the mantle xenoliths they studied was in sulphides, the amount of sulphide required would be on the order of only 0.15 wt %. Halliday et al. (1995) proposed sulphide fractionation as the main cause of fractionation of Ce/Pb and U/Pb and the production of the extreme values found in nephelinites in Atlantic intraplate basalts. Sims and DePaolo (1997) showed from their global Pb and Ce data, that sulphide strongly influences the partitioning of Pb either during shallow fractionation or as a mantle residue. How sulphide fractionates chalcophile elements has been discussed by Yi et al. (2000): Once sulphur solubility in silicate melts is exceeded, immiscible sulphide will form and its removal will fractionate and deplete chalcophile elements. It has been argued that sulphide liquids would affect platinum group elements (Greenland and Aruscavage, 1986) and Te (Rehkamper et al., 1999) even if they are not present in large quantities.

More recently, Hart and Gaetani (2006) have proposed that sulphide fractionation during mantle melting might resolve “the Third Pb Paradox.” The Third Pb Paradox is based on the relatively uniform Ce/Pb ratio in MORBs and OIBs over a wide range of

absolute concentration. This should define the element ratio of the mantle but it is distinct from the well-established bulk silicate earth value inferred from Pb isotopes. Sulphide liquids can not only coexist with silicate melt but also be much denser, and they will segregate if their size is sufficient (Czamanske and Moore, 1977). With their modelling, Hart and Gaetani (2006) suggested that sulphide melts might be likely to aggregate or pond at depth near the sulphide solidus because of their greater density relative to silicate melt; this strips Pb from silicate liquids and solids. Sulphide inclusions in MORB have indeed been shown to be exceedingly unradiogenic in their Pb isotopic composition (Burton et al., 2012) and to represent a potentially important reservoir in solving the “first Lead Paradox” (which is known as mantle reservoirs have more radiogenic Pb isotope compositions than the geochron of bulk earth) as well.

Therefore, sulphide fractionation can explain the variability in $\delta^{98/95}\text{Mo}$ and its correlations with Mo/Pr, Mo/Ce, Ce/Pb and U/Pb in intraplate magmas (Figure 3.5 and 3.6). The scatter in Mo/Pr ratio for a given [Pr] might also be due to sulphide fractionation as mentioned by Newsom et al. (1986). They claimed that a sulphide fraction on the order of 0.1 wt. % would be sufficient to explain observed Mo/Pr variability basalts. As discussed earlier, the only sample plotting off the correlation in Figure 3.5c and 3.5d is a hauyne nephelinite (C152), which has a high Mo abundance. However this still agree with the suggestion that sulphide plays an important role for

Mo/Pr variation. Hauyne is a tectosilicate mineral with sulfate, and it occurs as major phenocrysts in sample C152. Molybdenum might be enriched with sulphide in the parental magma of C152, and this caused the high Mo/Pr value in the bulk chemical composition. In addition, C152, like many Etinde nephelinites, contains perovskites phenocrysts. Separation of these could easily fractionate Mo from LREE. Furthermore, leaching experiments from basalts indeed confirm that sulphide is isotopically heavy relative to coexisting silicates (Voegelin et al., 2012). Therefore, sulphide fractionation is the most likely cause of the variability in $\delta^{98/95}\text{Mo}$ and the correlations with Mo/Pr, Mo/Ce, Ce/Pb and U/Pb in intraplate magmas.

3.6 Summary

1. Molybdenum content and isotopic composition are varying in ocean island basalts, even within a single locality. This variation is higher than previously observed values for magmatic rock in the literature.
2. Molybdenum isotope fractionation is neither related to fractional crystallization nor degree of partial melting. Source effects seem not relevant to Mo isotope signature within our sample set.
3. From the relationships between $\delta^{98/95}\text{Mo}$ and Ce/Pb, U/Pb, Mo/Ce, and Mo/Pr (Figure 3.5) it is proposed that sulphide not only fractionates chalcophile elements, but also preferentially incorporates heavier Mo isotopes.

4. It is likely immiscible sulphides retained in the mantle are a store of Mo as well as Pb and fractionate Mo isotopes in basaltic magmas.

CHAPTER FOUR



The molybdenum isotopic composition of the mantle and bulk silicate Earth

4.1 Introduction

Based on their geochemical affinity, elements can be classified into several different categories, e.g. atmophile, lithophile, siderophile, and chalcophile (Goldschmidt, 1937). During core formation, this different behaviour of elements leads to depletions of the siderophile and chalcophile elements in Earth's silicate portion with respect to lithophile elements. As a moderately siderophile and refractory element, molybdenum is thought to be an ideal target for investigating and distinguishing possible processes during core-mantle differentiation (Jones and Drake, 1986). Some of the first data on molybdenum abundances in different types of rocks and meteorites were published by Kuroda and Sandell (1954) using a colorimetric technique.

More precise Mo abundance measurements on terrestrial samples by improved analytical technique were systematically carried on since 1980s, which allowed some constraints on the Mo abundance of the mantle. Newsom and Palme (1984) published Mo contents for a number of terrestrial samples and estimated the Mo abundances in the mantle. Due to good correlations of Mo with Ce, Pr, and Nd, their estimation was based on the relative consistency of Mo/Nd ($0.043 \pm 30\%$). By using carbonaceous chondrite Nd/Al values and assuming the upper mantle Al content is 2.38%, they estimated a value of 59ppb for the upper mantle abundance of Mo (Newsom and Palme, 1984). McDonough (1990) presented elemental data for 375

ultramafic xenoliths from continental basalts, and attempted to constrain the composition of the continental lithospheric mantle. Although they present an average Mo abundance in these ultramafic xenoliths of 50 ± 30 ppb (1σ), only *three* of these 375 samples actually have Mo data.

A more commonly accepted estimation of the Mo budget in the mantle was presented by Sims et al. (1990). They analyzed a number of oceanic basalts ranging from depleted MORBs to enriched OIBs for their trace element compositions and obtained a good correlation between Mo and Ce abundances. Because the Mo/Ce ratio is relatively constant while absolute concentrations vary over a factor of 20, they concluded that the Mo/Ce ratio in the depleted mantle is 0.032 ± 0.009 (1σ), and used that ratio to estimate an abundance of Mo in the primitive mantle of 45 ± 13 ppb (1σ). Furthermore, together with their results of for the continental crust, they estimated that the Mo/Ce ratio and absolute Mo abundance of the primitive mantle are 0.027 ± 0.012 (1σ) and 47 ± 20 ppb (1σ), respectively (Sims et al., 1990). Additional evaluations of the Mo budget in the mantle were made more recently (Palme and O'Neill, 2007; Salters and Stracke, 2004), however, the Mo/Ce value published by Sims et al. (1990) is still generally accepted.

No work has been published on the isotopic composition of Mo in the mantle so far. The first data on Mo isotopic variation in ocean island basalts (OIB) is presented in this study (chapter 3). In this chapter, Mo isotopes and trace elements compositions

of ten mid-ocean ridge basalts (MORB) and seven ultramafic rocks from various localities are presented, in order to investigate how Mo isotopes behave under relatively large degrees of partial melting of the mantle. Furthermore, based on slightly different incompatibilities of Mo and Ce (Sun and McDonough, 1989), as well as Mo isotope data from this study, the average content of Mo in the bulk silicate earth (BSE) is re-evaluated.

4.2 Samples

Well characterised samples including 12 mafic and 7 ultramafic rocks (as listed in the Table 4.1) were selected from a variety of localities. Four of these are mantle-derived USGS standards which also provide quality control.

Among the 12 mafic rocks, BCR-2 and BHVO-2 are basalt standards, which were collected from Hawaii (OIB) and Oregon (continental intraplate basalt), respectively. And the other 10 samples are Mid-ocean ridge basalts. Mid-ocean ridge basalts (MORBs) are thought to be derived from an upper mantle source and have radiogenic isotopic compositions that reflect a time integrated history of melt depletion. The sample set comprises 10 fresh MORB glasses including samples from the Mid-Atlantic Ridge, Southwest Indian Ridge, and East Pacific Rise (Gannoun et al., 2007; Niu and Batiza, 1997; Schiano et al., 1997).

The ultramafic xenoliths were sampled from the Lashaine volcano, which is a tuff

cone that forms part of the Neogene volcanic province in northern Tanzania and stands astride the eastern Rift Valley of East Africa (Dawson et al., 1970). The Lashaine tuff cone is composed of ankaramitic scoria and carbonatite tuff, and contains a wide variety of remarkably fresh ultramafic xenoliths (Dawson et al., 1970). These xenoliths can be roughly divided into two groups: a) a series of peridotitic rocks consisting of lherzolite, harzburgite, dunite, garnet harzburgite, and garnet lherzolite (Dawson et al., 1970), and b) a suite of pyroxenitic rocks including alkali clinopyroxenite, websterite, mica dunite and iron –rich lherzolite (Dawson and Smith, 1973). The selected five xenoliths are well characterized in terms of their mineral, major and trace element composition (Dawson, 2002; Dawson et al., 1970; Dawson and Smith, 1973; Reid et al., 1975; Rhodes and Dawson, 1975), and include both pyroxenitic and peridotitic rocks (Table 4.1) (Dawson and Smith, 1973; Reid et al., 1975).

In addition, two well-characterized USGS ultramafic rock standards DTS-1 and PCC-1 have also been included. PCC-1 is a peridotite from the Cazadero ultramafic massif located in California and DTS-1 is a dunite from Twin Sisters area of Washington State (Flanagan, 1967). The Twin Sisters dunite has large olivine crystals which partly recrystallized and/or mylonitized in the upper mantle, as well as chromite pods and lenses (Onyeagocha, 1978).

4.3 Methods

Each MORB glass sample was hand-picked under the microscope and cleaned by rinsing in water. Before digestion, all ultramafic xenoliths were crushed with a tungsten carbide ball mill to avoid Mo contamination from steel crushers. MORB glasses are easily digested in concentrated acid, therefore samples were not crushed before digestion.

The detailed analytical methods are described in chapter 2. All samples were spiked with a double isotope tracer (^{100}Mo , ^{97}Mo) prior to digestion in order to have best correction of instrumental and laboratory mass fractionation. All of the mafic rocks were dissolved with a mixture of HF and HNO_3 in sealed Teflon vials on a hotplate at 140°C for at least 3 days. Ultramafic rocks that might contain refractory minerals were digested using mini-Teflon hexagonal screw top bombs (Prytulak et al., 2011). For Mo purification, The samples were then taken up in 6M HCl for chemical separation. Samples were loaded on 2 ml of Biorad AG1-X8 anion exchange resin rinsed with 6M HCl to remove most of the matrix and then eluted with 1 M HCl. The eluents were dried and then passed through 2 ml Biorad AG50W-X8 cation resin in 0.5 M HCl to remove Fe (Chapter 2).

Trace element concentration of ultramafic xenoliths and some MORBs were measured on Thermo Scientific® ELEMENT® ICP-MS, while Mo isotopic compositions were measured on a Nu instruments® MC-ICPMS at the Department of Earth

Sciences, University of Oxford. All Mo isotopic variations are represented by the delta notation as the deviation in per mil (‰):

$$\delta^{98/95}\text{Mo} = \left(\frac{(^{98}\text{Mo}/^{95}\text{Mo})_{\text{sample}}}{(^{98}\text{Mo}/^{95}\text{Mo})_{\text{standard}}} - 1 \right) \times 1000$$

One or two aliquots of basaltic USGS standard BHVO-2, occasionally with BCR-2, were processed with each batch of samples. Both BCR-2 and BHVO-2 show very good reproducibility with average $\delta^{98/95}\text{Mo}$ values of 0.00 ± 0.04 ‰ (2s.d.) and 0.01 ± 0.03 ‰, respectively (during the same period of time when the samples used in this chapter were analyzed).

To facilitate interlaboratory comparisons all data reported here have been normalized to the NIST SRM3134 value. More details about analytical protocol, external standard reproducibility, and data normalization are described in chapter 2.

4.4 Results

The Mo isotopic compositions for all samples are shown in Table 4.1. The errors given are 2 standard deviations of all replicates of each sample, and each duplicate analysis always consisted of a repeat of the entire procedure in a different day from the same crushed rock sample. If only one aliquot of the sample was measured the error is given as 2 standard deviations of the Alfa Aesar standard solution during the measurement at the same measurement session Figure 4.1

Table 4.1 Molybdenum concentration and isotope compositions of ultramafic rocks and mid-ocean ridge basalts (MORB).

Sample	Locality	n ^a	Mo (ppm)	Mo/Ce	$\delta^{98/95}\text{Mo}_{\text{SRM1314}}$		
					replicates	average	2 s. d. ^b
Ultramafic Rocks							
DTS-1	Dunite	2	0.05	1.00	0.45, 0.60	0.53	0.21
PCC-1	Peridotite	3	0.05	0.88	0.39, 0.28, 0.28	0.32	0.13
BD744	Alkali pyroxenite	2	1.03		0.40, 0.42	0.41	0.02
BD774	Lherzolite	2	1.09	0.36	0.34, 0.38	0.36	0.07
BD822	Spinel harzburgite	2	0.43	0.46	0.35, 0.36	0.35	0.02
BD825	Fe-rich chromite dunite	2	1.02		0.24, 0.34	0.29	0.15
BD1542	Chromite harzburgite	1	0.95		0.37	0.37	0.03 *
Ultramafic xenolith average			0.91			0.36	0.09
Mid-Ocean Ridge Basalts (MORB)							
Southwest Indian Ridge							
MD34 D6	Basaltic glass	1	0.62	0.030	0.08	0.08	0.05 *
Mid-Atlantic Ridge							
45N	Basaltic glass	1	0.43	0.032	0.06	0.06	0.04 *
ALV 518 3-1	Basaltic glass	2	0.42	0.036	0.06, 0.03	0.05	0.04
ALV 518 3-2	Basaltic glass	2	0.43	0.035	0.00, -0.04	-0.02	0.05
ARP 1974 12-19	Basaltic glass	2	0.32	0.038	0.04, 0.02	0.03	0.02
East Pacific Rise							
CY82 18-01	Basaltic glass	1	0.46	0.027	-0.01	-0.01	0.06 *
DR 7-1	Basaltic glass	2	0.93	0.035	0.01, 0.00	0.01	0.01
R82-1	Basaltic glass	2	0.23	0.043	0.06, 0.07	0.06	0.01
R93-7	Basaltic glass	2	0.58	0.036	0.02, 0.01	0.02	0.01
Searise 2 DR07	Basaltic glass	1	0.40	0.026	0.07	0.07	0.06 *
MORBs average			0.49			0.03	0.07

^a Number of duplicates for the same sample.^b The errors are 2 standard deviations of all duplicates of each sample.

* Only one aliquot successfully analysed for these samples, so the errors are given as 2 standard deviation of standard measurements in each measuring session.

Table 4.2 Major and trace element compositions of ultramafic rocks and mid-ocean ridge basalts (MORB), abundances in ppm.

	Mg#	V	Ni	Ga	Rb	Sr	Y	Zr	Nb	Ba	La	Ce	Pr	Nd	Sm
Ultramafic Rocks															
DTS-1 ^a	0.92	11	2360		0.095	0.32		0.11	0.042	0.3	0.025	0.05	0.0063	0.027	0.0039
PCC-1 ^a	0.91	31	2380		0.068	0.38		0.13	0.042	0.68	0.039	0.057	0.0085	0.03	0.008
BD774	0.92 ^b	32.3	2167	1.9 ^b	0.7 ^b	8.3 ^b	1.30	7.77	2.49	90.0	3.03	3.02	0.506	1.96	0.360
BD822	0.93 ^b	12.9	2344	3.6 ^b	1.7 ^b	8.1 ^b	0.0935	1.83	0.96	19.8	0.399	0.928	0.086	0.299	0.0611
BD825 ^b	0.85			2	1.3	9.1	0.5	6.6	13						
BD1542 ^b	0.92			2.7	3	214	1.1	7.1	2.4						
Mid-Ocean Ridge Basalts (MORB)															
Southwest Indian Ridge															
MD34 D6 ^c	0.50	337	45.4	17.4	3.16	138	37.9	113	8.25	65.4	8.60	20.80	3.06	15.5	4.68
Mid-Atlantic Ridge															
45N ^c	0.63	281	154	15.2	4.86	103	22.0	54.2	8.10	55.9	5.81	13.3	1.80	8.69	2.61
ALV 518 3-1 ^d	0.58	251	69.9	13.3	3.06	120	21.4	48.2	7.45	41.3	4.97	11.7	1.72	8.34	2.48
ALV 518 3-2 ^d	0.59	248	74.3	13.2	2.69	129	22.3	53.3	8.87	40.8	5.25	12.4	1.79	8.49	2.64
ARP 1974 12-19 ^c	0.57	329	66.6	15.3	0.753	81.2	32.6	77.2	1.67	7.92	2.59	8.34	1.55	9.36	3.40
East Pacific Rise															
CY82 18-01 ^d	0.56	301	77.5	16.8	2.41	160	33.8	137	5.55	25.6	5.64	16.8	2.79	13.8	4.28
DR 7-1 ^c	0.54	309	65.9	19.1	8.16	268	30.5	139	14.8	115	11.2	26.8	3.74	17.9	4.87
R82-1 ^e	0.65	217	123	15.4	0.50	88.6	20.3	40.6	1.16	7.18	1.64	5.35	0.95	5.15	1.96
R93-7 ^e	0.65	207	122	16.6	2.01	177	24.7	106	5.93	25.1	6.16	16.2	2.32	10.74	3.14
Searise 2 DR07 ^d	0.44	464	48.3	19.0	1.03	91.3	53.3	151	3.16	8.98	4.75	15.6	2.77	15.7	5.43

a Reference data from Govindaraju (1994) and Ionov et al. (1992)

b Reference data from Rhodes and Dawson (1975)

c Unpublished data from K. W. Burton, Department of Earth Sciences, Durham University, Science Labs, Durham, UK

Table 4.2 (continued).

	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Pb	Th	U
Ultramafic Rocks														
DTS-1 ^a	0.0013	0.0063	0.001	0.0085	0.0016	0.0074	0.0013	0.01	0.0022	0.0046	0.0021	7.5	0.0083	0.0038
PCC-1 ^a	0.0018	0.008	0.0015	0.01	0.0038	0.0123	0.0025	0.0215	0.0049	0.0055	0.003	8.2	0.0095	0.0042
BD774	0.0973	0.356	0.0483	0.253	0.0453	0.135	0.0168	0.115	0.0198	0.226	0.353	0.537	0.178	0.278
BD822	0.0156	0.0493	0.0060	0.0231	0.0044	0.0112	0.0008	0.0063	0.0010	0.0506	0.389	0.317	0.0687	0.0155
BD825 ^b														
BD1542 ^b														
Mid-Ocean Ridge Basalts (MORB)														
<i>Southwest Indian Ridge</i>														
MD34 D6 ^c	1.59	6.01	1.02	7.19	1.49	4.32	0.631	4.38	0.633	3.08	0.471	0.983	0.772	0.193
<i>Mid-Atlantic Ridge</i>														
45N ^c	0.942	3.29	0.563	4.07	0.847	2.46	0.358	2.54	0.368	1.57	0.493	0.498	0.611	0.185
ALV 518 3-1 ^d	0.900	3.48	0.611	4.07	0.836	2.44	0.363	2.33	0.345	1.80	0.540	0.373	0.510	0.183
ALV 518 3-2 ^d	0.970	3.39	0.616	4.09	0.837	2.46	0.339	2.38	0.345	1.72	0.582	0.410	0.569	0.199
ARP 1974 12-19 ^c	1.21	4.78	0.832	6.04	1.27	3.73	0.551	3.75	0.551	2.39	0.119	0.325	0.126	0.038
<i>East Pacific Rise</i>														
CY82 18-01 ^d	1.46	5.31	0.948	5.86	1.25	3.70	0.501	3.55	0.507	3.35	0.387	0.763	0.364	0.130
DR 7-1 ^c	1.69	5.45	0.866	5.88	1.18	3.34	0.474	3.29	0.468	3.43	0.944	1.06	0.927	0.316
R82-1 ^e	0.77	2.62	0.49	3.34	0.72	2.05	0.32	2.11	0.30	1.38	0.08	0.26	0.08	0.03
R93-7 ^e	1.15	3.73	0.65	4.21	0.90	2.53	0.38	2.50	0.36	2.40	0.39	0.57	0.36	0.14
Seairise 2 DR07 ^d	1.87	7.78	1.42	9.27	2.02	6.03	0.863	5.63	0.851	4.33	0.315	0.608	0.216	0.081

^d Data from Sutcliffe (2013)^e Reference data from Niu and Batiza (1997)

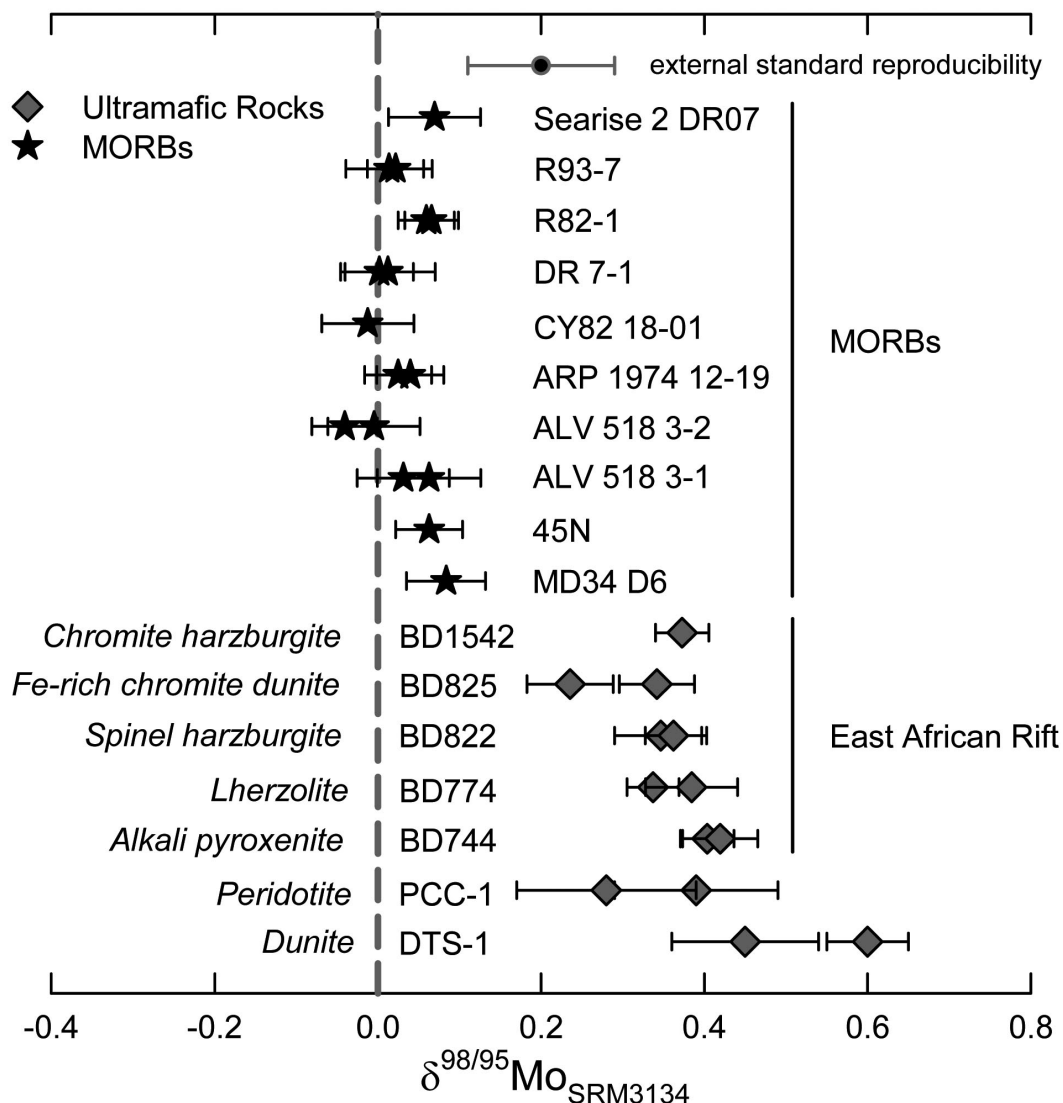


Figure 4.1. The Mo isotope compositions of ultramafic rocks and mid-ocean ridge basalts, showing the degree of replication achieved for each sample. Errors given are 2 standard deviations of standard measurements in each measuring session. The long term external standard reproducibility of $^{98}\text{Mo}/^{95}\text{Mo}$ is $\pm 0.09\text{‰}$.

shows the degree of replication achieved for each sample with two standard deviations for each analysis. The trace element abundances for parts of samples are summarized in Table 4.2, and the accuracy of ICP-MS concentration measurements are better than $\pm 10\%$.

The USGS ultramafic rock standards, DTS-1 and PCC-1, have low Mo contents (0.05

ppm), causing inferior reproducibility relative to basaltic standards, and the average $\delta^{98/95}\text{Mo}$ is 0.53 ± 0.21 ‰ (2s.d.) for DTS-1 and 0.32 ± 0.13 ‰ for PCC-1. Mo concentrations in the East African ultramafic xenoliths are higher (0.4 to 1.1 ppm) with an average $\delta^{98/95}\text{Mo}$ of 0.36 ± 0.09 ‰ ($\delta^{98/95}\text{Mo} = 0.29\text{--}0.41$ ‰), which means they are within error identical to those of the ultramafic rock standards. Mo concentrations of MORBs are intermediate (0.23 to 0.93 ppm) between those of the much depleted North American peridotites and the less depleted East African peridotites. As with ultramafic rocks the $\delta^{98/95}\text{Mo}$ of all MORBs is relatively uniform ranging between 0.08 and -0.02 ‰.

4.5 Discussion

4.5.1 Molybdenum isotopic uniformity of the mantle

Compared to the variation in OIBs (Chapter 3), the Mo isotopic compositions of MORBs and ultramafic rocks are each surprisingly uniform though distinct. The Mo abundances in the East African ultramafic xenoliths are at least 10 times higher than in the USGS ultramafic rock standards (Table 4.1) and this might reflect a cumulate origin for the latter. On the other hand, there is no obvious relationship of $\delta^{98/95}\text{Mo}$ with mineralogy or chemical composition. Different ultramafic rock types (alkali pyroxenite, lherzolite, spinel harzburgite, chromite harzburgite, and iron-rich chromite dunite) are included in our sample set, and all of their Mo isotopic results

overlap within error. One of the xenoliths (BD825) is extremely iron-rich (Rhodes and Dawson, 1975), but its $\delta^{98/95}\text{Mo}$ is still 0.29 ± 0.15 ‰. Furthermore, the fact that the samples and standards are from North America and East Africa provides some evidence that the mantle may be relatively uniform in Mo isotopic composition.

Mid-ocean ridge basalts are thought to be derived from a higher degree of partial melting of the upper mantle than OIBs. Therefore, while Mo is behaving as an incompatible element (Sun and McDonough, 1989), the Mo abundances of MORBs are generally lower than OIBs (Table 4.1 and Table 3.1). The MORB samples are from various oceans and ridges, and represented by 4 normal (N-type) and 6 enriched (E-type) samples (Figure 4.2). However, their Mo isotopic composition is uniform regardless of degree of trace element enrichment (Table 4.1, Figure 4.2). This is consistent with the argument from Chapter 3 that Mo isotopic fractionation is not likely related to source effects and that the isotopic variations might actually reflect magmatic processes associated with MORB and OIB production and differentiation. This also gives support to the view obtained from the ultramafic rock data that the mantle is relatively uniform in Mo isotopic composition. However, the average $\delta^{98/95}\text{Mo}$ of all MORBs analyzed is $+0.03 \pm 0.07$ ‰ and is clearly light relative to the compositions of peridotites (0.53 ± 0.21 to 0.29 ± 0.15 ‰). Therefore, there appears to be a systematic Mo isotopic fractionation associated with partial melting of the mantle.

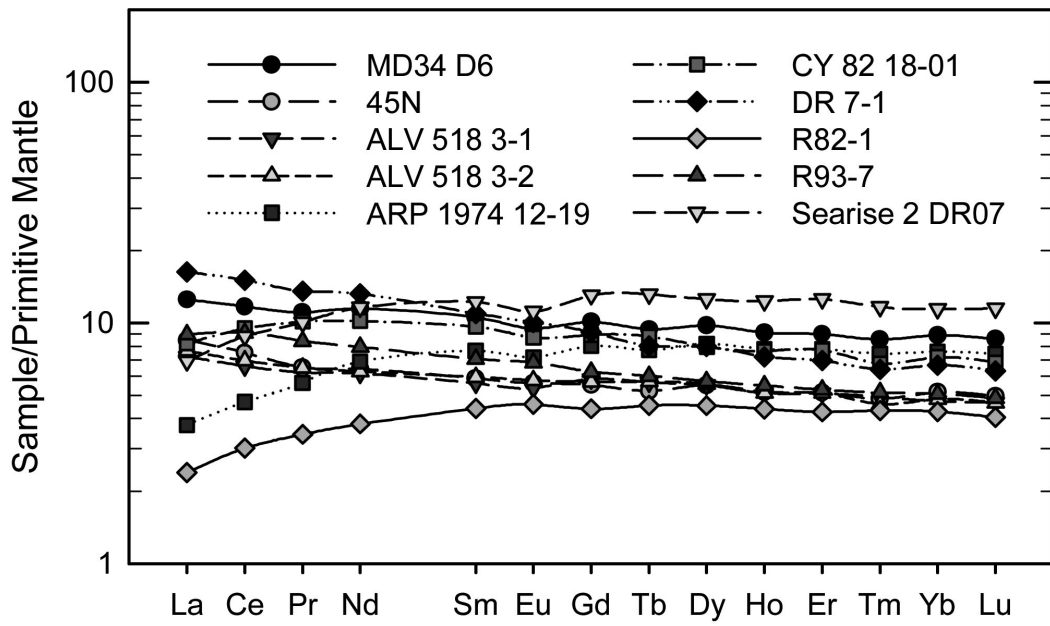


Figure 4.2 Plot of rare earth element concentrations normalized to the value of primitive mantle for our MORB samples.

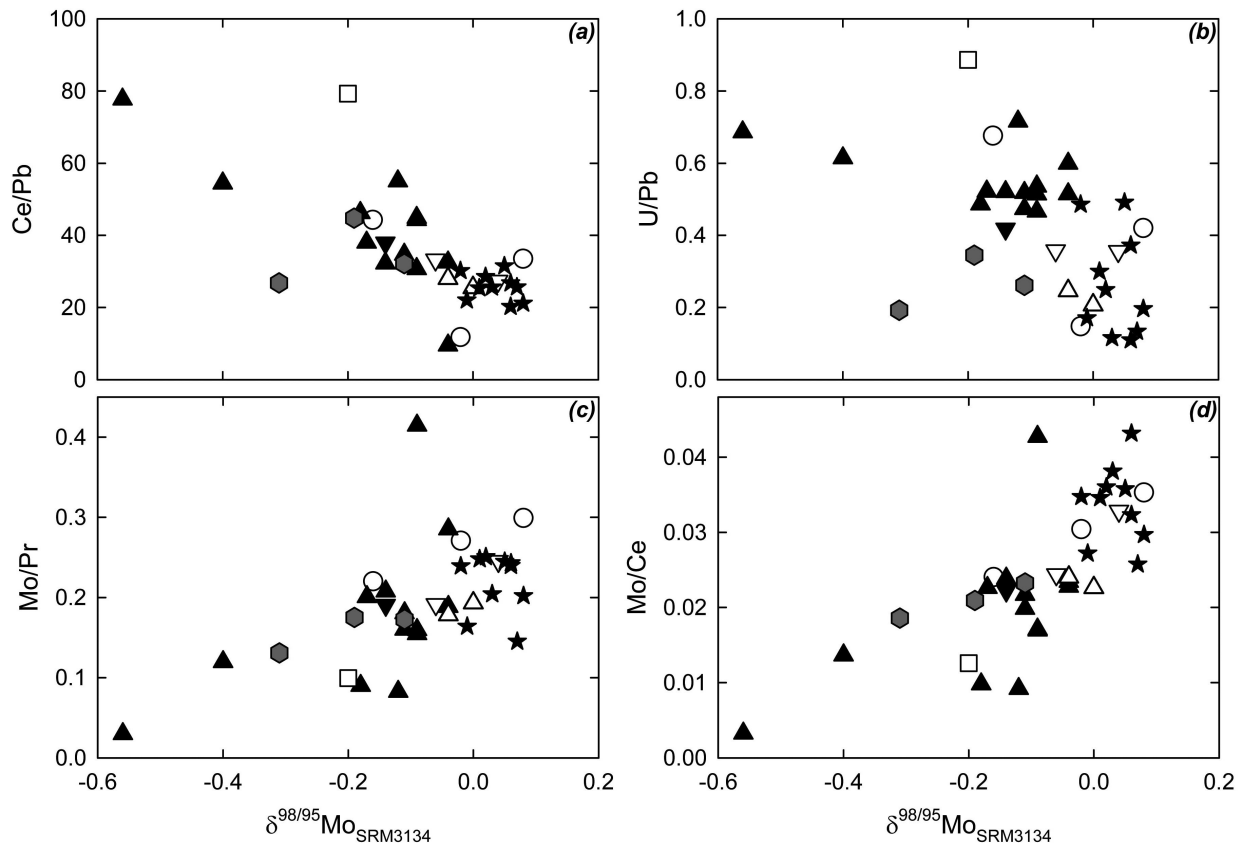


Figure 4.3 Plots of (a) Ce/Pb, (b) U/Pb, (c) Mo/Pr, and (d) Mo/Ce against $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ values for OIBs and MORBs samples. Data from Table 3.1, 3.2, 4.1, and 4.2. Symbols as in Figure 3.2 and 4.1.

A major conclusion from Chapter 3 was that sulphide preferentially incorporates heavier Mo isotopes and fractionates both chalcophile elements and Mo isotopes. This assumption was based on correlations between $\delta^{98/95}\text{Mo}$ and Ce/Pb, U/Pb, Mo/Ce, and Mo/Pr. Results from MORBs are plotted along with OIBs to test this argument in Figure 4.3. The MORB results fit into the previously observed trends. This observation supports the idea that sulphide fractionation is the most likely cause of the variability in $\delta^{98/95}\text{Mo}$ and the correlations with Mo/Pr, Mo/Ce, Ce/Pb and U/Pb in intraplate magmas as well as differences between MORB and ultramafic rocks, in particular mantle xenoliths (Figure 4.1 and 4.3).

While immiscible sulphides retained in the mantle during partial melting was proposed as the reason of Mo isotopic fractionation in OIBs (Chapter 3), Hart and Gaetani (2006) and Burton et al. (2012) also suggested sulphide fractionation based on Pb content and isotopic composition in MORBs and OIBs. Hart and Gaetani (2006) suggested because of the greater density than silicate melt, sulphide melts might be likely to aggregate or pond at depth near the sulphide solidus, and this strips Pb from the silicate phase. This is consistent with the difference in $\delta^{98/95}\text{Mo}$ between ultramafic samples and basalts (Table 3.1, and 4.1, Figure 3.2 and 4.1), which means there is a ubiquitous hidden residue of Mo bearing sulphide left from partial melting. If so, then the Mo/Ce ratio of most basalt should reflect buffering by a coexisting sulphide liquid phase during partial melting.

4.5.2 Molybdenum budget of the mantle

Molybdenum abundance in the mantle was estimated by Newsom and Palme (1984) based on the relative consistency of Mo/Nd they found in a number of terrestrial samples. In addition, the Mo/Ce values in MORBs seem to be uniform and have been used for estimating the Mo abundance of the primitive mantle (Sims et al., 1990). However, Mo is known to be more incompatible than Nd and less incompatible than Ce between the partitioning of silicate mineral and silicate melt (Sun and McDonough, 1989). It was generally thought that Mo/Pr values are uniform in both MORBs and OIBs, although Mo may be slightly more incompatible than Pr (Newsom et al., 1986). However, both Mo content and Mo/Pr values vary in ultramafic samples (Table 4.1 and 4.2). Molybdenum prefers a monosulphide solid solution over sulphide liquid in silicate melts (Li and Audetat, 2012), and the partition coefficient of Mo between sulphide and silicate melt changes as a function of sulphur and oxygen fugacity (Li and Audetat, 2012; Lodders and Palme, 1991). This might explain why the Mo content and Mo/Pr values in ultramafic samples vary dramatically, but their isotopic composition remains relatively constant. In different sulphur and oxygen fugacity, the partition coefficient of Mo between sulphide and silicate melt changes over two orders of magnitude (Li and Audetat, 2012; Lodders and Palme, 1991), which causes Mo heterogeneity in the mantle. However, the residual sulphide still dominates the Mo budget of the mantle leading to a uniform heavy Mo isotopic

composition.

Although Mo/Pr and Mo/Ce seem not to fractionate in a systematic fashion in oceanic basalts (Newsom et al., 1986; Sims et al., 1990), in reality the significant scatter in Mo/Ce for a given Ce probably reflects variable retention of Mo in residual sulphide (Figure 4.4). Therefore, in the presence of residual sulphide, both Pr and Ce are likely more incompatible than Mo during bulk mantle melting, and the real Mo budget of the primitive mantle would be higher than has previously been deduced on the basis of basalt Mo/Pr and Mo/Ce. This is consistent with the fact that the so estimated Mo abundance of 39 ppb for the primitive mantle (Palme and O'Neill, 2007) and 25 ppb for the depleted mantle (Salters and Stracke, 2004) is more than an order of magnitude lower than the mean measured Mo content in our mantle xenoliths (910 ppb, Table 4.1).

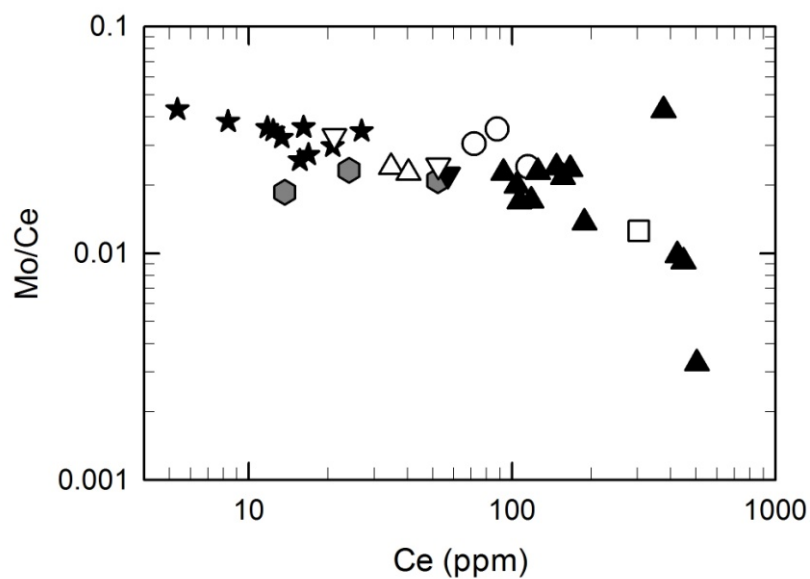


Figure 4.4 Plot of Mo/Ce versus Ce abundances of OIBs and MORBs samples. Data from Table 3.2, and 4.2. Symbols as in Figure 4.5.

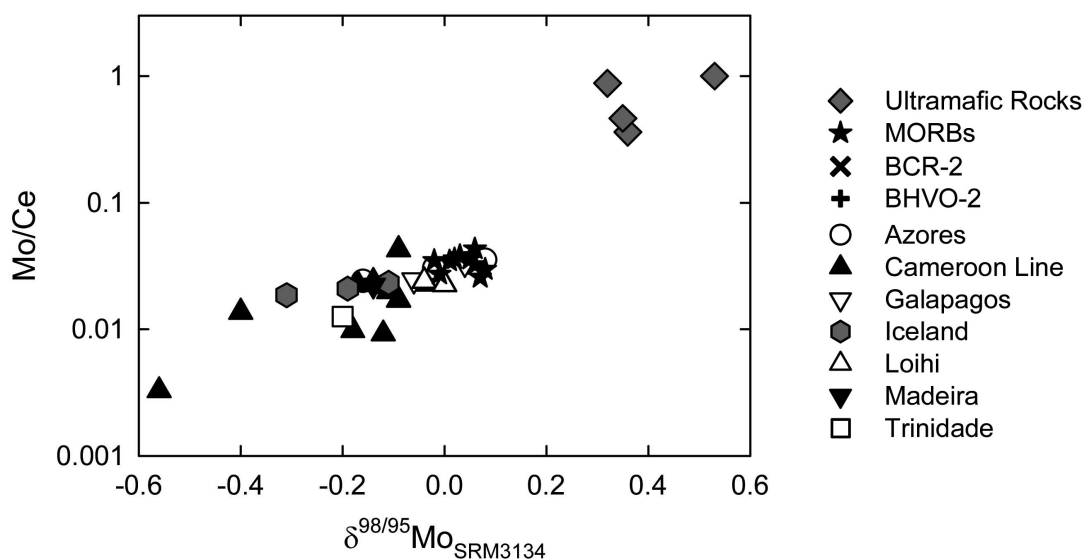


Figure 4.5 Plot of Mo/Ce versus $\delta^{98/95}\text{Mo}$ values of OIBs, MORBs and ultramafic samples. Data from Table 3.1, 3.2, and 4.1.

Isotopic data for mantle sulphides should allow this corrected mantle molybdenum concentration to be determined more precisely through mass balance. In the absence of such studies a first estimate can be derived from the limited amount of data for ultramafic rocks. Within the ultramafic samples studied here, the most depleted one (DTS-1) has the highest Mo/Ce ratio (~ 1). The lowest Mo/Ce value is > 0.3 , which contrasts with basaltic values of < 0.1 (Figure 4.5). Very few reliable data for other ultramafic rocks are available. Molybdenum concentrations (without REE data) were reported for a range of rock types by Kuroda and Sandell (1954) (Table 4.3 and 4.4). They noted that Mo concentrations were broadly similar through all igneous rock types from ultramafic to felsic (Table 4.4), which would be consistent with some level of buffering by sulphides. Limited data for komatiites are also available and these display a range from basaltic like to higher Mo/Ce (0.01-0.19)

(Sims et al., 1990). However, due to there is only little information provided about these komatiites, we cannot exclude the possibility that these high Mo/Ce ratio might actually be affected by crustal contamination (Mo/Ce = 0.18 (Rudnick and Gao, 2003)). Data are available for anomalous enriched assemblages (MARID-like rocks) in the suboceanic mantle (Gregoire et al., 2000). These four samples have highly variable Mo/Ce ranging between 0.02 and 0.16 consistent with their high levels of enrichment. They are almost certainly not representative of the depleted mantle. Based on the available data the Mo/Ce and Mo concentration of the depleted mantle may therefore have been significantly underestimated.

Table 4.3 Molybdenum abundances in ultramafic rocks reported by Kuroda and Sandell (1954)*

Rock type	n	Range of [Mo] (ppm)	average of [Mo] (ppm)
Pyroxenite	1	0.6	0.6
Peridotite	3	0.5-1.3	0.9
Dunite	3	0.0-0.5	0.3
Serpentine	10	0.0-0.4	0.3
Antigorite	1	0.1	0.1
Kimberlite	1	0.9	0.9

Table 4.4 Molybdenum abundances in different type rocks reported by Kuroda and Sandell (1954)*

Rock type	average of Mo abundance (ppm)
Granitic rocks	1.0
Intermediate Rocks	0.7
Basalts and diobases	1.1
Gabbros and related rocks	0.6
Ultramafic rocks	0.4

* The precision of the method in this study is estimated to correspond to 0.1-0.2ppm average deviation for 0-1ppm Mo; above 1-2ppm Mo, it is approximately $\pm 10\%$.

This is illustrated in Figure 4.5, which shows the Mo isotopic compositions of mantle derived samples as a function of their Mo/Ce ratio. The isotopic composition of ultramafic rocks is consistently heavy regardless of Mo concentration (Table 4.1, Figure 4.1). Therefore, the average of the precisely determined data for Tanzanian ultramafic xenoliths provides a best estimate of the mantle $\delta^{98/95}\text{Mo}$ (0.36 ± 0.09 ‰). The best estimate of the mantle Mo concentration is based on the average Mo/Ce of the 4 ultramafic samples in Figure 4.5 (between 0.36 and 1.0) and literature data of ultramafic rocks (Gregoire et al., 2000), which is approximately 0.36 as the Mo/Ce for depleted mantle, or roughly an order of magnitude higher than previously reported values of 0.033 for the depleted mantle (Salters and Stracke, 2004) and 0.027 for the Primitive Mantle or BSE (Palme and O'Neill, 2007). Even using these earlier estimates the mantle is the major (>80%) repository for Mo in the silicate Earth. As such the mantle composition as measured in ultramafic rocks provides the most robust constraints on the overall composition of the primitive mantle or bulk silicate Earth (BSE).

The new estimation of the Mo abundance in Earth's primitive mantle basically follows the model proposed by Sims et al. (1990). Assuming the Earth's primitive mantle has been differentiated into the depleted mantle and continental crust, a mass balance between these two reservoirs can be used to model the primitive mantle abundance of Mo. The mass balance model for a primitive mantle ratio

$(A/B)_{pm}$ can be expressed as following

$$(A/B)_{pm} = \frac{(A/B)_{dm} \times [B_{dm} \times (1 - X_{cc})] + (A/B)_{cc} \times [B_{cc} \times X_{cc}]}{[B_{dm} \times (1 - X_{cc})] + [B_{cc} \times X_{cc}]} \quad (4.1)$$

where pm, dm, cc refer to primitive mantle, depleted mantle, and the continental crust, respectively; A is the element of interest (Mo); B is the normalizing element (Ce); X_{cc} is the mass fraction of continental crust. Within our modeling, the estimate of X_{cc} is based on assuming only upper mantle was involved in the differentiation of the crust, and the value of X_{cc} is 2.0% (DePaolo, 1988). The concentrations of Ce and Mo in the continental crust follow the summarized results presented by Rudnick and Gao (2003), which are 43 and 0.8ppm respectively. Workman and Hart (2005) estimated the chemical composition of the depleted MORB mantle and suggested a value of 0.55ppm for Ce. Because the average Mo/Ce ratio of the depleted mantle is approximately 0.36 as mentioned earlier, the calculated Mo/Ce value of primitive mantle is around 0.15. However, estimates of the Ce content of primitive mantle could be varied. McDonough and Sun (1995) and Palme and O'Neill (2007) proposed a Ce content of the primitive mantle between 1675 and 1786 ppb, respectively. Taking this into account, the calculated Mo abundance of primitive mantle should be between 251 and 268 ppb, significantly higher than proposed in literatures (Palme and O'Neill, 2007; Sims et al., 1990) reflecting the higher Mo/Ce values found in this study.

The $\delta^{98/95}\text{Mo}$ value and revised Mo concentration of the BSE so estimated is given in Table 4.5 together with that of the depleted mantle, and the oceanic and continental crust. To estimate the Mo isotopic composition of oceanic crust we have used the MORB average from this study ($\delta^{98/95}\text{Mo} = 0.03 \pm 0.07\text{‰}$). The Mo content of continental crust is as recommended previously (Rudnick and Gao, 2003), but the data for Mo isotopic compositions are still quite limited. From available granites data (Siebert et al., 2003; Voegelin et al., 2012; Yang et al. 2012), the $\delta^{98/95}\text{Mo}$ of average continental crust is estimated to be marginally heavier than that of oceanic crust. This $\delta^{98/95}\text{Mo}$ value of the BSE and the mantle is 0.3‰ heavier than that estimated for the continental crust (which is resolvable due to our long-term external instrument reproducibility is 0.09‰). If heavy Mo is indeed retained in sulphides in the mantle then the value is consistent with this fractionation during mantle melting.

Table 4.5 Estimates of Mo content and $\delta^{98/95}\text{Mo}$ value of the BSE.

	Mo abundance (ppb)	$\delta^{98/95}\text{Mo}$
Continental Crust	800 ^a	0.08
Oceanic Crust	480	0.03
Mantle	250-265	0.36
Bulk Silicate Earth	251-268	0.35

^a Rudnick and Gao (2003)

In the modern Earth, the major rivers have relatively heavy Mo isotope compositions ($\delta^{98/95}\text{Mo}$ up to 2.3‰, Archer and Vance, 2008; Neubert et al., 2011). Neubert et al. (2011) explained this by incongruent weathering of sulphides from basalts. If a similar process has been operating for other continental lithologies since the Archean,

then removal of isotopically heavy Mo with or from the continents since the Archean over time could also drive the continental crust to an isotopically lighter overall composition. The fractionation of Mo isotopes in subduction zones is currently poorly understood. Further work is needed to confirm the main reasons for an apparent difference between the crust and the mantle.

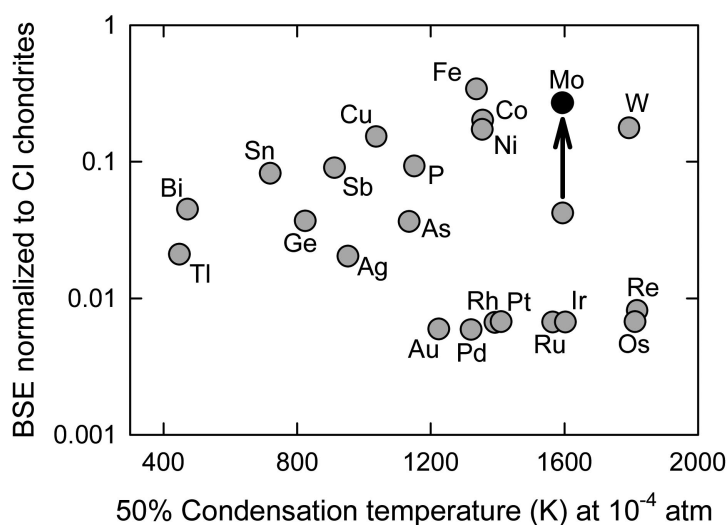


Figure 4.6 Abundances of siderophile elements in the bulk silicate earth (normalized to CI chondrites) versus condensation temperatures. Data from Table 4.5 and Palme and O'Neill (2007).

Finally, the revised Mo abundance for the BSE dramatically changes the constraints that exist on core formation. The prior high degree of depletion of Mo relative to Ni, W and Co was hard to explain without removal by sulphide during the end of core formation (Lodders and Palme, 1991; Wade et al., 2012). The revised estimate for the BSE is shown in Figure 4.6 relative to these elements. It can be seen that Mo is now no more depleted than other moderately siderophile elements and requires no special late removal mechanisms. As such there is no evidence from Mo that the

later stages of accretion were particularly sulphur or sulphide rich.

4.6 Summary

1. The Mo isotopic composition of ultramafic rocks is quite uniform and distinctly heavy relative to mantle-derived basalt.
2. Both Mo content and isotopic composition are uniform within MORB with respect to OIB.
3. The relationships between $\delta^{98/95}\text{Mo}$ and Ce/Pb, U/Pb, Mo/Ce, and Mo/Pr in OIB also hold true for MORB (Figure 4.3), giving additional support for the idea that sulphide fractionation might be the key factor for the fractionation of chalcophile elements and Mo isotopes.
4. Sulphide is the dominant phase of the Mo budget in the mantle, and the fact that Mo is only moderately incompatible. This implies that the isotopic composition of the mantle represents the bulk silicate Earth. The Mo concentration in the BSE is provisionally estimated to be an order of magnitude higher than previously assumed and the Mo isotope composition ($\delta^{98/95}\text{Mo} = 0.35\text{‰}$) is heavy relative to the crust ($\delta^{98/95}\text{Mo} = 0.03\text{--}0.08\text{‰}$).

CHAPTER FIVE



Molybdenum isotope fractionation in meteorites and planet formation

5.1 Introduction

Isotopic variations in bulk meteorite samples can provide important information about early Solar System evolution. For example, core segregation is one of the most important events in the history of planetary bodies, and radiogenic isotope studies give some idea of timing of this event (Kleine et al., 2002; Yin et al., 2002b). The actual physical conditions during core-mantle differentiation, e.g. oxygen fugacity or temperature, have more limited constraints. During core-mantle differentiation, the lighter silicates and associated lithophile elements remain in the mantle while siderophile elements sink in dense metallic and sulphide liquids to the centre to form the core. Although it is impossible to sample Earth's core directly, primitive chondritic meteorites offer a proxy for the bulk Earth (Allègre et al., 1995; McDonough, 2003; Palme and O'Neill, 2007) such that the core's composition can be inferred from the difference relative to the silicate Earth. Core formation results in depletions in the abundances of siderophile elements in the primitive mantle or bulk silicate Earth (BSE) relative to chondrites, depending on the strength of the partitioning into metallic liquids.

Differences in bonding between metallic or sulphur-rich liquids and silicate or silicate liquids are likely to generate small but potentially measurable isotopic effects. On this basis, Georg et al. (2007) presented the first isotopic evidence for the composition of the core by demonstrating silicon (Si) isotopic fractionation in the Earth's mantle,

which appears to be residual to the segregation of Si-bearing metal. Similarly, Moynier et al. (2011) present measurements of Cr stable isotopes in a range of meteorites and argue that Cr partitioning into Earth's core prefers light isotopes. Many previous studies had already shown that the chemical composition of Earth's mantle could provide critical information about the physicochemical conditions at the time of core formation. The degree of depletion of slightly siderophile elements, such as V, Cr, Mn and Nb, has become an indicator of planetary core formation conditions such as oxygen fugacity. Many studies have tried to investigate the conditions under which these elements partition into the core (Chabot and Agee, 2003; Wade and Wood, 2005; Wood et al., 2008), and very reducing conditions appear necessary to explain the budgets in the silicate Earth (Wood et al., 2008).

As the most strongly depleted moderately siderophile and refractory element in the bulk silicate Earth, molybdenum (Mo) should be an ideal element for studying the processes of core-mantle differentiation. Its factor of >50 depletion (Palme and O'Neill, 2007) is problematic. Based on experimental results the only way to achieve such a high degree of depletion of Mo in the mantle is with the addition of 2% of S in to the core during the final stages of accretion (Wade et al., 2012). The partition coefficient of Mo between sulphide and silicate melt has been shown changing as a function of sulphur and oxygen fugacity (Lodders and Palme, 1991). Due to the increasing S content, Mo will be more strongly partitioned into the metal, making it

much more depleted in the BSE than W, Ni, Co, V, Cr and Nb (Wade et al., 2012). Based on a recent study (this thesis, Chapter 4), the Mo budget in the BSE may have been under-estimated. The Mo mass-dependent isotope fractionation study in the mantle (chapter 4) indicates a Mo abundance that may be as much as 6 times higher than previously estimated. Therefore, the degree to which S rich metallic liquids are really needed at the end of core formation is less clear.

Isotopic studies of Mo in meteorites are mainly focused on mass-independent isotope variations. Molybdenum has seven isotopes and most of them have roughly equal abundances, but importantly, it has three isotopes produced by each of *p*-, *s*-, and *r*-process only. These facts make molybdenum an ideal element for studying isotopic heterogeneity in the Solar System, and especially useful for discussing incomplete homogenization of diverse nucleosynthetic components for different isotopes (Burkhardt et al. 2011). The abundances of elements and their isotopes in our Solar System show significant variations, and these isotope anomalies might occur as a result of heterogeneity of the protosolar nebula or in some cases (especially oxygen) fractionation processes occurring during Solar System formation (Clayton, 2003; Truran Jr and Heger, 2003). These variations contrast with the uniformity of stable isotope abundances for many elements in the Solar System, which implies processes existed that efficiently homogenized the dust and gas from different stellar sources within the young solar nebula. Isotopic heterogeneity has

been recognized on the subcentimetre scale in primitive meteorites, indicating that these might preserve a compositional memory of their stellar sources (Lewis et al., 1994; Lugaro et al., 2003; Savina et al., 2004). Differentiated meteorites, e.g., achondrites, stony-irons, and iron meteorites, also provide key information on earliest Solar System history, because they are the products of the early metal-silicate differentiation, partial melting, as well as metamorphic events in newly formed planetary bodies (McKeegan and Davis, 2007).

Murthy (1962) and Wetherill (1964) first reported mass-independent isotope variations of Mo in some iron meteorites as early as 1960s. Yin et al. (2002a) demonstrated that the molybdenum isotopic compositions of bulk carbonaceous chondrites are distinct from the accepted average Solar value. Additional studies have observed small variations for Mo isotopes in the Allende meteorite and in iron meteorites, mesosiderites, and pallasites (Becker and Walker, 2003; Dauphas et al., 2002b, c; Fujii et al., 2006). Dauphas et al. (2002b, c) provide evidence for Mo heterogeneity between bulk iron meteorites, mesosiderites, pallasites, and chondrites. The presence of molybdenum isotope anomalies is thought to reflect a mixture of different nucleosynthetic components that have survived planetary-scale homogenization in the proto-solar nebula, leading to a conclusion that this isotope heterogeneity is the “cosmic chemical memory” inherited from the interstellar environment from which the Solar System was formed (Dauphas et al., 2002b).

Little is known about mass dependent fractionation of Mo isotopes in our Solar System. Most of the geochemical Mo mass dependent fractionation discussion in the literatures is about redox-related processes happening on earth's surface, (e.g. Colodner et al., 1995; Morford and Emerson, 1999; Neubert et al., 2011; Siebert et al., 2003), and our knowledge of the fractionation happening at high temperatures is still quite limited.

In this study, the mass dependent variations of Mo in the inner Solar System were investigated by analyzing different bulk meteorites (carbonaceous chondrites, ordinary chondrite, enstatite chondrites and iron meteorites). This was done for the first time using the double spike technique. The results are compared with terrestrial values using mass balance arguments to provide information on metal silicate separation and core formation.

5.2 Samples

Several well studied meteorites have been chosen as a sample set, including 1 carbonaceous chondrite, 4 ordinary chondrites, 4 enstatite chondrites, and 9 iron meteorites (Table 5.1). Before determining the mass dependent isotope variation in meteorites, the nucleosynthetic mass independent isotope composition needs to be known. Clayton et al. (1991); Clayton et al. (1984) have pointed out that enstatite chondrites have oxygen isotopic compositions that lie on the terrestrial fractionation

line. This overlapping of oxygen isotopic compositions between enstatite chondrites and terrestrial samples might indicate that material similar to enstatite chondrites built our planet (Javoy et al., 1986). However, this is highly contentious because many features of enstatite chondrite chemistry are hard to reconcile with the composition of the BSE.

Several previous studies (Becker and Walker, 2003; Dauphas et al., 2002a; Yin et al., 2002a) were not able to resolve Mo isotopic differences between terrestrial samples, ordinary and enstatite chondrites. Burkhardt et al. (2011) reported Mo isotopic anomalies for ordinary and enstatite chondrites although these were generally smaller than (or equal to) their analytical uncertainties. Thus ordinary and enstatite chondrites would be straightforward material to represent Earth-like material for our purposes. One of the enstatite chondrites studied here, Abee, was magnetically separated, and only the remaining non-magnetic (largely silicate) part has been analyzed in this study. (The remainder was consumed in another study.)

Magmatic iron meteorites are thought to represent fragments of cores of differentiated asteroids. Nine well characterized magmatic iron meteorites have been studied, each classified into 5 different chemical groups (Table 5.1). Some of these have been analyzed for their Mo mass independent isotopic anomalies, but no resolvable effects were reported (Becker and Walker, 2003; Dauphas et al., 2002b; Yin et al., 2002a). More recent data (Burkhardt et al., 2011) confirmed that Mo

isotope anomalies in iron meteorites do exist but are very small ($< 2\epsilon$ in all the Mo isotopes). Among these nine iron meteorite samples, Sikhote-Alin is the only sample with two separate small fragments. All analyzed samples were visually fresh, with no weathered crust remaining.

Finally, the composition of bulk Ivuna-like carbonaceous chondrites (CI) are viewed as a measure of average Solar-System abundances and are used as a reference planetary composition for many materials, while other classes of carbonaceous chondrites display more significant nucleosynthetic differences relative to Earth (Burkhardt et al., 2011). Therefore, one CI chondrite (Orgueil) is included in the sample set.

5.3 Methods

All chondrites were hand crushed in an alumina mortar and pestle, then dissolved with a mixture of HF and HNO₃ in sealed Teflon vials on a hotplate at 140°C for at least 3 days. All samples are analyzed as bulk meteorites, with the exception of Abee(EH4) as noted above. All chondrite samples were digested with mini-Teflon hexagonal screw top bombs as described in Prytulak et al. (2011). In order to make certain that all refractory components were dissolved, this bomb digestion technique was repeated up to 5 times for some samples. Iron meteorite samples were polished with SiC sandpaper, and then washed with Milli-Q water. Then they were leached

with 6M HCl for an hour at least 3 times before being digested with 6M HCl. After the polishing and leaching procedures, all of these iron meteorite samples still had more than 90% of the material remaining.

Molybdenum purification follows the techniques described in chapter 2. Iron meteorites were processed through the cation chemistry several times to remove all Fe before anion column chemistry. However this method cannot separate Ru from Mo completely, so additional cation column chemistry with TRU-spec resin used by Burkhardt et al. (2011) was applied to all of the samples.

The details about analytical protocol, external standard reproducibility, and data normalization are described in chapter 2. All Mo isotopic variations are represented by the delta notation as the deviation in per mil (‰).

$$\delta^{98/95}\text{Mo} = \left(\frac{(^{98}\text{Mo}/^{95}\text{Mo})_{\text{sample}}}{(^{98}\text{Mo}/^{95}\text{Mo})_{\text{standard}}} - 1 \right) \times 1000$$

One or two aliquots of basaltic USGS standard BHVO-2 were processed with each batch of samples. The basaltic standard BHVO-2 shows very good reproducibility with average $\delta^{98/95}\text{Mo}$ values of -0.00 ± 0.06 ‰ (2s.d.) during the same period of time when the samples used in this chapter were analyzed.

In order to investigate mass-dependent fractionation, mass independent variation caused by nucleosynthetic effects must be calculated out. The mass independent Mo isotopic anomalies in each bulk CI chondrite and all the iron meteorites among our

sample set have been well determined (Burkhardt et al., 2011), and these values were applied for normalization calibration. There might be some risk for this normalization calibration due to heterogeneous mass independent isotopic variation or alteration in the bulk meteorite. Therefore, in this study, only the fresh pieces of sample were applied. And those meteorites known for their heterogeneous isotopic variation (i.e. Murchison) were not included in the sample set. Furthermore, because the external standard reproducibility of $^{98/95}\text{Mo}$ in this study is 0.09‰, only the meteorites having mass independent variations in ^{95}Mo , ^{97}Mo , and ^{100}Mo (normalized to $^{96}\text{Mo}/^{98}\text{Mo}$) smaller than 0.9‰ were included in the sample set in order to minimize the possible effect of heterogeneous isotopic variation. The Mo isotopic anomalies in ordinary and enstatite chondrites are consistent and smaller than analytical uncertainties, so the average isotopic anomalies published by Burkhardt et al. (2011) were applied to their normalization.

5.4 Results and Discussion

The results of the measurements of mass dependent Mo isotopic fractionation for all samples are given in Table 5.1 (relative to NIST SRM3134). Errors are given as 2 standard deviations of all duplicates of each sample. If only one aliquot of a sample was measured successfully, the error is given as 2 standard deviations of Alfa Aesar standard measurements during the same measurement session as the sample. All of the results are also summarized in Figure 5.1.

Table 1 Molybdenum concentration and isotope compositions of meteorites.

Table 2. Molybdenum concentration and isotope compositions of meteorites.

Sample	Classification	n ^a	Mo (ppm)	$\delta^{98/95}\text{Mo}_{\text{SRM3134}}$		
				replicates	average	2 s. d. ^b
USGS standard						
BHVO-2	Basalt	7	3.54	0.01, 0.00, -0.05, 0.01, 0.00, -0.02, 0.00	-0.01	0.06
Carbonaceous Chondrite						
Orgueil	CI	4	0.95	-0.05, -0.07, -0.08, -0.18	-0.09	0.11
Ordinary Chondrite						
Bremervörde	H/L3	1	1.01	-0.12	-0.12	0.05 *
Barratta	L4	4	0.79	-0.10, -0.14, -0.10, -0.12	-0.11	0.04
Bruderheim	L6	1	0.78	-0.11	-0.11	0.05 *
Parnallee	LL3	5	0.63	-0.12, -0.10, -0.09 -0.11, -0.08	-0.10	0.03
Enstatite Chondrite						
Abee	EH4	2	0.38	-0.09, -0.08	-0.08	0.01
Indarch	EH4	2	1.27	0.06, 0.02	0.04	0.06
Hvittis	EL6	1	0.93	0.08	0.08	0.06 *
Khairpur	EL6	2	0.90	0.13, 0.14	0.13	0.02
Iron meteorite						
Arispe	IC	1	6.37	-0.09	-0.09	0.04 *
Negrillos	IIAB	1	6.11	-0.10	-0.10	0.04 *
North Chile	IIAB	1	6.60	-0.08	-0.08	0.04 *
Sikhote-Alin A	IIAB	1	6.78	-0.21	-0.21	0.03 *
Sikhote-Alin B	IIAB	1	6.14	0.11	0.11	0.03 *
Sikhote-Alin mean			6.46	0.06	-0.06	
Charcas	IIIAB	1	6.56	-0.08	-0.08	0.04 *
Henbury	IIIAB	1	5.39	-0.14	-0.14	0.04 *
Clark County	IIIF	1	4.38	-0.06	-0.06	0.04 *
Duel Hill	IVA	1	5.70	0.31	0.31	0.04 *
Gibeon	IVA	1	5.20	-0.08	-0.08	0.04 *

^a Number of duplicates for the same sample.^b The errors are 2 standard deviations of all duplicates of each sample.

* Only one aliquot successfully analysed for these samples, so the errors are given as 2 standard deviation of standard measurements in each measuring session.

Table 5.2 Major and trace element compositions of iron meteorites. Abundance in ppm except Ni in %.

	Cr	Co	Ni	Cu	Ga	Ge	As	Ru	Rh	Pd	Sb	W	Re	Os	Ir	Pt	Au
Arispe	14 ^l	4600 ⁱ	6.54 ⁱ	112 ^l	54 ⁸	243 ⁸	5.3 ^l	15.2 ^f	3 ^f	2.84 ^f	0.12 ^l	2.34 ^f	0.922 ^f	8.16 ^f	11 ^f	22.9 ^f	0.771 ^f
Negrillos	92°	4490°	5.25°	136°	57.5°	179°	3.55°	23.1 ^e	3.49 ^f	1.83 ^f		3.72°	4.89°	66.8 ^f	47.4°	33.1°	0.477°
North Chile	45°	4540°	5.6°	131°	58.5°	177°	4.81°	17.7 ^a	3.1 ^a	1.95 ^a	0.5 ^a	2.58°	0.212°	1.12 ^a	3.43°	21.8°	0.617°
Sikhote-Alin	31°	4790°	6.03°	117°	53.7°	158°	9.4°	4 ^c	1.73 ^c	2.23 ^c	0.093 ^c	0.74°			0.024°	5.5°	1.05°
Charcas	29 ^l		7.86 ^k	151 ^l	19.4 ^k	41.4 ^k	4.8 ^l			2.4 ^l	0.027 ^l		0.149 ^b	1.09 ^b	1.9 ^k	12.5 ^b	
Henbury	135 ⁿ	4920 ⁿ	7.47 ^f	152 ⁿ	18.4 ⁿ	33.7 ⁿ	3.1 ^l	14 ^f	2.25 ^f	2.35 ^f	0.028 ⁿ	1.32 ⁿ	1.58 ⁿ	16 ^f	13.4 ⁿ	15.8 ⁿ	0.486 ⁿ
Clark County	1565 ^l		7 ^m	80 ^l	6.8 ^m	0.96 ^m	0.79 ^b	5.9 ^e	0.88 ^b	2.7 ^l	0.018 ^l	1.77 ^j	0.65 ^e	9.3 ^e	6.5 ^e	9.7 ^e	0.302 ^e
Duel Hill	34 ^p	4290 ^p	10.5 ^p	209 ^p	2.1 ^p	0.111 ^p	14.4 ^p	1.88 ^d	0.67 ^d	7.1 ^d		0.28 ^p	0.032 ^d	0.23 ^d	0.362 ^p	3.1 ^d	2.76 ^p
Gibeon	210 ^p	3850 ^p	7.78 ^p	169 ^p	2.04 ^p	0.111 ^p	3.46 ^p	4 ^f	1.2 ^f	3.75 ^f	0.011 ^l	0.63 ^p	0.285 ^p	3.09 ^f	2.52 ^p	5.9 ^p	0.882 ^p

a. Campbell et al. (2002); b. Cook et al. (2004); c. D'Orazio and Folco (2003); d. McCoy et al. (2011); e. Pernicka and Wasson (1987); f. Petaev and Jacobsen (2004); g. Reed (1972); h. Ryan et al. (1990); i. Scott (1977); j. Scott (1978); k. Scott et al. (1973); l. Smales et al. (1967); m. Wasson (1967); n. Wasson et al. (1998); o. Wasson et al. (2007); p. Wasson and Richardson (2001)

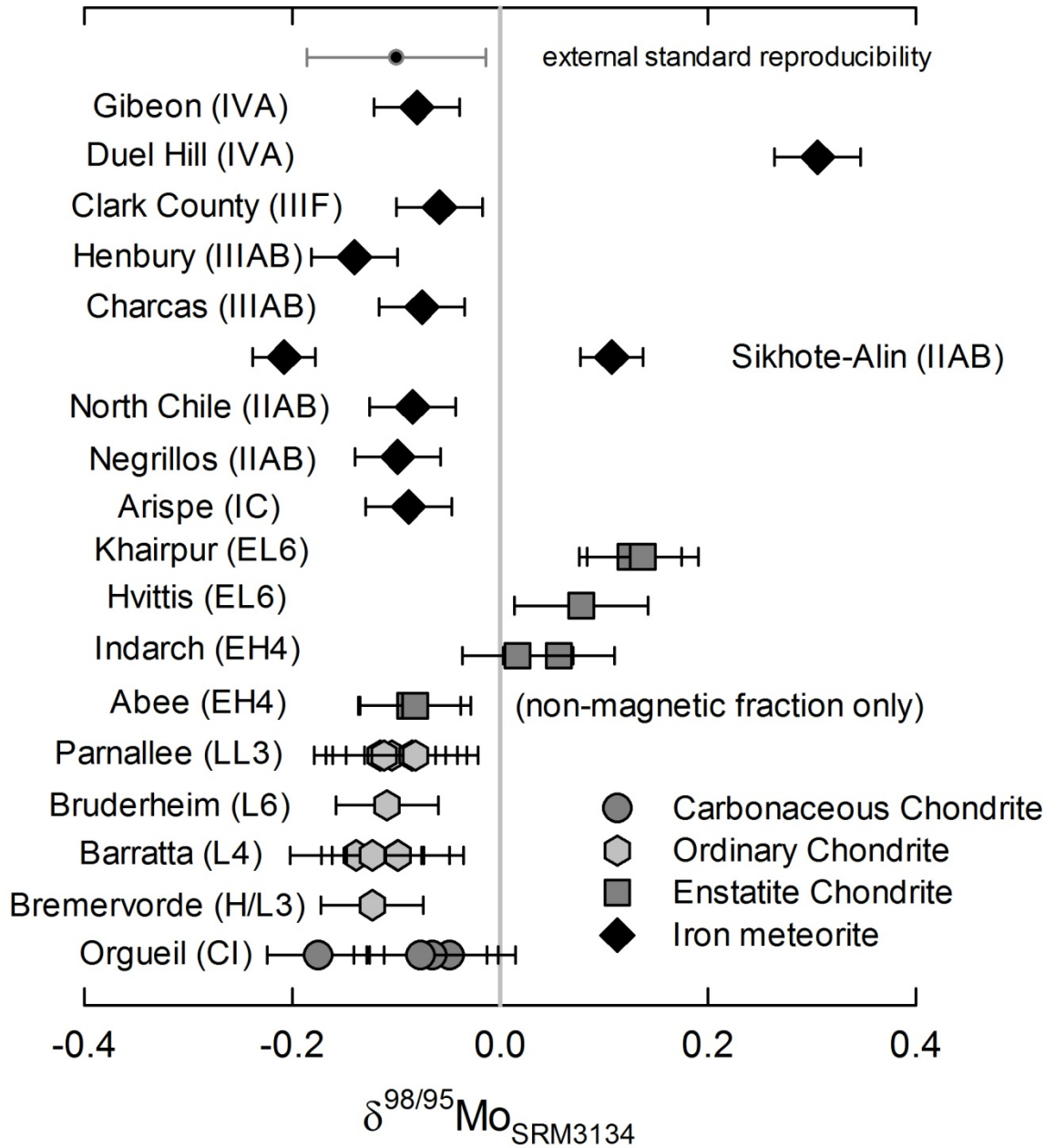


Figure 5.1 The Mo isotope compositions of meteorites, showing the degree of replication achieved for each sample. Errors given are 2 standard deviations of standard measurements in each measuring session. The long term external standard reproducibility of $^{98}\text{Mo}/^{95}\text{Mo}$ is $\pm 0.09\%$ based on Alfa Aesar standard solution.

5.4.1 Homogeneity between ordinary and CI carbonaceous chondrite

Different groups of ordinary chondrites (from H to LL) were included in the sample set. Their Mo contents gradually decrease from H group to LL group, which is

consistent with a positive relationship between refractory siderophile element concentrations and bulk iron contents (Table 5.1). The Mo contents vary by a factor of 2, but all the investigated ordinary chondrites have uniform $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ ranging between -0.12 ± 0.05 and $-0.10 \pm 0.03\%$. Siderophile element abundances should decrease and oxidation state increase through the sequence H–L–LL (Krot et al., 2007), so Mo behaves in a manner consistent with its siderophile affinity. The Mo isotope composition appears unaffected by the oxidation state of the parent asteroids and there is no evidence that differing proportions of metallic iron fractionate Mo isotopes.

The Mo isotopic composition of the analyzed CI chondrite ($\delta^{98/95}\text{Mo}_{\text{SRM3134}} = -0.09 \pm 0.11\%$) is also identical with the values observed in ordinary chondrite (-0.12 to -0.10%). Generally, CI chondrites are thought to be the most primitive meteorites compositionally and provide the best match to the solar photosphere, although they also contain some secondary mineral phases that provide a record of extensive and multistage aqueous alteration on their parent body (Endress and Bischoff, 1996; Endress et al., 1996; McSween and Richardson, 1977). However, the results for the CI chondrite indicate that these processes do not fractionate Mo isotopes significantly (or within the error), and lead to identical values for CI and ordinary chondrites. Similar results are reported by Burkhardt et al. (2013); they obtain indistinguishable $\delta^{98/95}\text{Mo}_{\text{SRM 3134}}$ values of ordinary and carbonaceous chondrite with the exception of

CM and CK which have been deliberately avoided in our study. Their equivalent data average $-0.16 \pm 0.02\text{‰}$, which is within error of our results.

This common value of ordinary and CI chondrites is much lighter than the Mo isotopic composition of BSE ($\delta^{98/95}\text{Mo}_{\text{SRM3134}} = 0.35$, chapter 4). While ordinary chondrites are generally thought to be similar to the Earth chemically and CI chondrites are a close match of solar abundances for elements (Palme and Jones, 2003), the heavier Mo isotopic composition of the BSE possibly reflects stable isotope fractionation during core formation (Hin et al., 2013) as first proposed for Si (Armytage et al., 2011; Georg et al., 2007). On this basis, lighter Mo isotopes preferably partition into core-forming metallic and sulphidic liquids.

The evolution and accretion model presented by Wade et al. (2012), proposes that Mo strongly partitions into the core with sulphur during the end of core formation. It is thought that Mo in sulphides is isotopically heavy relative to silicates (chapter 4), so this process should produce an isotopically lighter BSE compared to ordinary and CI chondrites. They assumed very strong depletion of Mo abundance in BSE (Palme and O'Neill, 2007), but more recent estimates show that the Mo budget is actually higher (chapter 4). The revised estimate of the BSE Mo budget is similar to the levels of depletion in refractory siderophile elements such as W, Ni and Co, and fits the continuous accretion model proposed by the same group earlier (Tuff et al., 2011).

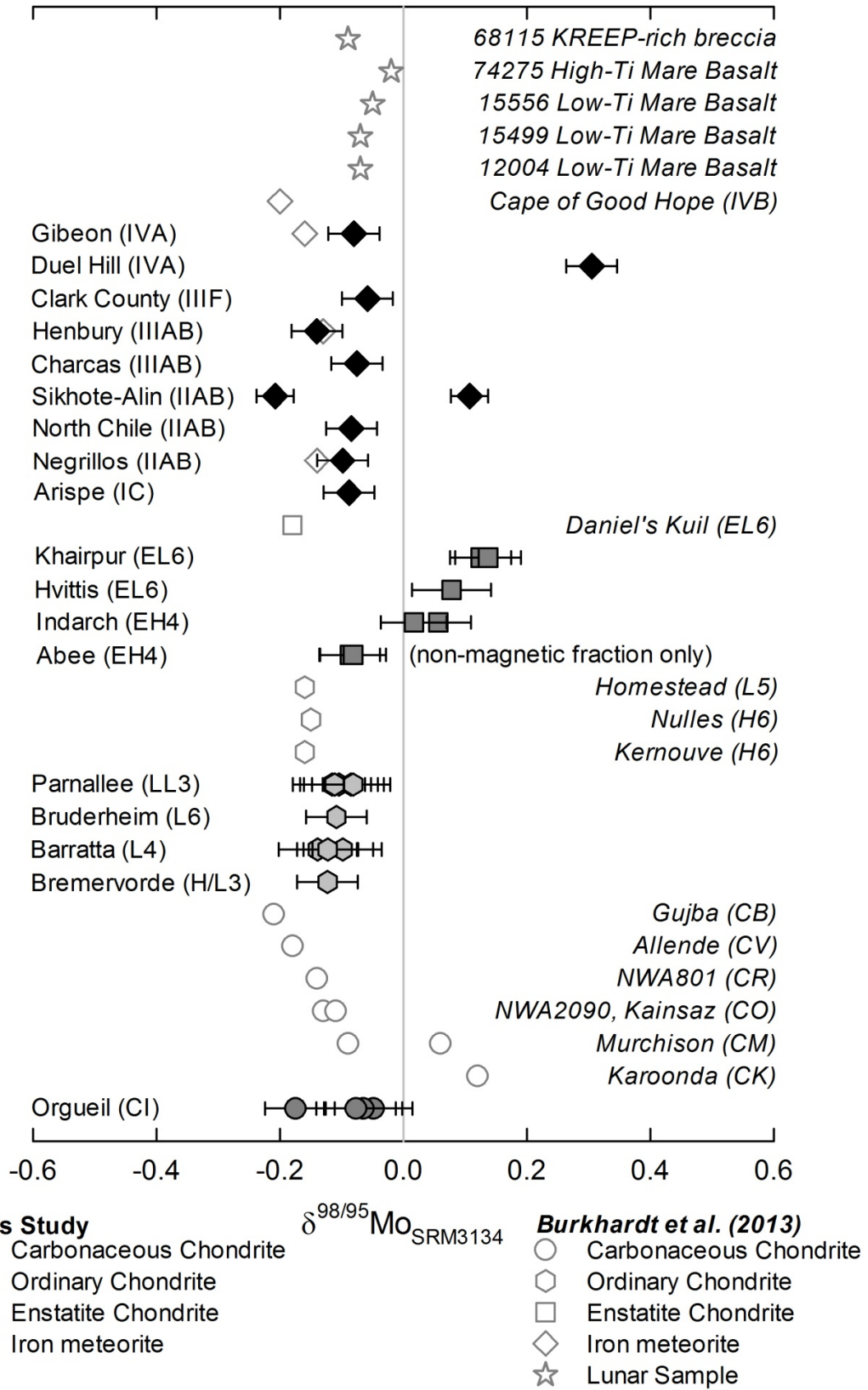


Figure 5.2 The Mo isotope composition of meteorites and results comparison between Burkhardt et al. (2013) and this study.

5.4.2 Isotopic fractionation within iron meteorite parent bodies

Due to its siderophile nature, the Mo contents in iron meteorites are higher than in chondrites. However, most of the $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ values are identical within error to ordinary and CI chondrites (Table 5.1). Three of these iron meteorites have also been analyzed by Burkhardt et al. (2013) and show comparable results except Gibeon (Figure 5.2). However, Gibeon has been demonstrated to be chemically heterogeneous between different pieces (Wasson and Richardson, 2001). Although these nine analyzed iron meteorites were selected from five different chemical groups, the results of seven of them ($-0.14 \pm 0.04\text{‰}$ (2s.d.) to $-0.06\text{‰} \pm 0.03\text{‰}$ (2s.d.)) are not significantly different from the values observed in CI and ordinary chondrites ($-0.09 \pm 0.11\text{‰}$ (2s.d.)). These results are not surprising because most Mo in the parent body of these irons must partition into their core, thus these irons should have Mo isotopic composition identical with the primitive asteroids from which the metallic core-forming liquids segregated. This is also consistent with the earlier indications that metallic iron does not fractionate Mo isotopes to any large extent.

The two fragments of Sikhote-Alin were processed separately from each other, and they show different Mo contents and $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ values demonstrating Mo isotopic fractionation within a single iron meteorite. Sikhote-Alin is classified as group IIAB, with a coarse octahedrite structure, which suggests these two analyzed pieces may represent different octahedrite phases. Trace elements partition between

the two phases during growth of kamacite (Rasmussen et al., 1988). There is about 10 % Mo content difference between them, and the piece with lower Mo concentration is heavier isotopically. This indicates that fractionation can take place internally during trace element partitioning. The fractionation is sizable (0.3‰ on $\delta^{98/95}\text{Mo}$) between different phases (Table 5.1). The calculated average $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ value (-0.06‰) of Sikhote-Alin from these two pieces is in the range of most other iron meteorites (Table 5.1, Figure 5.1).

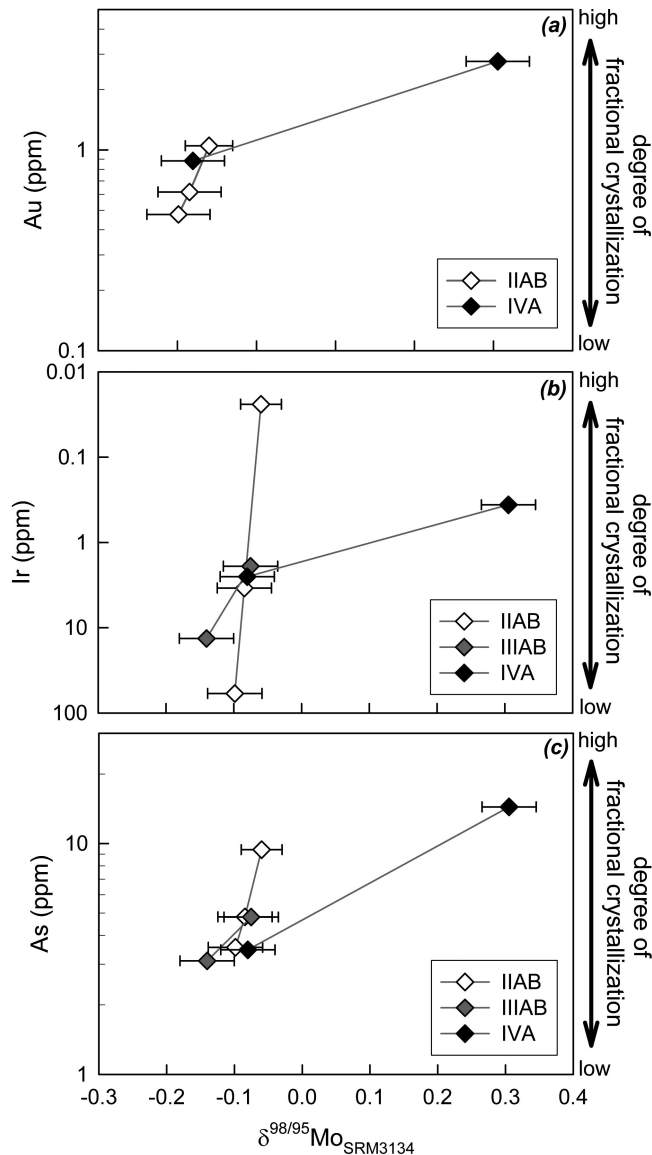


Figure 5.3 Plots of (a) Au, (b) Ir, and (c) As contents against $\delta^{98/95}\text{Mo}$ values for IIAB, IIIAB, and IVA iron meteorites. Data from Table 5.1, and 5.2.

Duel Hill has the heaviest Mo isotopic composition of all analyzed meteorites ($\delta^{98/95}\text{Mo}_{\text{SRM3134}} 0.31 \pm 0.04\text{‰}$). It is classified as a IVA iron meteorite with fine kamacite with a bandwidth of approximately 0.3mm. Although Schaudy et al. (1972) suggested that IVA irons might be formed in two different parent bodies, Wasson and Richardson (2001) show an extensive compositional data set and conclude that the IVA irons must originate in a single parent body core. In fact, the other IVA iron meteorite (Gibeon) in our sample set has a Mo isotopic composition consistent with the other groups, therefore, this unique isotopic signature of Duel Hill must relate to something else rather than its bulk parent body composition. Based on its trace elements composition, Duel Hill seems to have formed around the end of the IVA fractional crystallization trend, at which point the core was approximately 80% crystallized. This contrasts with Gibeon which is a sample of core material that had crystallized between 30 and 50% (Wasson and Richardson, 2001). Therefore, Mo isotopes might be fractionated during core fractional crystallization.

The Au, Ir and As concentrations of iron meteorites have been used for modeling the degrees of fractional crystallization (Wasson, 1999; Wasson and Richardson, 2001). Molybdenum contents show a very limited range of variation between different groups of iron meteorites and their degrees of fractional crystallization (Petaev and Jacobsen, 2004). However, the $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ values of iron meteorites from a single group (IIAB, IIIAB, and IVA) seem to vary with these trace element parameters (Figure

5.3, Table 5.2). Although the variations of Mo isotopic composition in IIAB and IIIAB irons are not significant, the available data show that it is still most likely that the iron meteorite with the higher degree of fractional crystallization preserves a heavier Mo isotope composition (Figure 5.3). This isotopic variation might relate to sulphide as found in mantle partial melting (chapter 3 and 4). Sulphur is almost insoluble in solid metal, and the S content has been shown to increase during crystallization (Haack and Scott, 1993). During the early and intermediate stages of fractional crystallization, the effect on Mo isotopic fractionation might not be obvious because sulphur/sulphide contents had not increased greatly. At the end of fractional crystallization sulphur/sulphide abundance was high enough to play an important fractionating role and this could explain the remarkable heavy Mo isotope composition of Duel Hill.

5.4.3 Distinguishing Mo features of enstatite chondrites

Although most of enstatite chondrites are heavily shocked, the Mo isotopes fractionation might actually affect by shock effects. However, all the pieces of enstatite chondrite samples analyzed in this study are visually fresh. And in order to be representative, for each enstatite chondrites measured in this study, there are always at least 5 grams of materials being taken and crushed homogeneously.

Burkhardt et al. (2013) proposed that enstatite chondrites have identical Mo isotopic

signature with magmatic irons and ordinary chondrites, but this argument is based on one sample only. The $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ value of enstatite chondrites in this study range between $0.04 \pm 0.06\text{‰}$ to $0.13 \pm 0.02\text{‰}$, which is heavier than that of carbonaceous chondrites, ordinary chondrites, and most of the iron meteorites (with the exception of Abee, Figure 5.1). Enstatite chondrites are also anomalous in their Si isotopic composition (Armstrong et al., 2011; Georg et al., 2007; Savage and Moynier, 2013). Enstatite chondrites are thought to be formed under extremely reducing conditions (Brearley and Jones, 1998; Keil, 1968), and their unique mineralogy is characterized by high sulphide contents. Therefore, their Mo isotopic compositions are consistent with the theory proposed in chapters 3 and 4 that sulphide dominates Mo isotope fractionation. These samples are analyzed as bulk meteorites, so the process is more likely one of heavier Mo isotopes preserved in sulphide in the area of the solar nebula where enstatite chondrites formed.

Supporting evidence for this model is that, as mentioned earlier, only the non-magnetic fraction of Abee (EH4) was analysed. (The magnetic fraction had been completely consumed in other experiments.) Magnetic separation not only separates metal but also removes some sulphide from the original material. Therefore, the low Mo concentration observed for Abee relative to all other enstatite chondrites (Table 5.1) might be caused by removal of Mo with the metal and sulphide phases. Removal of heavy Mo isotopes with sulphide phases would explain

the lighter isotope composition of Abee and provide support for the argument that sulphide is the major fractionating phase for Mo in meteorites.

5.4.4 Molybdenum isotopic fractionation during the Earth evolution

The estimated $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ (0.34‰) of the BSE (chapter 4) is heavier and distinct from the isotope compositions of chondrites and iron meteorites, which, in the main, define a relatively narrow compositional range (-0.14 to -0.06‰).

The most obvious explanation for this is that Mo isotopes were slightly fractionated during core-mantle differentiation (Burkhardt et al., 2013), in a similar fashion to that which has been demonstrated for Si (Armytage et al., 2011; Georg et al., 2007). Wade et al. (2012) showed that during metal–silicate partitioning, there is an exchange between oxidised Mo in the silicate and reduced Mo in the metal. In order to explain the BSE value, heavy Mo isotopes would have to prefer the oxidizing conditions in the silicate, leaving the metal phase light. No differences between metal and bulk chondrite are currently resolvable, but this is to be expected because most (>95%) of the Mo enters the metallic planetary core. The Mo isotopic compositions of the metallic cores of asteroids and planets could still be lighter than their silicate counterparts. For example, a difference of 0.46‰ between chondrites and Earth's silicate reservoir would be balanced by a difference of only 0.02‰ between Earth's core and chondrites assuming a depletion factor of between 4 and 24 for Mo in the

BSE (see Palme and O'Neill (2007) and Chapter 4). This is much smaller than can be resolved at present in the study of iron meteorites. Characterization of residual silicate reservoirs, other than the BSE, such as by studying HED or martian meteorites, should resolve this. Some shergottites, angrites and eucrites have been investigated (Burkhardt et al., 2013), but their Mo isotopic composition vary significantly (-0.3 to 0.9‰) and may reflect terrestrial weathering effect on these desert finds.

The opposite is found in reducing enstatite chondrites. Isotopically heavy Mo is associated with more reduced conditions, as in bulk enstatite chondrites, and is also associated with more metallic phases. In a similar vein, sulphides appear to fractionate Mo isotopes in mantle derived samples (chapter 4), an assumption that is consistent with leaching experiments from basalts (Voegelin et al., 2012).

It is also possible that equilibrium Mo isotopic fractionation during core-mantle differentiation is not significant or is at least overwhelmed by later effects. The Mo budget of the BSE is very low (0.04 to 0.27 times CI), and as such its isotopic composition is particularly susceptible to that of the latest material that was accreted, including post core formation. It is thought that highly siderophile elements in the BSE were accreted in a late veneer (Chou, 1978; Dale et al., 2012; Walker, 2009). The exact mass of this late veneer is unclear and in particular what proportion of siderophile and atmophile elements were introduced post core formation (see Albarede, 2009; Albarede et al., 2013; Halliday, 2008, 2013; Wood et al., 2008; Wood

et al., 2006). If there were late accretion of material having relatively heavy Mo isotopic composition in the late stages of accretion it would make the BSE heavier in Mo isotopes.

There are two possible candidates for such putative isotopically heavy late -accreted Mo. One is enstatite or CM/CK carbonaceous chondrites, because they are the chondritic meteorite groups that have been found to possess heavier Mo isotopic compositions. The Mo isotopic composition of these chondrites are still slightly lighter than BSE and the CM and CK meteorites have a different nucleosynthetic composition. Nevertheless, more work is needed to determine if this is representative.

The second possibility is that isotopically heavy sulphide liquids from accreted planetary core material dominate the BSE. If, during accretion, impactors fragment into different liquid phases, such as silicate-, metal- and sulphur-rich components, it is conceivable that the metal mixes with Earth's core and that there is no bulk equilibration with the BSE (Dahl and Stevenson, 2010; Deguen et al., 2011; Halliday, 2004; Samuel, 2012; Samuel et al., 2010). This being the case the residual silicate Earth could be dominated by accreted dregs of sulphur rich liquids added at a late stage. The difficulty with this model is that it does not explain the depletion of S in the BSE, which is even more depleted than refractory highly siderophile elements.

Finally it is also possible that the Mo isotopic composition of the Solar System is heterogeneous in a mass dependent fashion such that heavier Mo isotopes were enriched in the section of the disk from which Earth accreted. This could also explain the similarity to the Mo isotopic composition of enstatite chondrites.

5.5 Summary

1. A uniformity of Mo isotopic composition among ordinary chondrite, CI carbonaceous chondrite, and most of iron meteorites investigated in this study has been found with $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ values between -0.14 and -0.06‰. This range of Mo isotopic composition might represent the common feature of bulk planetary bodies in the inner solar system. Variability in the proportion of metallic iron-rich components does not appear to generate isotopic variations.
2. Mass dependent Mo isotopic fractionation takes place within the cores of iron meteorite parent bodies. Within our sample set, it seems not only do the different octahedrite phases have different Mo isotopic compositions, the Mo isotopes appear to be fractionated during fractional crystallization of the asteroidal core. However, further work is needed to provide more evidence.
3. Enstatite chondrites have Mo isotopic compositions that are distinct from the consistent values found between ordinary chondrites, CI carbonaceous chondrites, and most iron meteorites. Their heavier composition might

correlate with their higher sulphide contents as they were formed under extremely reducing conditions.

4. It is unclear why the BSE has heavier Mo isotopic composition than all the meteorites analyzed in this study. Based on the latest experimental results, Hin et al. (2013) conclude that there is equilibrium fractionation of Mo isotopes between liquid metal and liquid silicate and silicate has heavier Mo isotopic composition. They also propose this fractionation is temperature dependent. However, these experiments did not include sulphur/sulphide under any experimental conditions, despite the fact that it has been shown the partition coefficient of Mo between core forming metallic and sulfidic liquids and silicate melt changes as a function of sulfur and oxygen fugacity (Li and Audetat, 2012; Lodders and Palme, 1991; Wade et al., 2012). Core formation is a possibility but if Mo is mainly removed late S-rich liquids one would expect the residual BSE to be isotopically light rather than heavy. It is also possible that Earth simply accreted Mo that is isotopically heavier from this region of the Solar System, in an analogous fashion to that found in enstatite chondrites. Further work is needed in order to better constrain these hypotheses.

CHAPTER SIX



Conclusion and outlook

6.1 Conclusion of this thesis

The objective of this research project and DPhil thesis was to investigate the precise mass dependent isotopic behaviour of molybdenum during high temperature processes and during formation of the inner Solar System. To achieve this the chemical purification procedure had to be improved; the ion exchange chromatography used by Siebert et al. (2001) and Siebert et al. (2006) cannot fully separate Mo from Ru, which has three isobaric interferences with Mo and is more abundant in extra-terrestrial samples than in terrestrial samples. My modification allowed for chemical separation of Mo and Ru in meteorites with widely different matrices (i.e. stony and iron meteorites).

In order to produce high precision Mo isotope data in a wide variety of different sample types, I employed the double spike technique method for correcting the analytical mass fractionation (Siebert et al., 2001). By choosing double spiking, I achieved a long term reproducibility of $\pm 0.09\%$ on $^{98}\text{Mo}/^{95}\text{Mo}$ (2s.d.) for the in-house reference standard solution, and a long term reproducibility for $^{98}\text{Mo}/^{95}\text{Mo}$ on USGS basaltic rock standards (BCR-2 and BHVO-2) of $\pm 0.04\%$ (2s.d.) through entire measurements of this research.

This study presents the first detailed study of Mo isotopic variations in mantle-derived rocks. In contrast to former studies that did not find significant

variations in subduction volcanics and granites (e.g. Siebert et al., 2003; Voegelin et al., 2012), $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ values for mafic samples presented in this study vary significantly from -0.56 to 0.13 ‰. There is no correlation between $\delta^{98/95}\text{Mo}$ and radiogenic Sr, Nd and Pb isotope compositions and no evidence that the Mo isotope variability has some relationship with the nature of the source. Neither is there any relationship between Mo isotopes and Mg# or La/Yb in our samples, making it is unlikely that Mo isotope fractionation is simply controlled by degree of partial melting or fractional crystallization.

However, $\delta^{98/95}\text{Mo}$ does correlate with Ce/Pb, U/Pb, Mo/Pr, and Mo/Ce values, providing evidence that sulphide plays an important role in fractionating chalcophile elements and Mo isotopes. Sulphide fractionation has been proposed for resolving “the Third Pb Paradox” (Hart and Gaetani, 2006), and on the order of 0.1-0.15wt.% sulphide fractionation can explain the variations in Mo/Pr ratio of oceanic basalts (Newsom et al., 1986) and U/Pb and Ce/Pb in ultramafic xenoliths (Meijer et al., 1990). Fractionation might happen during removal of excess immiscible sulphide from silicate melts. The same process has been proposed to explain abundances of platinum group elements and Te in basalts (Greenland and Aruscavage, 1986; Rehkamper et al., 1999; Yi et al., 2000). If these sulphides fractionate Mo to heavier values, all observed variations of Mo isotopes in the mantle samples could be explained. The assumption of heavy Mo fractionation into sulphides is reasonable

because Voegelin et al. (2012) has shown that sulphide are isotopically heavy relative to coexisting silicates in leaching experiments with basalts.

The isotope compositions ($\delta^{98/95}\text{Mo}_{\text{SRM3134}}$) of ultramafic rocks range between 0.29 and 0.53 ‰, the heaviest group in our sample set. In addition, the $\delta^{98/95}\text{Mo}$ of all MORBs is relatively uniform (0.08 to -0.02 ‰) but seems isotopically fractionated relative to the mantle represented by ultramafic xenoliths. Since ultramafic rocks are isotopically uniform but heavier relative to oceanic basalt, it is proposed that immiscible sulphides retained in the mantle play an important role for Mo and Pb abundance and Mo isotope fractionation in basaltic magmas. If so, then sulphide is the dominating phase of the Mo budget in the mantle. Molybdenum prefers a monosulphide solid solution over sulphide liquid in silicate melts, which has been confirmed by experiments (Li and Audetat, 2012). The above arguments indicate that Mo is only moderately incompatible during partial melting of the mantle, and the provisionally estimated Mo abundance of the BSE based on Mo/Ce ratios in oceanic basalt needs to be re-considered. I made a new estimate of the Mo content in the bulk silicate Earth of 251 to 268 ppb, which is 6 times higher than previously deduced (Palme and O'Neill, 2007; Sims et al., 1990) and has significant impact on the interpretation of how the Earth formed in its late stages.

Therefore the levels of depletion of Mo during core formation should be similar to other refractory siderophile elements such as W, Ni and Co. The values of

$\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ in ordinary and CI carbonaceous chondrites are identical (from -0.12 to -0.09‰) but lighter than the BSE (0.35‰), which possibly reflects stable isotope fractionation during core formation.

Base on the results so far in this study, Mo isotopes in iron meteorites shows that Mo isotopic fractionation occurs during fractional crystallization and between different phases within a single iron meteorite. Most iron meteorites we have investigated have a common value of $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ (-0.14 to -0.06‰) identical to ordinary and CI carbonaceous chondrite. Since Mo is a siderophile element, most of the Mo would partition into the core. Therefore, the Mo isotopic composition of the metallic core would have similar values with those primitive meteorites that they were accreted from. In contrast, enstatite chondrites have heavier $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ (0.04 to 0.13‰) and are more sulphide enriched than other groups of meteorites in this study, which could be explained by their formation under reducing conditions and the possible presence of sulphide. However, more future work is need for providing further evidence for these hypotheses.

Based on the data in this study, different scenarios can be proposed to explain the heavy $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ values of the BSE. The first is related to core-mantle differentiation. While Mo should strongly partition into the core, heavier Mo isotopes could preferentially remain in the silicate melt as has been found for Si. Core formation would appear less likely as an explanation for the isotopic fractionation if

Mo removal is dominated by S rich liquids as has been proposed. Heavy Mo isotopes are preferably retained in sulphide, so it would be expected that the residual BSE would be isotopically light. Another possibility is that the Mo isotope signature of the BSE is caused by a late veneer during late accretion. Bombardment by enstatite chondrites (or other group of chondrites with a heavy Mo isotope composition) or sulphur-rich components from differentiated objects could have mixed that heavy composition into the silicate mantle, and left to an isotopically heavy bulk silicate Earth. The difficulty with this model is that it does not explain the much greater depletion of S relative to Mo in the BSE. The third possibility is the Mo isotopic composition of the Solar System is heterogeneous in a mass dependent fashion such that heavier Mo isotopes were enriched in the section of the disk from which Earth accreted. However, the process behind this assumption needs further investigation.

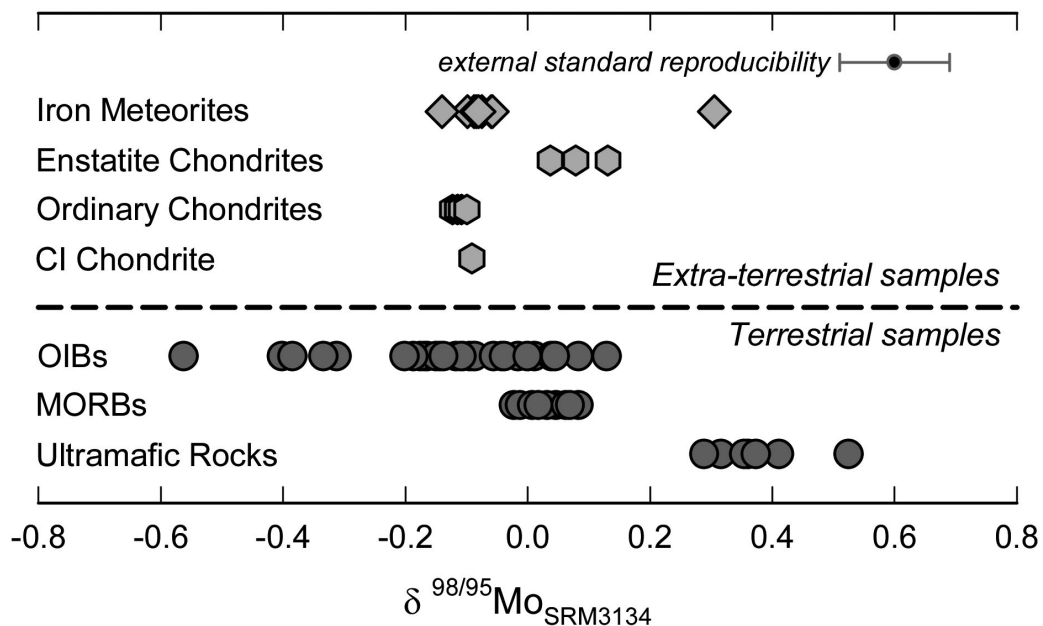


Figure 6.1 Summary of Mo isotopic variation in all samples discussed in this thesis.

6.2 Outlook of future work on molybdenum isotope geochemistry

Double-spiking coupled with MC-ICPMS measurements have been demonstrated to be a powerful technique to analyse a range of terrestrial and extra-terrestrial samples for their Mo isotopic composition. Future work concerning high temperature processes and Mo isotopes should include fractionation by different mineral phases. I proposed that sulphide plays a critical role for both Mo isotopic fractionation and elemental distribution. Analysis of sulphides from samples in different geological settings could confirm this model.

A further important research path would be to link Mo isotopic measurements with experimental work. Wade et al. (2012) proposed an accretionary model for Earth's evolution, which adds 2% of S into the core during the final stages of core formation based on their experimental result. This model would require that Mo strongly partitions into the core and led to a more depleted BSE. However, applying their model to my observations, heavy Mo isotopes should partition into the core with sulphide and make the silicate Earth isotopically lighter, in direct contrast to my data. Therefore, combining experimental work and isotopic measurements is an opportunity for resolving these major remaining questions.

Furthermore, additional studies are needed to investigate the average $\delta^{98/95}\text{Mo}_{\text{SRM3134}}$ value of continental crust, the compositional variation between

upper and lower continental crust, the recycling of Mo isotope during subduction, etc. This work will allow us to erect a concise model for the global Mo cycle.

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