Transition metal isotope fractionation in marine hydrothermal deposits of the Mohns Ridge, North Atlantic Ocean

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“Dr. Evil! I didn’t spend six years in Evil Medical School to be called ‘Mister’, thank you very much.”

— Dr. Evil in *Austin Powers: International Man of Mystery*

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Abstract

Seafloor hydrothermal vent systems form along mid-ocean ridges in all of the Earth's oceans. They have a major impact on the chemical exchange between the lithosphere and the hydrosphere, as vast volumes of seawater cycle through these systems, thereby interacting with young, oceanic crust. Furthermore, seafloor hydrothermal vent systems provide an excellent environment for organisms to thrive, resulting in diverse and unique vent faunas. Due to their favourable ecological conditions and their existence throughout Earth's history, they are regarded as a potential cradle where life on Earth could have emerged.

Transition metals, such as iron, copper and zinc, are essential nutrients for all organisms on Earth and, thus, metabolic processes have direct influence on cycling of these elements in the environment. The development of high-resolution multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) in the mid-1990s enabled the use of transition metal stable isotope variations in nature as geochemical tracers. Studies on Fe, Cu and Zn isotope variations have revealed that metabolic reactions are capable of fractionating stable isotopes of these transition metals. Consequently, researchers have tried to find distinct isotopic fingerprints that allow identifying remnants of biological activity in geological samples, since DNA or microfossil structures are often missing in especially ancient samples due to later geological overprint. Unambiguous biological transition metal isotope signatures, however, have not been discovered so far.

The objective of this thesis is to better understand fractionation of Fe, Cu and Zn isotopes in seafloor hydrothermal vent systems in general, and whether isotope variations of these transition metals may help to unravel (biological) formation processes of ancient hydrothermal deposits in particular. For this purpose, analytical methods were developed to determine Cu and Zn isotope variations in Fe-rich hydrothermal samples. Copper and zinc were purified from the sample matrices using a two-step ion-exchange chromatographic procedure. It was shown that no fractionation of Cu isotopes occurred during chromatographic separation of copper by applying a standard addition approach with an enriched ^{65}Cu spike. Furthermore, a new ^{64}Zn-^{67}Zn double spike was calibrated in order to correct for instrumental mass bias during Zn isotope ratio determinations by MC-ICP-MS. Cu and Zn isotope measurements of international reference materials and inter-laboratory data comparison between the isotope laboratories at the University of Bergen and the Imperial College, London, confirmed the accuracy and applicability of the established analytical methods.

The samples investigated in this thesis derived from the Jan Mayen and the Loki's Castle vent fields, situated along the Mohns Ridge, North Atlantic. Low temperature hydrothermal venting at the Jan Mayen vent fields leads to the formation of extensive microbial mats that mediate the precipitation of layered, siliceous Fe oxyhydroxide deposits. These deposits exhibit substantial amounts of encrusted filaments of the Fe-oxidising bacterium *Mariprofundus ferrooxidans*. Fe isotopic compositions of the siliceous Fe oxyhydroxides span a range from -2.09 to -0.66 ‰ in δ^{56}Fe, which is most likely the result of partial oxidation of hydrothermal $Fe(II)_{aq}$ by low concentrations of free oxygen in fluid-filled cavities within the deposits and/or by microbial iron oxidation. The Jan Mayen samples are enriched in the heavy Zn isotopes relative to the low temperature hydrothermal fluids, most likely caused by isotope fractionation during adsorption of Zn aquo complexes onto the surfaces of the siliceous Fe oxyhydroxides. Cu isotopes in the Jan Mayen samples, on the other hand, are fractionated towards lower δ^{65}Cu values relative to igneous rocks. Here, Cu isotope fractionation might be caused by partitioning of copper into different organic and inorganic complexes and subsequent preferential, pH-dependent adsorption of Cu aquo complexes onto siliceous Fe oxyhydroxides and/or by assimilation and adsorption of isotopically light copper by microorganisms. Isotope variations in the modern Jan Mayen siliceous Fe oxyhydroxide deposits were compared to those in Ordovician jasper beds from the Løkken ophiolite complex, Norway, which are interpreted to have formed from white smoker hydrothermal fallout deposits. Fe isotope variations in the Løkken jaspers, ranging from -0.38 to +0.89 ‰ in δ^{56}Fe, point to partial oxidation of $Fe(II)_{aq}$ in the hydrothermal plume. The isotopic compositions of copper and zinc in the jaspers are comparable to those of the modern siliceous Fe oxyhydroxide deposits from the Jan Mayen vent fields, and isotope fractionation might have been caused by similar (bio)chemical reactions despite different formation pathways of the two deposits. However, interpreting reactions causing the observed Cu and Zn isotope fractionations in these hydrothermal systems remains speculative.

Besides low temperature deposits, hydrothermal sulphides which formed in high temperature white smoker chimneys at the Jan Mayen vent fields and in black smoker chimneys at the Loki's Castle vent field were investigated. In these environments, fractionation of transition metal isotopes is mostly driven by inorganic chemical reactions. Variations of Fe, Cu and Zn isotopes were used to trace reaction pathways of sulphide formation. Isotopically light iron is incorporated into iron mono- and disulphides, such as pyrrhotite and marcasite, respectively, reflecting kinetic Fe isotope fractionation during sulphide precipitation. Kinetic isotope effects are most likely also responsible for low δ^{56}Fe and δ^{66}Zn values in sphalerite solid solution, compared to δ^{56}Fe and δ^{66}Zn values of high temperature hydrothermal fluids. A correlation between FeS concentration and Zn isotopic composition in sphalerite was found, which might indicate an impact of zinc substitution for iron on Zn isotope fractionation. Equilibrium isotope fractionation of copper and iron between hydrothermal fluids and sulphides was identified during formation of isocubanite and chalcopyrite. Here, isotope fractionation is most likely driven by changes in the oxidation states of iron and copper. Overall, the results are in agreement with experimental studies published in literature.

The findings of this thesis show that transition metal isotope variations can be successfully used to trace chemical reactions in hydrothermal vent systems. However, the results also confirm that investigations solely based on Fe isotope variations are not suitable to distinguish between microbial and inorganic oxidation of reduced $Fe(II)_{aq}$, which is an important reaction in oceanic and terrestrial low temperature environments. Combined studies of isotope fractionation of different transition metals, as presented in this thesis, are certainly a better approach to unravel formation reactions of minerals and hydrothermal deposits. However, the results of this thesis also emphasise the need of further research on metal isotope fractionation both in nature and laboratory experiments to enhance our knowledge of transition metal isotope fractionation and, thus, to allow accurate interpretations of measured isotope variations in nature.

Authorship statement

The candidate is the principle investigator and author of all chapters of this thesis. There are co-author contributions to chapters II to IV; however, the candidate is sole author of chapter I. An overview of the candidate's contributions to each manuscript is given below. Acknowledgements of the contributions of others are included at the end of the individual manuscripts.

Chapter II

Moeller, K., Schoenberg, R., Pedersen, R.-B., Weiss, D. and Dong, S., *in press*. Calibration of the New Certified Reference Materials ERM-AE633 and ERM-AE647 for Copper and IRMM-3702 for Zinc Isotope Amount Ratio Determinations. Geostandards and Geoanalytical Research, doi: 10.1111/j.1751-908X.2011.00153.x.

The candidate was responsible for method development with concept and guidance by R. Schoenberg as well as for data acquisition. Data were mainly interpreted by the candidate with discussions with R. Schoenberg. In-house standards 'Imperial Zn', 'London Zn', 'Romil Zn' and 'Romil Cu' and the international reference material NIST SRM 976 were provided by D. Weiss and S. Dong. Data collection for laboratory comparison at the Imperial College, London, was performed by S. Dong. R. Schoenberg, D. Weiss and R.-B. Pedersen provided with manuscript review.

Chapter III

Moeller, K., Schoenberg, R., Grenne, T., Thorseth, I. H., Pedersen, R.-B., *in preparation*. Comparison of Transition Metal Isotope Variations of Modern and Ordovician Siliceous Fe Oxyhydroxide Deposits.

Samples were collected by K. Moeller, R. Schoenberg, T. Grenne and I. H. Thorseth (Løkken jaspers) and by I. H. Thorseth and R.-B. Pedersen (modern Fe oxyhydroxide mounds). Data were produced by the candidate (Cu and Zn isotopes) and R. Schoenberg (Fe isotopes). Interpretation of the data was mainly performed by the candidate with discussions with R. Schoenberg. Manuscript review was performed by R. Schoenberg, T. Grenne, I. H. Thorseth and R.-B. Pedersen.

Chapter IV

Moeller, K., Schoenberg, R., van Zuilen, M. A., Pedersen, R.-B., *in preparation*. Transition Metal Isotope Fractionation during Formation of Hydrothermal Sulphides.

Samples were taken by the candidate and R.-B. Pedersen. The candidate was solely responsible for collection of isotope data. Acquisition of Raman data and mineral identification were performed by M. A. van Zuilen and the candidate. Interpretation of isotope data was done by the candidate. R. Schoenberg, M. A. van Zuilen and R.-B. Pedersen provided with manuscript review.

Scientific environment

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Chapter I

Introduction

1. Objectives

Seafloor hydrothermal vent systems are thought to be one of the places where first organisms may have emerged (e.g., Baross and Hoffmann, 1985; Holm, 1992; Russell and Hall, 1997; Martin et al., 2008) and, thus, play an important role in understanding the evolution of early life on Earth. Stable isotope variations of 'light elements', such as carbon and sulphur, have proven to be useful to trace the presence of organisms in geological samples, even if visible remnants, i.e., fossils, are missing (e.g., Canfield and Raiswell, 1999; Schidlowski, 2001; Shen et al., 2001; House et al., 2003). With the development of high-resolution multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) in the mid-1990s, it became possible to accurately determine isotope variations of elements with higher masses, such as transitions metals, which play an important role in microbial nutrient cycles. However, more than a decade of research conducted on the fractionation of iron, copper and zinc isotopes has still not led to unambiguous conclusions if and how these isotope systems can be used to indentify biological processes. Especially in the case of copper and zinc, stable isotope research may still be considered as being in its infancy.

The aim of this thesis is to better understand how iron, copper and zinc isotopes are fractionated in seafloor hydrothermal vent systems. For this purpose, three foci were set:

1) Establishment of analytical procedures to accurately and precisely determine copper and zinc isotope variations in hydrothermal samples;

2) Investigation of transition metal isotope variations in low temperature, diffuse venting areas, where Fe-oxidising bacteria form extensive Fe oxyhydroxide deposits;

3) Investigation of transition metal isotope fractionation during precipitation of sulphide minerals in high temperature black and white smoker chimneys.

First, a general overview of seafloor hydrothermal vent systems and the particular vent sites that were investigated will be given in this chapter. Furthermore, principles of stable isotope fractionation will be outlined, including brief literature reviews on iron, copper and zinc isotope fractionation and variations in nature.

2. Seafloor hydrothermal vent systems

The ocean floor is pervaded by oceanic spreading centres along divergent tectonic plate boundaries, forming a continuous, approximately 80,000 km long network of mid-ocean ridges (MOR). New, permeable oceanic crust is formed at these sites. Along the MOR, seafloor hydrothermal vent fields occur as a result of seawater penetrating through the crust and interacting with crustal rocks at high temperatures (Fig. 1). The circulation of fluids through the oceanic crust has a major impact on heat transport between lithosphere and hydrosphere and also influences the chemical composition of the crust and the seawater.

A short outline of reactions in hydrothermal systems below the seafloor will be given based on the article by Alt (1995). Seawater enters the oceanic crust through cracks and fissures. In the so-called recharge zone, the seawater is heated up and first reactions with the surrounding rocks take place. Dissolved oxygen carried with the seawater oxidises the rocks, resulting in formation of Fe oxyhydroxides, which replace olivine and primary sulphides in the crustal rocks and fill pores and veins. Due to heating of the seawater below the seafloor, calcium and sulphate precipitate as anhydrite. The alkali metals K, Rb and Cs as well as B are removed from the water and incorporated into micas and clay minerals. With increasing penetration depth, the evolving fluids become depleted in Mg^{2+} and OH^{-}, which form components of smectite and chlorite. The extraction of OH^{-} leads to decreasing pH values, causing leaching of Ca, Na, K, Cu, Zn and other elements from the surrounding oceanic crust. In the reaction zone, the fluids are considered to experience the highest temperatures. Here, transition metals and sulphur are leached from the rocks and become enriched in the fluids. Phase separation into a vapour-rich and a brine phase may occur when the temperature and pressure conditions exceed those of the boiling curve for seawater (Von Damm et al., 1997). Due to the high pressure and temperatures in the reaction zone, density and viscosity of the evolved fluids decrease. As a result, the fluids become buoyant relative to cold seawater and rise rapidly towards the seafloor. Hydrothermal fluids either rise through focused or diffuse upflow zones. Focused upflow zones are characterised by massive sulphide deposits (VMS) and associated high temperature vents at the seafloor. Dependent on fluid temperature, either black or white smoker type chimneys form. In diffuse upflow zones, the hydrothermal fluids mix with seawater that penetrates into the crust below seafloor. Low temperature diffuse venting (< 50 °C), which often occurs in peripheral parts of hydrothermal vent sites, results in precipitation of Fe oxyhydroxides, Mn oxides and silica (Hannington et al., 1995). Both focused and diffuse venting with moderate to high temperatures release warm buoyant plumes into the water column. In black smoker plumes, sulphide particles precipitate from dissolved metals and H_2S carried in the hot hydrothermal fluids upon mixing with the cold ambient seawater. Successive oxidation results in formation of Fe oxyhydroxide particles (e.g., Mottl and McConachy, 1990).

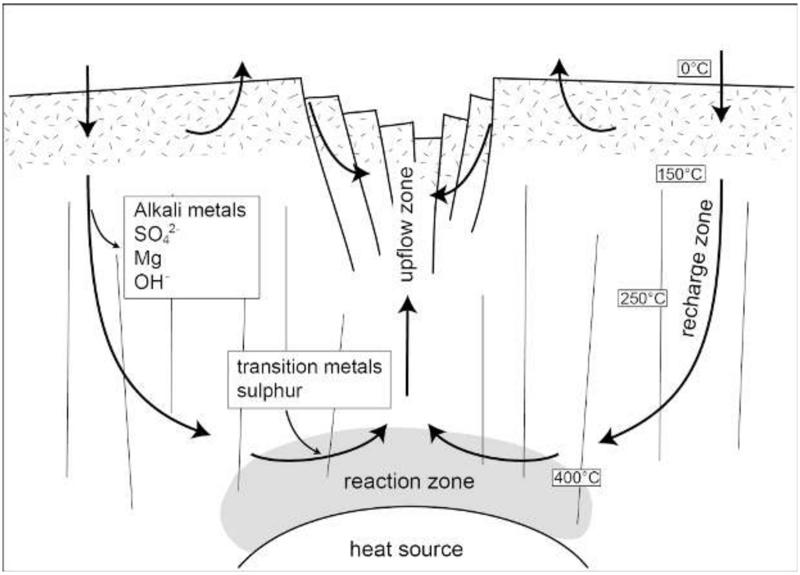

Fig. 1. Schematic cross section through a MOR. Fluid flows are indicated by black arrows. Seawater penetrating through the crust becomes depleted in alkali metals, sulphate, Mg and OH^- in the recharge zone. At higher temperatures in the reaction zone, transition metals and sulphur are leached from the oceanic crust. Rising hydrothermal fluids may mix with circulating seawater in the upflow zone.

Black smoker chimneys form from focussed high temperature hydrothermal fluids, commonly emanating through one central conduit (Fig. 2a). The formation of black smoker chimneys was first described by Haymon (1983). In a first stage of chimney growth, anhydrite precipitates due to mixing of hydrothermal fluids with ambient seawater, isolating the hot fluids against the cold seawater. Anhydrite is then gradually replaced by Cu-Fe sulphides, mainly chalcopyrite, isocubanite and pyrrhotite, which line the inner walls of the chimney (Hannington et al., 1995).

Hydrothermal fluids that form white smoker chimneys carry less sulphur and metals, either because fluid temperatures are not high enough or because of conductive cooling or sub-seafloor mixing with seawater, resulting in precipitation of sulphides below the seafloor. In contrast to black smoker chimneys, anhydrite is less common in white smoker chimneys, and the structures are commonly cemented by silica and barite (Hannington et al., 1995). Sulphides, which precipitate inside the chimneys, are mostly marcasite, pyrite and sphalerite. Some white smokers may consist almost entirely of sphalerite. The chimney walls, however, remain porous and cold seawater can penetrate into the interior of the chimney, causing steep thermal and chemical gradients (Hannington et al., 1995). White smoker chimneys do not exhibit one distinct conduit (Fig. 2b), but rather a network of entangled, narrow channels with diameters of usually less than 1 cm (Tivey, 1995). In the late stage of chimney growth, silica precipitates in the open spaces and channels, eventually clogging the interior and cutting the chimney off from the hydrothermal flow.

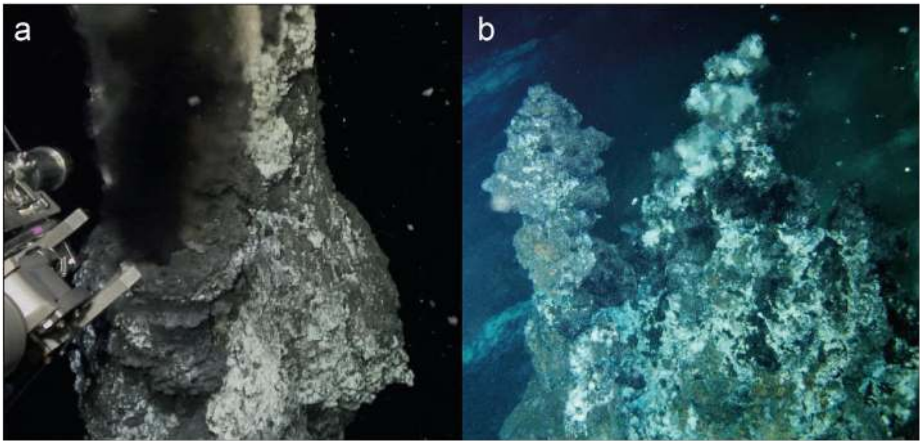

Fig. 2. Photographs of high temperature hydrothermal chimneys. (a) Hydrothermal fluids emanate from one distinct orifice of a black smoker chimney at Loki's Castle, forming a black plume due to precipitation of sulphide particles in contact with ambient seawater. (b) White smoker chimney at the Jan Mayen vent fields consists of several, irregular spires from which almost clear hydrothermal fluids emanate.

2.1. Study areas

Samples investigated in this thesis derived from two seafloor hydrothermal vent sites along the ultraslow spreading Arctic Mid-Ocean Ridges (AMOR) (Fig. 3). The black smoker type hydrothermal vent field Loki's Castle is situated at the transition of the Mohns Ridge into the Knipovich Ridge at about 2400 m water depth (Pedersen et al., 2010b). Four black smoker chimneys were discovered, hosted by two hydrothermal sulphide mounds (Pedersen et al., 2010a). In contrast, the Jan Mayen vent fields, located near the southwestern termination of the Mohns Ridge, consist of two venting sites, both exhibiting white smoker type chimneys in water depth between approximately 550 and 700 m (Pedersen et al., 2010b). Distal to the northern vent field called Troll Wall, diffuse low temperature venting leads to the formation of siliceous Fe oxyhydroxide deposits which spread over several hundred metres. Microbial communities with abundant Fe-oxidising bacteria are thought to mediate the precipitation of the Fe oxyhydroxides.

In addition, transition metal isotope variations were analysed in Ordovician jasper beds from the Løkken ophiolite complex, western Trondheim region, Norway. The jasper beds were interpreted to have formed from siliceous Fe oxyhydroxide gel precursors, which cumulated as fallout deposits around mainly white smoker type venting sites in a back arc basin (Grenne and Slack, 2003; Grenne and Slack, 2005).

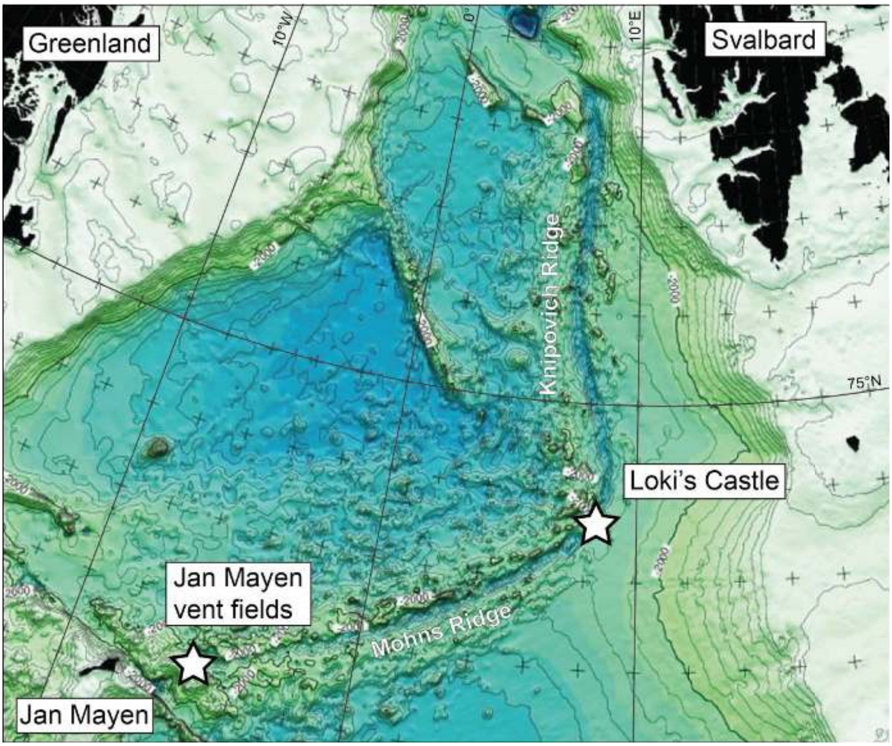

Fig. 3. Location of the investigated hydrothermal vent sites Loki's Castle and the Jan Mayen vent fields along the Arctic Mid-Ocean Ridges.

3. Principles of stable isotope fractionation

Isotopes are atomic variants of a chemical element with equal numbers of protons, but different numbers of neutrons in the nucleus. They can either be stable or unstable, depending on the ratio of protons to neutrons in their nuclei. Unstable isotopes are radioactive, i.e., they decay under emission of high-energy radiation into nuclides of a different chemical element. 'Stable' isotopes, on the other hand, are either truly stable, i.e., they do not decay, or they are radioactive by theory with extremely long half-lives.

The abundances of stable isotopes of a chemical element are variable. Partitioning of isotopes between two substances or phases with different isotope ratios is called 'isotope fractionation'. Mass-dependent isotope fractionation is caused by differences in mass between the isotopes of an element. For elements heavier than H, C, N, O and S, which are widely used stable isotope systems since the 1950s, or elements with high ionisation potentials, accurate measurements of isotope ratios could not be performed before new innovations in mass spectrometry. In particular, the introduction of multicollector mass spectrometers with inductively-coupled plasma (MC-ICP-MS) in the mid-1990s has enabled isotope ratio measurements of elements such as Li, Mg, Ca, Cr, Fe, Cu, Zn, Se, Mo and Cd (see reviews of Johnson et al., 2004a (2004) and Anbar and Rouxel (2007)), which are often described as 'non-traditional' isotope systems.

Differences in the stable isotope abundances of a particular element A are commonly given as the ratio R of two isotopes of the element:

$$R = \frac{{}^{heavy}\mathrm{A}}{{}^{light}\mathrm{A}} \tag{1.1}$$

Due to the rather small variations of isotope abundances in nature, these are reported in the δ-notation relative to a reference material as per mill deviation by multiplying with a factor of 10^3:

$$\delta^{heavy/light}\mathrm{A} = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \tag{1.2}$$

The fractionation of isotopes of an element A between educt E and product P is described by the fractionation factor α, which is defined as

$$\alpha_{P,E} = \frac{R_P}{R_E} \tag{1.3}$$

In isotope studies, isotope fractionation between two substances is often given as the difference Δ between their measured isotopic compositions:

$$\Delta_{A-B} = \delta_A - \delta_B \qquad (1.4)$$

where α is related to Δ by

$$\Delta \approx 10^3 \ln \alpha \qquad (1.5)$$

Mass-dependent fractionation of stable isotopes can be caused by two different processes, i.e., equilibrium and kinetic isotope fractionation. A brief summary of the theory of stable isotope fractionation based on recent reviews of Chacko et al. (2001) and Schauble (2004) is given below.

Equilibrium isotope fractionation

Mass-dependent equilibrium isotope fractionation is a quantum mechanical phenomenon, which is mainly caused by differences in vibrational energies of molecules containing atoms of different masses (Urey, 1947). These differences in vibrational energies are associated with differences in the zero-point energy (*ZPE*) of the chemical bonds in the molecules, and thus with bond strength. The energy associated with atomic motion is distributed over translation, rotation and vibration. In general, the *ZPE* is predominantly determined by the vibrational frequency of a bond, whereas rotational and translational frequencies have subordinate effects. For a simple harmonic vibration, the vibrational energy is defined as

$$E_{vib} = \left(n + \frac{1}{2}\right)hv \qquad (1.6)$$

where n (= 0, 1, 2, …) is the quantum number, h is the Planck's constant and υ the oscillation frequency of the vibration. As an approximation, the *ZPE* (i.e., n = 0) of a simple diatomic gas molecule (AB) can therefore be written as

$$ZPE = \frac{1}{2}hv \qquad (1.7)$$

The vibrational frequency υ can be approximated by a harmonic oscillator:

$$v = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad (1.8)$$

where k is the effective spring constant and μ is the reduced mass of the molecule AB, which is defined by the masses of the atoms A and B, m_A and m_B, as

$$\mu = \frac{m_A m_B}{m_A + m_B} \tag{1.9}$$

Therefore, the *ZPE* is a function of the masses of the atoms A and B and is greater for bonds involving a light isotope than for bonds with a heavier isotope. The larger the difference between *ZPE* and the energy of the dissociated atoms (Fig. 4), the stronger is the bond. Thus, the bond strength increases when a heavier isotope substitutes for a lighter one.

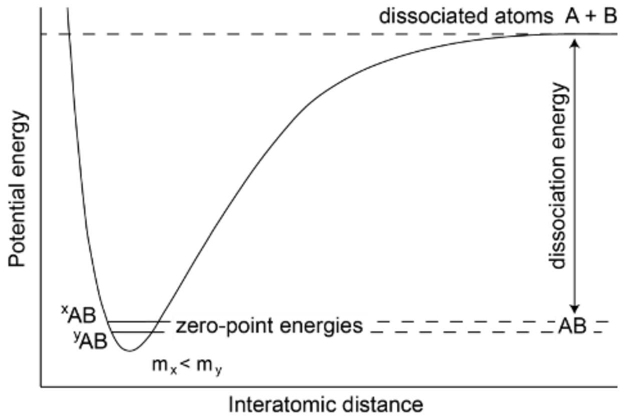

Fig. 4. Schematic energy curve for a diatomic molecule AB. B is monoisotopic. The zero-point energy (*ZPE*) for the molecule with the heavier isotope y incorporated (^{y}AB) is lower than the *ZPE* for the molecule with the lighter isotope x (^{x}AB). A lower *ZPE* means higher dissociation energy and, thus, stronger chemical bonds.

Equilibrium isotope fractionation can be calculated using the approach of Urey (1947), which assumes harmonic vibrations, as described above, rigid-body rotation and simplified rotation energies. These assumptions are reasonable for most geochemical applications (Schauble, 2004).

A simple isotope exchange reaction can be defined by

$$^{x}AB + ^{y}A \Leftrightarrow ^{y}AB + ^{x}A \tag{1.10}$$

where x and y are two isotopes of the element A, and B is in this case monoisotopic. The equilibrium constant k_{eq} of this reaction is defined as the quotient of the activities of the products and educts:

$$k_{eq} = \frac{\{{}^{y}\mathrm{AB}\}\{{}^{x}\mathrm{A}\}}{\{{}^{x}\mathrm{AB}\}\{{}^{y}\mathrm{A}\}} \tag{1.11}$$

which is equivalent to the equilibrium isotope fractionation factor $\alpha_{AB,A}$:

$$k_{eq} = \alpha_{AB,A} = \frac{{}^{x}\mathrm{AB}/{}^{y}\mathrm{AB}}{{}^{x}\mathrm{A}/{}^{y}\mathrm{A}} \tag{1.12}$$

The equilibrium constant is related to the free energies of the products and educts with

$$\Delta G^{0} = -RT \ln k_{eq} \tag{1.13}$$

giving

$$k_{eq} = \exp\left(\frac{-\Delta G^{0}}{RT}\right) \tag{1.14}$$

where ΔG^0 is the Gibbs free energy of the reaction, R is the molar gas constant and T is the absolute temperature.

During isotope exchange reactions, the bond structure, and thus the potential energy of each molecule, is unaffected. Therefore, only energy associated with atomic motion has to be considered for the calculations. Furthermore, isotope exchange does, in general, not affect pressure (P) and the molar volumes (V). Therefore, the Gibbs free energy G is equivalent to the Helmholtz free energy F:

$$G = F + PV \quad \text{and} \qquad \Delta G \approx \Delta F \tag{1.15}$$

The basic expression for the equilibrium constant can, thus, be given as

$$k_{eq} = \exp\left(\frac{-\Delta F}{RT}\right) \tag{1.16}$$

As an approximation, the atomic motion can be described by a harmonic oscillator. Here, the energy difference ΔF equals approximately the difference in zero-point energies ΔZPE, which can be calculated using Eqn. 1.7,

$$\Delta F \approx \Delta ZPE = \sum\left(\frac{1}{2}h\nu\right)_{Products} - \sum\left(\frac{1}{2}h\nu\right)_{Educts} = \frac{1}{2}h\Delta\nu \qquad (1.17)$$

This illustrates that equilibrium isotope fractionation between two substances is mainly driven by the differences in vibrational frequency $\Delta\upsilon$, which is related to the mass of the isotopes (Eqns. 1.8 and 1.9).

As mentioned before, the above described approach solely considers molecules in their ground vibrational state, which is an oversimplification. Partition functions Q describe the total energy of a system of molecules, including vibrational, rotational and translational energies, as the sum over all energy states and the probabilities that the molecule will occupy a particular state. Q is related to the Helmholtz free energy by

$$F = -RT\ln Q \qquad (1.18)$$

The vibrational partition function Q_{vib} describes the sum over all vibrational energies E_n in a molecule:

$$Q_{vib} = \sum_n \exp\left(-E_n/kT\right) \quad \text{with} \quad E_n = \left(n+\frac{1}{2}\right)h\nu \qquad (1.19)$$

where k is the Boltzmann's constant and n (= 0, 1, 2, …) describes the energy state, i.e., the quantum number, of the vibrational degree of freedom.

The partition functions for rotation Q_{rot} and translation Q_{trans} in a molecule can be approximated by

$$Q_{rot} = \frac{8\pi^2 IkT}{h^2} \quad \text{and} \qquad (1.20)$$

$$Q_{trans} = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \qquad (1.21)$$

where I is the moment of inertia, V the volume and m the mass of the molecule.
The total energy of atomic motion is

$$F = -RT\ln\left(Q_{vib} * Q_{rot} * Q_{trans}\right) \qquad (1.22)$$

resulting in the following expression of the equilibrium constant k_{eq} and the equilibrium fractionation factor α:

$$k_{eq} = \alpha = \exp\left(\frac{-\Delta F}{RT}\right) = \exp\left[\frac{-\left(F_{Prodcuts} - F_{Educts}\right)}{RT}\right]$$

$$= \exp\left[\sum\nolimits_{Products} \ln\left(Q_{vib} * Q_{rot} * Q_{trans}\right) - \sum\nolimits_{Educts} \ln\left(Q_{vib} * Q_{rot} * Q_{trans}\right)\right]$$

$$= \frac{\prod_{Products}\left(Q_{vib} * Q_{rot} * Q_{trans}\right)}{\prod_{Educts}\left(Q_{vib} * Q_{rot} * Q_{trans}\right)} \tag{1.23}$$

Inserting the partition functions in the equation above, the equilibrium fractionation factor $\alpha_{AB,A}$ can be calculated as

$$\alpha_{AB,A} = k_{eq} = \frac{Q_{trans}\left({}^{x}\mathrm{A}\right)}{Q_{trans}\left({}^{y}\mathrm{A}\right)} * \frac{Q_{trans} * Q_{rot} * Q_{vib}\left({}^{y}\mathrm{AB}\right)}{Q_{trans} * Q_{rot} * Q_{vib}\left({}^{x}\mathrm{AB}\right)}$$

$$= \left(\frac{m_{{}^{x}A}}{m_{{}^{y}A}}\right)^{3/2} * \left(\frac{m_{{}^{y}AB}}{m_{{}^{x}AB}}\right)^{3/2} * \frac{I_{{}^{y}AB}}{I_{{}^{x}AB}} * \frac{\exp\left(-\frac{h\nu_{{}^{y}AB}}{2kT}\right)}{1-\exp\left(-\frac{h\nu_{{}^{y}AB}}{kT}\right)} * \frac{1-\exp\left(-\frac{h\nu_{{}^{x}AB}}{kT}\right)}{\exp\left(-\frac{h\nu_{{}^{x}AB}}{2kT}\right)} \tag{1.24}$$

if the vibrational frequencies υ and the moment of inertia I are known.

The fractionation factor α between two substances P and E can be expressed as partition function ratios:

$$\alpha_{P,E} = \frac{Q_{{}^{x}P}/Q_{{}^{y}P}}{Q_{{}^{x}E}/Q_{{}^{y}E}} \tag{1.25}$$

Calculated partition function ratios are usually reported as reduced partition functions (β-factors), which ignore rotational and translational energies. Using these β-factors, equilibrium fractionation factors can be calculated with

$$\alpha_{P,E} = \frac{\beta_P}{\beta_E} \quad \text{or} \tag{1.26}$$

$$1000 \ln \alpha_{P,E} = 1000 \ln \beta_P - 1000 \ln \beta_E \tag{1.27}$$

Schauble (2004) summarised a few simplified qualitative rules governing equilibrium isotope fractionation. These rules predict large isotope fractionation between two substances with marked differences in oxidation state, bond strength, electron configuration and coordination number at low temperature:

- Equilibrium fractionation decreases with increasing temperature, roughly with $1/T^2$.
- Fractionation is largest for elements with low atomic masses and large relative mass differences between the isotopes of interest.
- Heavy isotopes are preferentially incorporated in the substance where they form the stiffest, i.e., short and strong, chemical bonds. Bond stiffness correlates with high oxidation state, bonding partners near the top of the periodic table, highly covalent bonds, low-spin electronic configuration number for transition metals and low coordination number.

Kinetic isotope fractionation

In contrast to equilibrium isotope fractionation, kinetic fractionation between two substances can occur during incomplete isotope exchange reactions. In most cases, these are unidirectional, such as evaporation, diffusion or dissociation reactions. The kinetic isotope effect is caused by differences in the reaction rate constants of different isotopes of an element, which is the result of the mass dependence of the dissociation energy, and, thus, of the bond strength (Fig. 4).

The mass of a molecule or atom *m* affects its velocity *v*. For an ideal gas, where the translational kinetic energy E_{kin} is equivalent for all molecules or atoms, this can be illustrated by

$$E_{kin} = \frac{3}{2}kT = \frac{1}{2}mv^2 \tag{1.28}$$

where *k* is the Boltzmann's constant and *T* the absolute temperature. The velocities of molecules or atoms with different masses differ according to

$$\frac{m_{light}}{m_{heavy}} = \frac{v_{heavy}^2}{v_{light}^2} \tag{1.29}$$

This means that the heavier isotope reacts more slowly than the lighter one. Therefore, in many kinetic, i.e., non-equilibrium, reactions, the light isotopes are enriched in the reaction product.

3.1. Stable iron isotopes

Iron (Fe) is the second most abundant element on Earth. As most of the iron is cumulated in the Earth's core, it represents the fourth most abundant element in the Earth's crust (Rudnick and Gao, 2004). Besides metallic Fe^{0}, it occurs mainly as reduced ferrous Fe^{2+} and oxidised ferric Fe^{3+} in nature. Iron is an essential nutrient for almost all known terrestrial and oceanic organisms. Furthermore, it is a major element in many rock-forming minerals. Due to its importance to biological and inorganic processes, fractionation of iron isotopes has become the focus of an increasing number of studies over the last decade.

Iron has four stable isotopes (with approximate natural mole fractions by de Laeter et al. (2003)): ^{54}Fe (5.85%), ^{56}Fe (91.75%), ^{57}Fe (2.12%) and ^{58}Fe (0.28%). Some researchers prefer to report Fe isotopic compositions of natural samples in the δ-notation (Eqn. 1.2) relative to the average isotopic composition of igneous rocks (e.g., Beard et al., 2003a; Johnson et al., 2005; Johnson et al., 2008a; Beard et al., 2010; Percak-Dennett et al., 2011; Wu et al., 2012). However, Fe isotopic compositions are usually given relative to the reference material IRMM-014 (Taylor et al., 1992), certified for its isotope abundances and distributed by the Institute for Reference Materials and Measurements (IRMM) in Geel, Belgium, expressed in per mill (‰) by multiplying with a factor of 10^3:

$$\delta^{56}Fe_{IRMM-014} = \left(\frac{{}^{56}Fe/{}^{54}Fe_{sample}}{{}^{56}Fe/{}^{54}Fe_{IRMM-014}} - 1 \right) \tag{1.30}$$

The first attempts to measure stable Fe isotopic compositions in natural samples were made using thermal ionisation mass spectrometry (TIMS) (e.g., Völkening and Papanastassiou, 1989; Dixon et al., 1993; Walczyk, 1997; Johnson and Beard, 1999). However, significant analytical difficulties, such as large instrumental mass bias drift, hampered accurate Fe isotope ratio determinations. Although the precision of measurements could readily be improved by using Fe double spikes to correct for instrumental mass bias, analytical uncertainties were still in the order of ±0.2 to 0.3 ‰ (1 standard deviation) on $\delta^{56}Fe$ values (Johnson and Beard, 1999). More precise and accurate Fe isotope measurements with reproducibilities of around ±0.05 ‰ (2 standard deviation) on $\delta^{56}Fe$ could be achieved with the development of the MC-ICP-MS in the late 1990s (e.g., Belshaw et al., 2000; Weyer and Schwieters, 2003; Arnold et al., 2004; Schoenberg and von Blanckenburg, 2005). Since then, a lot of research has been done on determining Fe isotope fractionation factors for biological and inorganic reactions using experimental (e.g., Bullen et al., 2001; Skulan et al., 2002;

Welch et al., 2003; Brantley et al., 2004; Icopini et al., 2004; Wiesli et al., 2004; Crosby et al., 2005; Johnson et al., 2005; Schuessler et al., 2007; Mikutta et al., 2009; Wu et al., 2011) and theoretical approaches (e.g., Schauble et al., 2001; Anbar et al., 2005; Hill and Schauble, 2008; Polyakov and Soultanov, 2011). Comprehensive reviews on experimentally obtained Fe isotope fractionation factors and Fe isotope variations measured in nature have recently been published (Anbar, 2004; Beard and Johnson, 2004; Johnson et al., 2004b; Dauphas and Rouxel, 2006; Johnson and Beard, 2006; Anbar and Rouxel, 2007; Johnson et al., 2008b). Here, a short overview of the for this study most important reactions causing Fe isotope fractionation as well as about known Fe isotope variations of selected natural systems will be given.

A collection of samples from chondrites, meteorites from Mars and Vesta, lunar rocks and igneous rocks from the Earth has given evidence for the assumption that the planetary bodies of our solar system are relatively homogenous in their Fe isotopic composition (Zhu et al., 2001; Beard et al., 2003a; Poitrasson et al., 2004; Poitrasson and Freydier, 2005; Weyer et al., 2005; Schoenberg and von Blanckenburg, 2006). For bulk igneous rocks on Earth, an average δ^{56}Fe value of 0.09 ± 0.08 ‰ relative to IRMM-014 has been proposed (Beard et al., 2003a). Magmatic differentiation, however, can cause slight Fe isotope fractionation between minerals within melts and rocks (e.g., Poitrasson and Freydier, 2005; Schuessler et al., 2007; Teng et al., 2008; Williams et al., 2012).

Equilibrium isotope fractionation decreases with increasing temperature, thus, the largest Fe isotope effects are expected to occur in low temperature environments. In the biosphere, fractionation of Fe isotopes is driven by metabolic processes. Microorganisms are able use iron for assimilatory and dissimilatory redox processes, both as electron donor and acceptor (e.g., Kappler and Straub, 2005). Therefore, extensive research has been done on Fe isotope fractionation during dissimilatory iron reduction (DIR) (Beard et al., 1999; Crosby et al., 2005; Johnson et al., 2005; Crosby et al., 2007; Wu et al., 2009; Tangalos et al., 2010; Percak-Dennett et al., 2011) as well as during Fe(II) oxidation by anoxygenic photoautotrophic (Croal et al., 2004) and acidophilic chemolithotrophic bacteria (Balci et al., 2006). Furthermore, it has been shown that most plants significantly fractionate Fe isotopes during Fe uptake and plant growth, getting increasingly depleted in the heavy Fe isotopes relative to its source in soils (Guelke and von Blanckenburg, 2007).

The largest inorganic (equilibrium) fractionation effects are associated with redox reactions and, thus, changes in the oxidation state of iron. In aqueous solutions, oxidation of $Fe(II)_{aq}$ to

$Fe(III)_{aq}$ causes fractionation by ~3 ‰ in $\Delta^{56}Fe_{Fe(III)-Fe(II)}$ (Welch et al., 2003). Enrichment of the heavy Fe isotopes has also been observed during precipitation of Fe(III)-oxyhydroxides from reduced solutions (Bullen et al., 2001; Beard et al., 2010; Wu et al., 2011; Wu et al., 2012). Apart from redox reactions, considerable Fe isotope fractionation occurs during precipitation of carbonates (Wiesli et al., 2004) and sulphides (Butler et al., 2005; Guilbaud et al., 2011a; 2011b) due to equilibrium and/or kinetic effects. Adsorption of iron onto mineral surfaces (Icopini et al., 2004) and isotope exchange between absorbed and reactive Fe in the outer crystal layers (Crosby et al., 2005; Crosby et al., 2007; Jang et al., 2008; Mikutta et al., 2009) may further alter the Fe isotopic compositions of minerals and surrounding aqueous solutions.

In marine environments, isotopically light $Fe(II)_{aq}$ is produced in anoxic sediment pore waters and released into the water column along continental margins (Severmann et al., 2006; Staubwasser et al., 2006). Alteration of oceanic crust by hydrothermal fluids causes preferential leaching of isotopically light Fe(II) from the basaltic rocks, shifting the Fe isotopic composition of altered basalts towards higher $\delta^{56}Fe$ values (Rouxel et al., 2003). As a consequence, high temperature end member fluids of hydrothermal vent systems are depleted in the heavy Fe isotopes relative to the host rocks (Sharma et al., 2001; Beard et al., 2003b; Severmann et al., 2004; Rouxel et al., 2008; Bennett et al., 2009). Precipitation of sulphides from hydrothermal fluids tends to kinetically fractionate iron, causing especially iron mono- and disulphides to be even further depleted in the heavy Fe isotopes (Rouxel et al., 2004b; Rouxel et al., 2008). Associated with hydrothermal activity in Precambrian oceans, large deposits of banded iron formations (BIF) formed (e.g., Klein, 2005 for review). BIFs are characterised by highly variable Fe isotopic compositions, with $\delta^{56}Fe$ values ranging between around -2 and +2 ‰ (e.g., Johnson et al., 2003; Yamaguchi et al., 2005; Frost et al., 2007; Whitehouse and Fedo, 2007; Johnson et al., 2008a; Steinhoefel et al., 2010; Planavsky et al., 2012), reflecting biogeochemical iron cycling during early sediment diagenesis (Yamaguchi et al., 2005; Johnson et al., 2008a) and/or temporal variations in the ocean's Fe isotopic composition (Rouxel et al., 2005).

3.2. Stable copper isotopes

Copper (Cu) is a trace element in igneous rocks and is present in the Earth's crust at concentrations of about 50 ppm (Hofmann, 1988; Rudnick and Gao, 2004). It occurs in nature mainly as metallic Cu^0, cuprous Cu^{1+} and cupric Cu^{2+}. In the biosphere, copper is cofactor of various enzymes and, therefore, an essential micronutrient. However, elevated concentrations of copper are toxic to most organisms.

Copper has two stable isotopes: ^{63}Cu (69.15%) and ^{65}Cu (30.85%) (de Laeter et al., 2003). Cu isotopic compositions are reported relative to the certified reference material SRM 976 from the National Institute of Standards and Technology (NIST):

$$\delta^{65}Cu_{SRM976} = \left(\frac{{}^{65}Cu/{}^{63}Cu_{sample}}{{}^{65}Cu/{}^{63}Cu_{SRM976}} - 1 \right) \tag{1.31}$$

Compared with iron, much less research has been done on Cu isotope fractionation in nature. Accurate measurements of Cu isotope ratios may be hampered by non-quantitative chromatographic separation of copper from the sample matrix, which causes significant Cu isotope fractionation (Maréchal and Albarède, 2002), and by difficulties in monitoring instrumental mass bias and isobaric interferences on the Cu masses, as it has only two stable isotopes. Therefore, most of the earlier studies focused on Cu isotope fractionation in, for instance, ore deposits (Zhu et al., 2000; Larson et al., 2003; Mason et al., 2005; Asael et al., 2007), as highly enriched or almost pure copper samples do not necessarily require extensive chemical purification before measurement. However, the pioneering study of Maréchal et al. (1999) has provided analytical routines to precisely determine Cu isotopic compositions of samples less enriched in copper. Since then, the analytical methods were successively refined and adapted to various sample matrices (e.g., Archer and Vance, 2004; Ehrlich et al., 2004; Mason et al., 2004a; Mason et al., 2004b; Bermin et al., 2006; Borrok et al., 2007; Peel et al., 2008; Larner et al., 2011).

Terrestrial igneous rocks seem to have limited Cu isotope variations with a mean $\delta^{65}Cu$ value of ~0 ‰ (Luck et al., 2003 and references therein; Herzog et al., 2009; Li et al., 2009; Moynier et al., 2010). Lunar rocks and soils, on the other hand, exhibit $\delta^{65}Cu$ values spanning a range of around 6 ‰, probably reflecting isotope fractionation of the moderately volatile copper due to vaporisation during impact events and/or sputtering (Moynier et al., 2006; Herzog et al., 2009).

Cu isotope fractionation factors have been experimentally determined for both inorganic and biologically mediated reactions. In inorganic systems, large Cu isotope fractionation is caused by redox reactions with $\Delta^{65}Cu_{Cu(II)-Cu(I)}$ values of ~3 ‰ (Ehrlich et al., 2004; Pekala et al., 2011). Chemical reactions without changes in the oxidation state of copper, however, may also result in significant isotope fractionation. Adsorption onto mineral surfaces enriches the adsorbed copper in the heavy isotope (Balistrieri et al., 2008; Pokrovsky et al., 2008). Furthermore, variations in Cu isotopic compositions associated with differences in coordination number, and thus bond strength, between coexisting aqueous copper complexes have been proposed based on experimental observations (Maréchal and Albarède, 2002; Zhu et al., 2002) and theoretical approaches (Seo et al., 2007). The same effect of chemical bonding has been suggested to fractionate Cu isotopes in the presence of organic ligands (Vance et al., 2008; Bigalke et al., 2010b). Experiments involving bacteria showed that Cu isotopes are fractionated during metabolic assimilation (Zhu et al., 2002; Navarrete et al., 2011) and adsorption onto cells (Mathur et al., 2005; Pokrovsky et al., 2008; Kimball et al., 2009; Navarrete et al., 2011).

A large fraction of the published literature focuses on Cu isotope variations in ore bodies, especially in porphyry copper deposits. Here, researchers have been investigating natural systems with emphasis on redox conditions (Asael et al., 2009; Asael et al., 2012) and cycling of copper within the ore deposits (Larson et al., 2003; Graham et al., 2004; Markl et al., 2006; Maher and Larson, 2007; Mathur et al., 2009; Mirnejad et al., 2010; Braxton and Mathur, 2011). In addition, leaching experiments revealed that oxidative dissolution of primary and secondary Cu minerals causes the released aqueous copper to be enriched in the heavy Cu isotope relative to the minerals by up to 3 ‰ in $\delta^{65}Cu$ (Mathur et al., 2005; Fernandez and Borrok, 2009; Kimball et al., 2009; Mathur and Schlitt, 2010; Wall et al., 2011).

In marine hydrothermal vent systems, secondary copper minerals are systematically enriched in the heavy Cu isotope relative to primary sulphides in black smoker chimneys as the result of oxidation of the primary copper sulphides in contact with ambient seawater (Zhu et al., 2000; Rouxel et al., 2004a). Reworking and dissolution of secondary copper minerals in sulphide deposits below the seafloor may release isotopically heavy Cu into high temperature vent fluids, causing variable isotopic compositions of the emanating hydrothermal fluids. The remobilisation of isotopically heavy copper was proposed as one reason for variable Cu isotopic compositions of primary sulphides in hydrothermal vent system, ranging from ca. -0.3 to +3.1 ‰ in $\delta^{65}Cu$ (Rouxel et al., 2004a).

3.3. Stable zinc isotopes

Zinc (Zn) is, as copper, a trace element in most rocks and occurs in the Earth's crust at concentrations of about 70 ppm (Rudnick and Gao, 2004). It is the second most abundant transition metal in organisms after iron and is a building block in numerous enzymes (Broadley et al., 2007).

Zinc has five stable isotopes: ^{64}Zn (48.27%), ^{66}Zn (27.98%), ^{67}Zn (4.10%), ^{68}Zn (19.02%) and ^{70}Zn (0.63%) (de Laeter et al., 2003). Initially, no reference material certified for Zn isotope abundances was available when the first methods for determining stable Zn isotope variations in natural samples by MC-ICP-MS were developed in the late 1990s and early 2000s. Therefore, Maréchal et al. (1999) introduced the in-house reference material 'JMC Lyon' prepared from the zinc metal Zn JMC 3-0749 L (Johnson Matthey$^{©}$), which was afterwards used by the majority of research groups. However, 'JMC Lyon' is no longer available from the Lyon-CNRS laboratory, and the new certified reference material IRMM-3702 was introduced as alternative reference material (Ponzevera et al., 2006), which gives a $\Delta^{66}Zn_{\text{JMC Lyon–IRMM-3702}}$ value of -0.30 ± 0.05 ‰ (Cloquet et al., 2006; Petit et al., 2008; Borrok et al., 2010; Moeller et al., 2012). Most laboratories still use 'JMC Lyon' to report Zn isotope ratios of samples. In this thesis, however, δ^{66}Zn values will be reported relative to both reference materials:

$$\delta^{66}Zn_{JMC\,Lyon} = \left(\frac{{}^{66}Zn/{}^{64}Zn_{sample}}{{}^{66}Zn/{}^{64}Zn_{JMC\,Lyon}} - 1 \right), \quad \delta^{66}Zn_{IRMM\text{-}3702} = \left(\frac{{}^{66}Zn/{}^{64}Zn_{sample}}{{}^{66}Zn/{}^{64}Zn_{IRMM\text{-}3702}} - 1 \right) \qquad (1.32)$$

Various terrestrial silicate rocks have been investigated for their Zn isotopic compositions, including basalts (Maréchal et al., 2000; Chapman et al., 2006; Cloquet et al., 2006; Viers et al., 2007; Herzog et al., 2009), granites (Viers et al., 2007) and andesites (Bentahila et al., 2008; Toutain et al., 2008). The data show a narrow range of δ^{66}Zn values, ranging from about 0.2 to 0.6 ‰ relative to 'JMC Lyon'. In contrast to this rather homogenous Zn isotopic composition of the silicate Earth, large variations in δ^{66}Zn have been found in extraterrestrial material, spanning a range of around 10 ‰ as the result of evaporation-condensation processes (Luck et al., 2005; Moynier et al., 2006; Herzog et al., 2009).

Except for its metallic form, zinc occurs almost exclusively as Zn^{2+} in nature. As shown above, the largest fractionations of iron and copper isotopes are related to changes in their oxidation states. In case of zinc, however, redox reactions do not influence Zn isotopic compositions in most environments. Instead, isotope fractionation was found to be associated, for instance, with adsorption of zinc onto mineral surfaces (Pokrovsky et al., 2005; Balistrieri et al., 2008; Juillot et al., 2008), diatoms (Gélabert et al., 2006; John et al., 2007) and organic matter (Jouvin et al., 2009), generally causing the adsorbed zinc to be enriched in the heavy isotopes relative to the remaining Zn in solution by up to ~0.5 ‰ in δ^{66}Zn. Complexation of aqueous zinc was suggested to create considerable isotope fractionation due to differences in chemical bonding (Fujii et al., 2010; Black et al., 2011; Fujii et al., 2011).

Due to its importance in metabolic processes, a number of studies focused on fractionation of Zn isotopes in biological systems. It was shown that translocation of zinc within higher plants favours the lighter Zn isotopes, resulting in leaves and shoots being enriched in the lighter Zn isotopes relative to the roots (Weiss et al., 2005; Viers et al., 2007; Moynier et al., 2009). Similar, diatoms preferentially assimilate isotopically light zinc (John et al., 2007).

A recent review by Weiss et al. (2008) emphasised the potential of Zn isotope variations to trace anthropogenic pollutant sources in natural environments. Fractionation of Zn isotopes during e.g. smelting (Mattielli et al., 2009) or combustion of coal (Borrok et al., 2010) enables to distinguish anthropogenic from natural zinc sources (Cloquet et al., 2006; Dolgopolova et al., 2006; Gioia et al., 2008; Sivry et al., 2008; Sonke et al., 2008; Chen et al., 2009; Bigalke et al., 2010a).

Zinc is one of the major metals that occur in seafloor hydrothermal vent systems. Precipitation of sulphides results in incorporation of isotopically light zinc from the hydrothermal fluids into the minerals, studied in modern, active vent systems (John et al., 2008) as well as in volcanic massive sulphide (VMS) ore deposits (Mason et al., 2005; Wilkinson et al., 2005; Kelley et al., 2009). As a consequence, formation of VMS below the seafloor may alter the Zn isotopic composition of the emanating fluids towards higher δ^{66}Zn values (John et al., 2008).

4. Synopsis of research findings

The research findings of this thesis are presented in the following three chapters.

Chapter II describes the two-step ion-exchange chromatographic protocol that was developed as part of this thesis at the University of Bergen in order to purify copper and zinc from matrices typical for the here investigated hydrothermal samples. Possible fractionation of Cu isotopes during the chromatographic separation was excluded by applying a standard addition approach with an enriched ^{65}Cu spike. Furthermore, the chapter presents analytical routines for measurements of Cu and Zn isotopic compositions by MC-ICP-MS. A new ^{64}Zn-^{67}Zn double spike was prepared and calibrated to correct for instrumental mass bias during measurements of Zn isotope ratios. The accuracy and applicability of the here developed analytical methods were assessed by inter-laboratory data comparison between the isotope laboratories at the University of Bergen and the Imperial College, London. Special emphasis was placed on calibrating new reference materials certified for Cu and Zn isotope abundances in order to maintain inter-laboratory comparison of Cu and Zn isotope data in the future.

Chapter III presents transition metal isotope variations of low temperature hydrothermal deposits. It focuses on the question whether biological processes leave a specific isotopic fingerprint, which may be used to detect traces of microorganisms in ancient rock sequences. The formation of the investigated siliceous Fe oxyhydroxide mounds from the Jan Mayen vent fields was mediated by extensive microbial mats mainly consisting of the Fe-oxidising bacterium *Mariprofundus ferrooxidans*. Fe isotope variations with $\delta^{56}Fe$ values spanning a range between -2.09 and -0.66 ‰ reflect partial oxidation of aqueous Fe(II), which derived from the low temperature hydrothermal fluids, due to low concentrations of free oxygen in fluid-filled cavities within the mounds and/or microbial activity of the Fe-oxidising bacteria. Fractionation of Cu and Zn isotopes is likely caused by adsorption of these elements onto the surfaces of siliceous Fe oxyhydroxides. Preceding partitioning of copper into different aqueous organic and inorganic complexes, followed by preferential adsorption of aquo complexes onto the Fe oxyhydroxides, might have shifted the Cu isotopic composition of the Jan Mayen samples towards lower $\delta^{65}Cu$ values relative to those of igneous rocks. Isotopic compositions of the modern Jan Mayen deposits were compared to those of Ordovician jasper beds from the Løkken ophiolite complex. $\delta^{56}Fe$ values of these jaspers ranging from -0.38 to +0.89 ‰ indicate partial oxidation of $Fe(II)_{aq}$ in the hydrothermal plume. The Løkken jaspers exhibit Cu and Zn isotope variations remarkably similar to the modern siliceous Fe oxyhydroxide mounds from the Jan Mayen vent fields, although formation processes of these two deposits are different. Overall, clear isotopic evidence for biological activity could neither be found in the modern Fe oxyhydroxide deposits nor in the jasper beds.

Chapter IV presents transition metal isotope investigations of high temperature hydrothermal sulphides from black and white smoker chimneys at the Jan Mayen and the Loki's Castle vent fields. Fe, Cu and Zn isotope variations were successfully applied to trace reaction pathways of sulphide formation. Iron mono- and disulphides, i.e., pyrrhotite and marcasite, respectively, are depleted in the heavy Fe isotopes relative to hydrothermal fluids, reflecting kinetic isotope fractionation during precipitation. Kinetic isotope effects are most likely also the reason for isotopically light iron and zinc incorporated into sphalerite solid solutions. In contrast, the Cu-Fe sulphides isocubanite and chalcopyrite form in isotopic equilibrium with the surrounding fluids. The results presented in this chapter confirm the findings of earlier experimental studies performed by other research groups (Ehrlich et al., 2004; Butler et al., 2005; Guilbaud et al., 2011a; Pekala et al., 2011).

5. Future perspectives

This thesis provides new insights into transition metal isotope fractionation in seafloor hydrothermal vent systems. In search of distinctive isotopic fingerprints to indentify biological activity, the here presented findings may help to give directions for future research. The use of Fe isotope variations to distinguish between inorganic and biologically mediated reactions has long been under debate. The results of chapter III of this thesis reinforce the difficulties to pinpoint biological iron oxidation solely based on Fe isotope data, as even in systems where the oxidation of iron is clearly microbially mediated, spontaneous inorganic oxidation by dissolved oxygen cannot be excluded. Variations of Cu and Zn isotopes may be a promising complement to further address the question of how to identify remnants of biological activity in the rock record by chemical proxies. However, very little is known about the fractionation of Cu and Zn isotopes, for instance, during interactions with microorganisms and complexation by organic and inorganic ligands. Furthermore, the findings of chapter III suggest that Cu and Zn isotope fractionation caused by microbial activity might be superimposed by isotope effects during inorganic reactions. Here, experimental studies are needed in order to understand individual isotope fractionation mechanisms in complex natural systems and how biological isotope signatures may be preserved.

Chapter IV of this thesis shows that fractionation of Fe, Cu and Zn isotopes are useful to trace pathways and mechanisms of sulphide formation. Although there are already a few experimental studies on isotope fractionation during iron and copper sulphide formation, fractionation of Fe and Zn isotopes during precipitation of sphalerite solid solutions has not yet been investigated, and the proposed kinetic effects are solely based on isotope variations measured in natural samples. Furthermore, this thesis shows that the knowledge of the Cu isotopic composition of hydrothermal fluids is a crucial aspect for understanding Cu isotope fractionation in high as well as low temperature hydrothermal systems. This, however, still remains unknown and should be addressed in future studies.

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