Characterization of hydrothermal sources of iron in the oceans

Constraints from iron stable isotopes

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Abstract

In recent years, iron (Fe) has been recognized as one of the key elements in Earth’s biogeochemical cycles, acting as an important micronutrient for photosynthetic organisms, and a limiting factor in regulating primary productivity. Consequently, the oceanic biogeochemical cycle of Fe is tightly linked to the global carbon cycle and hence global climate processes. This perception has triggered intense scientific interest in understanding the marine biogeochemistry of Fe and quantifying its spatial distribution and transport in the oceans, as well as the technological advancements necessary to facilitate high-precision analyses of Fe concentrations and Fe isotopic compositions of marine samples, including seawater.

Identifying the sinks, sources and transformations of Fe species in the global ocean, as well as lateral and vertical modes of transportation and ocean mixing, supplying dissolved Fe to areas away from Fe sources, are the main aims of current research campaigns. Multiple Fe sources, such as aerosol dust, contribute to the marine dissolved Fe budget and novel tools utilizing isotopic characterization of these sources and mass balance calculations are anticipated to facilitate resolution of the complex interplay of the various Fe fluxes. Hydrothermal discharge has received growing attention as a major source of dissolved Fe to the deep ocean, particularly in areas with little dust deposition. However, studies of Fe isotope fractionation in hydrothermal plumes have resulted in controversial findings with implications for constraining the isotopic signature/s of hydrothermally derived Fe and the role of hydrothermal Fe in the global oceanic Fe inventory.

In order to constrain Fe isotope fractionation within a submarine hydrothermal vent field and hydrothermal plume, this study aided in the development of new seawater preconcentration and separation protocols. These new methods facilitate direct Fe isotope analysis of dissolved Fe in plume samples, for the first time, utilizing double spiking techniques and multiple-collector ICPMS (MC-ICPMS) instrument settings specifically adapted to meet the requirements for analysis of low concentration samples. In order to provide a better understanding the Fe isotope systematics in submarine hydrothermal systems, the present study investigates the Fe isotopic compositions of hydrothermal fluids and precipitates from the newly discovered Nifonea vent field in
Vanuatu. Located in a young back-arc basin, Nifonea provides a unique opportunity to (1) study processes affecting Fe isotope fractionation, represented by the $^{56}\text{Fe}/^{54}\text{Fe}$ signature (reformulated as $\delta^{56}\text{Fe}$), in environments characterized by short-lived heat pulses and relatively low water depths, and (2) better constrain Fe isotope effects resulting from subsurface sulfide precipitation and phase separation. The results indicate the complex interplay of sulfide formation and phase separation producing large spatial variability of fluid Fe isotopic compositions with generally low $\delta^{56}\text{Fe}$. High temperatures from recent volcanic events are interpreted to facilitate slow precipitation of chalcopyrite with systematically higher $\delta^{56}\text{Fe}$ compared to hydrothermal fluids causing considerable Fe isotope effects. In addition, phase separation at relatively low pressure conditions produces low-Cl vapor phases and appears to strongly partition the Fe isotopes into vapor and liquid phases. For the first time, we demonstrate fractionation of Fe isotopes during phase separation with similar isotope effects as suggested from recent experimental studies (Syverson et al., 2014).

The processes controlling Fe isotope fractionation and Fe speciation during plume formation above Nifonea are approached by coupled Fe isotope analysis of dissolved and particulate Fe and the chemical composition (major and trace elements) of plume particles. Plume processes largely regulate the transport of dissolved Fe to the open ocean through mineral precipitation and redox processes. Removal and transformation of hydrothermally derived Fe from, or within, the plume also strongly fractionate the original Fe isotopic composition of dissolved hydrothermal Fe towards heavier isotopic compositions, resulting in $\delta^{56}\text{Fe}$ as low as -0.74‰ and up to -0.19‰ in more distal parts of the plume, as suggested in the presented study.

These results further support predictions from previous research (Bennett et al., 2009) however, they also reveal the very complex interplay of various processes affecting the Fe isotope systematics in hydrothermal plumes and preclude a generalized isotopic signature for hydrothermally derived Fe for input into mass balance models. Results of this thesis emphasize the need for further research investigating transformation processes of Fe within hydrothermal plumes, from near-field to far-field, thereby integrating dissolved and particulate Fe isotopic composition, and speciation, as well as particle geochemistry.
Authorship statement

The candidate is the principle investigator and author of all chapters of this thesis. Co-author contributions to chapters II to IV are listed below. In addition contributions of others are also included in front of the individual manuscripts (chapters III and IV).

For chapters I and V the candidate is the sole author.

Chapter II

Chapter II describes the theoretical background of multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) and the development of the instrumental parameters, the double spiking technique and chemical preconcentration and separation protocols. The candidate was responsible for the method development in close collaboration with postdoctoral fellow Dr. Melanie Gault-Ringold, including data acquisition, interpretation and discussion of Fe isotope data.

Establishment of chemical preconcentration and separation protocols intended to be utilized for seawater multi-element extraction was also achieved in joint collaboration with PhD candidate John Rolison.

The chapter was reviewed by Dr. Melanie Gault-Ringold, Assoc. Prof. Sylvia Sander and Assoc. Prof. Claudine Stirling

Chapter III


Iron isotope study of the Nifonea vent field, Vanuatu.

The author was solely responsible for collection of hydrothermal fluid and plume samples for Fe isotope analysis. Unprocessed whole rock samples were provided by Prof. Karsten Haase, Friedrich-Alexander University Erlangen-Nürnberg. Mineral (sulfide) separates from hydrothermal chimney fragments were kindly provided by Florian Häckel, Federal Institute for Geosciences and Natural Resources, Hannover, Germany.
Sample preparation of hydrothermal fluid, plume and sulfide samples as well as volcanic rock samples was performed solely by the candidate at the Centre for Trace Element Analysis, Department of Chemistry, University of Otago, Dunedin, New Zealand, with support from Dr. Melanie Gault-Ringold and Assoc. Prof. Claudine Stirling. Acquisition of Fe isotope data of fluid and plume samples was performed by the candidate under guidance of Dr. Michael Ellwood in the analytical facilities of the Research School of Earth Sciences, ANU, Canberra, Australia, whereas Fe isotope data of sulfide and rock samples was independently collected by the candidate at the Centre for Trace Element Analysis.

Concentration data of hydrothermal fluids was provided by Katja Schmidt (Research group of Andrea Koschinsky, Jacobs University Bremen, Earth and Space Sciences, Bremen, Germany) and Dieter Garbe-Schönberg (University of Kiel, Institute of Geosciences, Kiel, Germany) as part of a status report available for the whole science party of research cruise SO229. Concentration data of plume and sulfide samples was acquired at the Centre for Trace Element Analysis by Dave Barr. Interpretation of the data was mainly performed by the candidate with discussions with Andrea Koschinsky, Katja Schmidt, Dieter Garbe-Schönberg and Charlotte Kleint. Manuscript review was performed by Assoc. Prof. Sylvia Sander and Assoc. Prof. Claudine Stirling.

**Chapter IV**


Isotopic fractionation of iron in a hydrothermal plume above the Nifonea vent field, Vanuatu.

The candidate was solely responsible for collection and filtration of seawater samples. Handling of seawater preconcentration was assisted by Dr. Melanie Gault-Ringold and John Rolison, while the preparation of particle filters was performed solely by the candidate who also acquired all Fe isotope data independently at the Centre for Trace Element Analysis.

Concentration data of filter extracts was acquired at the Centre for Trace Element Analysis by Dave Barr; preliminary Fe concentrations of seawater samples were
obtained from flow-injection analysis by Ella Paterson. Fluid Rare Earth Element concentrations and advice for data reduction were provided by Katja Schmidt (Research group of Andrea Koschinsky, Jacobs University Bremen, Earth and Space Sciences, Bremen, Germany).
Assoc. Prof. Sylvia Sander and Assoc. Prof. Claudine Stirling reviewed the manuscript.

Scientific environment

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Chapter I

Introduction
1.1 Overview

In recent years, iron (Fe) has been recognized as one of the key elements in biogeochemical cycles, acting as an important micronutrient for photosynthetic organisms. However, in contrast to macronutrients, such as nitrogen (N) and phosphorus (P) that are widely available in most of the open ocean, Fe concentrations are severely depleted in certain regions of the world’s oceans, referred to as ‘high nutrient low chlorophyll’ (HNLC) areas, such as the Southern Ocean or the equatorial Pacific Ocean (figure 1.1). In these areas, Fe becomes a limiting factor regulating primary production (Archer and Johnson, 2000; 2007; Boyd et al., 2000; Pollard et al., 2007).

In 1990, Martin (1990) proposed a tight coupling between the oceanic Fe and carbon cycles to an extent where the availability of Fe would influence global climate. According to this “Iron Hypothesis”, Fe fertilization of the Southern Ocean strongly increased primary production, subsequently resulting in the massive draw-down of CO₂ that is widely attributed to have caused the last glacial maximum (Archer and Johnson, 2000; Lefevre and Watson, 1999; Martin, 1990; Martin et al., 1994). Consequently, the biogeochemical cycling of Fe has received much attention with intense international research aimed at understanding the marine biogeochemistry of Fe and quantifying its spatial distribution and transport in the oceans (Ussher et al., 2004), but also focused on improving trace

Figure 1.1
Surface concentrations of annually averaged (a) dissolved Fe [nM], (b) NO₃ [µM], (c) chlorophyll a [mg/m³], originating from the Pelagic Integration Scheme for Carbon and Ecosystem studies (PISCES) global ocean biogeochemistry model and published in Tagliabue et al. (2009). The PISCES model is fully described in Aumont and Bopp (2006). White ellipses mark major HNLC areas.
metal handling protocols and analytical procedures; e.g. Bruland et al. (1979); Biller and Bruland (2012). Identifying the sinks and sources and transformations of Fe species in the global ocean as well as lateral and vertical modes of transportation and ocean mixing, supplying dissolved Fe to areas away from dFe sources will greatly increase the understanding of the oceanic Fe cycle and its coupling to the carbon cycle and hence primary productivity.

1.2 Iron in the ocean

1.2.1 Distribution and speciation

Seawater Fe is generally separated in two different Fe pools, dissolved Fe (dFe) and particulate Fe. Dissolved Fe is operationally defined as being able to pass through a 0.2 (or 0.4) µm filter, while the particulate fraction is retained on such filters (Cullen et al., 2006). The dissolved Fe fraction can be further divided into colloidal and soluble Fe species (Bergquist et al., 2007; Wu et al., 2001). Both species are variable in the global ocean and have been shown to contribute equally to observed variability in dFe (Fitzsimmons and Boyle, 2014).

Concentrations of dissolved Fe in modern day oceans are on average very low, due to the insolubility of oxidized Fe and its consequential removal from solution, which is tightly coupled to the atmospheric oxygen content. As a result, Fe concentrations in today’s oxygenated oceans are more than 3 orders of magnitude lower than in the suboxic Archean (3.8 to 2.5 billion years) ocean (Johnson et al., 1997).

In the modern open ocean, dFe concentrations as low as 0.05 nM are commonly observed within the upper 100 m of the water column, sharply increasing to ~0.5 nM at the depths between 200 and 800 m (de Baar and de Jong, 2001; Johnson et al., 1997), while concentrations ranging from ~0.4 to 1 nM are typically observed in the deep ocean, depending on the local water mass (Bergquist and Boyle, 2006a; Boyle, 1997; Johnson et al., 1997). Iron occurs in both of its two oxidation states, Fe(II) and Fe(III), and as numerous chemical species in seawater; Fe(III) is the much less soluble than Fe(II) but is thermodynamically favored and thus the most abundant form of Fe in oxygenated seawater (e.g. Radic et al. (2011)). Additionally, more than 99% of the dissolved Fe fraction is thought to be present in complexes with organic ligands that
largely control its solubility (Johnson et al., 1997; Kuma et al., 1996; Rue and Bruland, 1995).

Particulate Fe, on the contrary, comprises biogenic phyto- and zooplankton, as well as organic matter and inorganic forms (Radic et al., 2011). All different forms of Fe interact through a range of processes in the marine environment, such as biological uptake/degradation, adsorption/desorption and precipitation/dissolution (de Baar and de Jong, 2001; Radic et al., 2011; Ussher et al., 2004).

1.2.2 Sources and sinks of marine Fe
The marine Fe budget is controlled by the balance between Fe sources and sinks. While the removal of Fe from the water column and into marine sediments by the settling of particles is the only Fe sink, there are numerous Fe sources whose individual importance remains controversially debated (Bennett et al., 2009; Radic et al., 2011; Ussher et al., 2004). The surface ocean is generally considered to be mainly supplied by dissolved Fe from dust deposition and dissolution (Duce and Tindale, 1991; Jickells et al., 2005; Jickells and Spokes, 2001), with minor contributions from rivers, groundwater and sediments in coastal areas (Elrod et al., 2004; Johnson et al., 1999; Wells et al., 1995; Windom et al., 2006).

Windblown soil dust is indeed the largest source of Fe by mass to the surface of the open ocean; however its solubility is significantly reduced compared to Fe from other aerosol sources (Jickells et al., 2005; Mackie et al., 2008; Mead et al., 2013). In fact, atmospherically-derived Fe appears to be largely maintained in the colloidal size fraction, as supported in a more recent study by (Fitzsimmons and Boyle, 2014). During experiments by Buck et al. (2013) carried out in the North Pacific, only 1.7% of the total aerosol Fe was found to be soluble aerosol Fe (II), comprising 26.2% of the soluble aerosol Fe in seawater. Therefore, solubility appears to be unrelated to the aerosol Fe concentration in the atmosphere (Buck et al., 2013). Iron isotope analyses of size-segregated aerosol samples collected on Bermuda revealed an important non-soil-dust source of Fe, which the authors attributed to biomass burning (Mead et al., 2013).

In the deep ocean, remineralization of sinking particles, as well as benthic inputs of dissolved Fe from seafloor sediments and hydrothermal discharge are major Fe sources. However, their relative impact has been the subject of on-going debate
Until recently, hydrothermal vents were not considered to significantly contribute to the marine dissolved Fe budget, however there is a growing body of evidence showing that some hydrothermal Fe persists in the dissolved phase and contributes to the global ocean inventory (see section 1.3.2).

Wind-driven upwelling of Fe-rich deep water along continental margins (Boyle et al., 2005; Coale et al., 1991; Coale et al., 1996; Lupton, 1998; Mackey et al., 2002; Winckler et al., 2010) or through Eddies (Adams et al., 2011; McGillicuddy et al., 2007) in turn fuels the surface ocean with dissolved Fe, but also diapycnal diffusion (diffusion across density surfaces) carries Fe rich deep water to the surface (Tagliabue et al., 2014). North Atlantic Deep Water (NADW) was shown to contain excess dFe after full biological utilization thereby acting as an important Fe source for biological production in the global ocean (Rijkenberg et al., 2014).

In areas with little landmass nearby and consequently reduced deposition of Fe-bearing dust and continental run off, such as the Southern Ocean, supply of dFe from deep water reservoirs is the dominant Fe source for surface waters (Tagliabue et al., 2014). Deep mixing in winter accounts for the supply of ten times more dFe to the surface ocean each year than diapycnal diffusion, as demonstrated by Tagliabue et al. (2014). The main source of Southern Ocean deep water dFe, in turn, was suggested to be hydrothermal input (see section 1.3.2).

Quantifying the relative impact each of these potential sources has on the dissolved Fe pool is extremely difficult (de Baar and de Jong, 2001), but new approaches utilizing Fe stable isotopes are being increasingly used as promising new tracers of oceanic Fe cycling (see section 1.5). This emerging tool has proven useful in tracing the processes that control inputs and losses of Fe to the ocean, biological cycling and speciation (Bennett et al., 2009; John and Adkins, 2010; Lacan et al., 2008; Radic et al., 2011; Severmann et al., 2004) as chemical and biological transformation processes leave behind distinctive shifts in the Fe isotopic signature. Moreover, the different sources of Fe can inherit these characteristic isotopic ‘fingerprints’ (Beard et al., 1999; Beard et al., 2003; Bullen et al., 2001; Conway et al., 2013; Conway and John, 2014; Homoky et al., 2013; Johnson et al., 2005; Johnson et al., 2002; Mead et al., 2013; Skulan et al., 2002).
1.3 Iron in hydrothermal systems

As discussed above, hydrothermal iron has been identified as an important source of dFe to the oceans. The number of discovered hydrothermal vent sites has been increasing steadily since their first discovery in the late 1970s (German and Von Damm, 2006), with known areas of active venting in a range of geotectonic settings, including mid-ocean ridges (e.g. Bach et al. (2002); Baker et al. (2004); Haase et al. (2007)), island arc (de Ronde et al., 2001; Massoth et al., 2007; Resing et al., 2009) and back-arc systems (James et al., 2014; Mottl et al., 2011; Reeves et al., 2011) as well as seamounts (e.g. Karl et al. (1988)). The nature of hydrothermal venting varies between geotectonic settings as a function of host rock, magmatic activity, heat flow and depth and produces distinctive fluids that differ in temperature, pH, metal and volatile content (German and Von Damm, 2006). Amongst all elements that are cycled through hydrothermal circulation cells, Fe is one of the main components, and along with sulfur, probably represents one of the most crucial elements for overall ocean chemistry because of its importance as a micronutrient (Boyd et al., 2007). Iron is highly enriched in hydrothermal fluids due to intense leaching from volcanic rocks with concentrations ranging from <2 µM (e.g. Menez-Gwen, Mid-Atlantic Ridge) up to 24 mM as reported from the Rainbow vent field also located on the Mid-Atlantic Ridge (Douville et al., 2002).

1.3.1 Hydrothermal circulation

Hydrothermal circulation cells are generally best described as cold seawater penetrating downwards in the oceanic crust where it undergoes transformation into a hot, acidic and reducing fluid that, due to its decreased density, rises back to the seafloor where it is expelled into the cold deep ocean. Fracture zones, rifts and oceanic detachment faults allow seawater to percolate downwards into the volcanic basement rock and the so called ‘recharge zone’, where metasomatic alteration of the crustal rocks occurring at lower temperatures (usually <150°C) transforms volcanic glasses and minerals to clays and oxyhydroxides (German and Von Damm, 2006; White, 2005). Also, anhydrite (CaSO₄) precipitation and the replacement of primary igneous minerals (for example plagioclase or pyroxene) and glass by Mg-rich secondary minerals, such as the clay mineral smectite (which replaces plagioclase) and chlorite (which replaces pyroxene) are typical reactions. Free protons are produced during the replacement of primary
igneous minerals causing the pH to drop (White, 2005). During downward percolation Ca, Mg and sulfate are stripped from the liquid and pH is lowered to a value of ~3-4, which greatly increases the leaching capacity of the fluid.

The recharge zone is followed by the ‘reaction zone’ where most of the metal leaching occurs. Here, the fluid reaches its closest proximity to the magma chamber heat source and is heated to temperatures above 350°C. Due to the reduction of sulfate to sulfide, the fluid becomes increasingly more acidic and reducing, with typical pH values of ~2 (German and Von Damm, 2006; White, 2005). Under these conditions, metals such as Cu, Zn, Fe and Mn, but also S, are readily leached from volcanic rocks, or released by the dissolution of metal sulfides, together with H₂S. When leached from the rocks, metals are more or less completely complexed by chloride anions, the most common anion under these pH conditions, as sulfide will be largely protonated (White, 2005).

The reaction zone is also the region where phase separation occurs. Phase separation below the critical point of seawater (at 298 bar and 407°C) is a common process associated with high-temperature hydrothermal vent systems causing seawater-derived fluids to separate into a gas rich, low chlorine and low density vapor phase and a dense deep circulating high chlorine liquid phase (or ‘brine’) at relevant temperature and pressure conditions (see figure 1.3). Phase separation above the critical point of seawater (supercritical phase separation) has only been observed in a single hydrothermal system so far (5°S on the Mid-Atlantic ridge) and was shown to produce differently evolving fluids than subcritical phase separation (Koschinsky et al., 2008).

Figure 1.2
Schematic illustration of a typical hydrothermal circulation cell and the main reactions occurring in the different stages. Adapted from White (2005)
With continuous boiling under subcritical conditions, the brine becomes progressively concentrated in Na, Cl and all elements forming chloride complexes (such as Fe), while the vapor phase is increasingly diluted (Foustoukos and Seyfried, 2007; Syverson et al., 2014; White, 2005). Consequently, the degree of phase separation controls the amount of Fe exported from a vent field. Time-displaced venting of both individual phases is generally assumed, whereby storage of the denser brine within the crustal rocks is required, but simultaneous venting of vapor and brine has been observed as well (Koschinsky et al., 2008; Von Damm et al., 1997; Von Damm et al., 2003). When venting occurs separately, the chemistry of the emanating fluid will change severely, from gas-rich, but metal depleted, towards a metal-rich fluid, with implications for vent communities, sediment formation and plume processes (White, 2005). In particular, in island arc settings and on seamounts, a contribution of magmatic volatiles (mostly sulfur species) to the hydrothermal fluid may be observed following volcanic eruptions (Von Damm, 2000).

Heating of the fluid significantly lowers its density and causes the fluid to ascend towards the surface, enriched in metal species such as Fe, Cu, Zn and Mn as well as gases like He, H₂, H₂S, CO₂ and methane. The ‘upflow zone’ accommodates only limited exchange between the fluid and crustal rocks but cooling of the fluids during ascent can induce subsurface precipitation of polymetallic sulfides (White, 2005).

1.3.2 Significance of hydrothermal Fe fluxes

Although total dissolved Fe fluxes from hydrothermal systems have been estimated to be $-9 \times 10^8$ mol dFe/yr (Bennett et al., 2008; Tagliabue et al., 2010), a significant export of Fe from hydrothermal systems has long been excluded (German et al., 1991; Mottl
and McConachy, 1990). This was because most of the dFe contained in vent fluids was regarded to be removed from the water column shortly after venting by the precipitation of Fe-sulfides and Fe-oxyhydroxides upon mixing with cold, oxygenated seawater. Accordingly, removal of up to 50% of the original Fe load and subsequent storage in hydrothermal sediments was proposed (Elderfield and Schultz, 1996; Feely et al., 1987; Rudnicki and Elderfield, 1993). More recently, however, evidence has increased showing that significant amounts of hydrothermally derived Fe persists in the dissolved phase and contributes a significant flux of dFe to the global ocean.

Increased dFe concentrations of 1.0-1.5 nmol/kg (about 0.4-0.9 nmol/kg higher than typical deep-sea dFe concentrations) near 2000 m depth in the abyssal southeast and southwest Pacific Ocean have been linked to hydrothermal activity, possibly along the southern East Pacific Rise thousands of kilometers away (Fitzsimmons et al., 2014; Resing et al., 2015). Furthermore, transformations of dFe, such as changes in size partitioning between the soluble and colloidal phases appear to continue even far from the vent source (Fitzsimmons et al., 2014). Similar observations of widespread hydrothermally derived dFe in the Indian Ocean (Nishioka et al., 2013) imply a greater longevity of hydrothermal dissolved Fe in the global deep ocean. Dissolved Fe persists over large distances and with sufficient magnitude to have far-field effects on the global dFe budget, estimated at four gigamoles per year, four times higher than previously thought (Bennett et al., 2008; Fitzsimmons et al., 2014; Resing et al., 2015; Tagliabue et al., 2010). In particular, the Southern Ocean, a region of critical importance for the global carbon cycle, may largely depend on hydrothermally derived Fe to sustain primary production (Beard et al., 2003b; Resing et al., 2015; Tagliabue et al., 2014b; Tagliabue et al., 2010).

Several mechanisms have been proposed to increase the longevity of dissolved Fe in the deep ocean. Nanoparticulate pyrite (< 200 nm), for example, formed during early stages of fluid discharge, are more resistant to oxidation than Fe(II)aq and FeS and are less likely to settle from the particle cloud, thereby increasing the chance of transportation over long distances (Yucel et al., 2011). Furthermore, organic ligands have been shown to complex with dissolved Cu and Fe, thereby reducing its reactivity because reducing microenvironments are maintained within the particle aggregates. This microbiologically mediated process prevents the precipitation of Fe minerals, and thus the
partitioning of Fe into the particulate phase, allowing for dispersion of dissolved Fe into the open ocean (Bennett et al., 2008; Lang et al., 2006; Sander and Koschinsky, 2011; Sander et al., 2007; Toner et al., 2009; Toner, 2012). According to Hawkes et al. (2013) up to 7.5% of hydrothermal dissolved Fe in a South Atlantic hydrothermal plume was sufficiently stabilized to make an impact on the deep ocean inventory.

Varying oxidation kinetics also modify Fe transport from hydrothermal vent sites. As shown by Field and Sherrel (2000) and Statham et al. (2005), oxidation rates progressively slow down along the thermohaline circulation, with significantly longer Fe(II)_{aq} oxidation half-lives in the Pacific ocean. This will significantly affect the magnitude of Fe loss due to particulate sulfide settling in the buoyant plume and thus transport of Fe to the distal parts of the plume. In contrast, prolonged Fe(II)_{aq} oxidation half-lives increases the time required for organic molecules to complex with Fe(II)_{aq} before its oxidation to less soluble Fe(III)_{aq} and subsequent precipitation.

Hydrothermal Fe fluxes are likely to remain approximately constant over long time periods (Chu et al., 2006) and consequently may act as a ‘buffer’ of the oceanic dissolved Fe inventory against shorter-term variations in dust deposition (Tagliabue et al., 2010).

1.4 Principles of stable Fe isotopes

Isotopes are atomic variants of a chemical element whose nuclei differ in the number of neutrons while the number of protons remains equal. Depending on the ratio of protons to neutrons, isotopes may either be stable or radioactive. Radioactive isotopes decay into nuclides of lower mass whereby high-energy radiation is emitted. Stable isotopes, in contrast, are either truly stable, in which case they do not decay, or they feature extremely long half-lives and are thus considered stable.

The abundances of isotopes of a specific element vary in nature; the preferential partitioning of light or heavy stable isotopes between co-existing compounds or phases during physicochemical reactions often gives rise to a shift in isotopic composition, referred to as ‘stable isotope fractionation’, as opposed to ‘radiogenic isotope fractionation’ where nuclear processes cause variations in the isotopic composition of elements.
On Earth, these variations are largely dependent on the mass of an isotope and the relative mass difference between two isotopes of one element (mass-dependent fractionation), but mass-independent isotope fractionation occurs as well, for example, creating oxygen and sulfur isotope variations in sulfate deposits (Bao et al., 2000; Michalski et al., 2004; Stosch, 1999).

Fractionation of the isotopic ratio \( R \) of a specific element A, defined as

\[
R = \frac{\text{heavy} A}{\text{light} A}
\]  

(Equation 1.1)

between reactant and product is described by a fractionation factor \( \alpha \), defined as:

\[
\alpha_{\text{Product, Reactant}} = \frac{R_{\text{Product}}}{R_{\text{Reactant}}}
\]  

(Equation 1.2)

Because variations in isotope abundances (of element A) in nature are rather small, isotope ratios are commonly reported in the \( \delta \)-notation relative to a reference material as per mill deviation by multiplying with a factor of \( 10^3 \).

\[
\delta_{\text{heavy/light} A} = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right)
\]  

(Equation 1.3)

Isotope fractionation between two compounds or phases (X and Y) is also expressed as the difference \( \Delta \) between their isotopic compositions:

\[
\Delta_{X,Y} = \delta_X - \delta_Y
\]  

(Equation 1.4)

whereby \( \alpha \) and \( \Delta \) follow the relationship:

\[
\Delta \approx 10^3 \ln \alpha
\]  

(Equation 1.5)

Two different fractionation mechanisms can cause mass-dependent isotope fractionation, kinetic effects and equilibrium effects. Both are briefly summarized below (based on White (2005)).

1.4.1 Equilibrium isotope fractionation

The majority of isotope fractionation results from equilibrium effects. Equilibrium fractionation effects are caused by translational, rotational and vibrational motions of atoms in crystals and molecules in liquids and gases because the energies associated with these motions are mass dependent (White, 2005). In order to minimize energy,
systems tend to transform and distribute their isotopes accordingly to minimize vibrational, rotational and translational energy. Vibrational energy contributes by far the most significantly to isotopic fractionation, because it is the only mode of motion available to atoms in solids. Vibrations of atoms in molecules and crystals approximate that of a simple harmonic oscillator (White, 2005) for which the vibrational energy is defined as:

\[ E_{\text{vibrational}} = (n + 1/2) \nu h \]  

(Equation 1.6)

where \( \nu \) is the vibrational frequency, \( h \) is Plank’s constant and \( n \) is the vibrational quantum number. The relationship between frequency and reduced mass in such an ideal harmonic oscillator is:

\[ \nu = \frac{1}{2} \sqrt{k/\mu} \]  

(Equation 1.7)

where \( k \) is the forcing constant, a function of the electronic configuration of a molecule, but not the isotope involved; \( \mu \) is the reduced mass of such a molecule, expressed as:

\[ \mu = \frac{1}{((1/m_1) + (1/m_2))} = \frac{(m_1 \cdot m_2)}{(m_1 + m_2)} \]  

(Equation 1.8)

The partition function for vibrational motion of a simple diatomic molecule such as \( \text{H}_2 \) is calculated as:

\[ Q_{\text{vibrational}} = \left( e^{\nu h/2 kT} / (1 - e^{\nu h/2 kT}) \right) \]  

(Equation 1.9)

Accordingly, as evident from equation 1.7, the vibrational frequency depends on the mass of atoms or isotopes involved in the bond. Consequently, since both the vibrational energy (equation 1.6) and the partition function (equation 1.9) are related to the vibrational frequency, these terms are mass-dependent as well (White, 2005). The zero point energy (ZPE), which is the energy level of vibration in a molecule’s ground state and hence at low temperature (White, 2005), is greater for bonds involving a light isotope than for bonds with a heavier isotope (figure 1.4). Consequently, the energy required for a molecule to dissociate differs between different isotopic combinations of one molecule, e.g. 440.6 kJ/ mol for \( ^2\text{H}_2 \) (a hydrogen molecule consisting entirely of deuterium), but only 431.8 kJ/mol for \( ^1\text{H}_2 \) (ordinary hydrogen); values from White (2005).
Bond strength increases with increasing difference between ZPE and the energy of the dissociated atoms and thus substitution of a heavier isotope for a lighter one will result in a stronger bond. In general equilibrium fractionation decreases with increasing temperature (T) and is largest for elements with low atomic masses where relative mass differences between isotopes are also larger, as summarized by Schauble (2004). Complexation of aqueous Fe (III) by organic ligands was suggested to result in equilibrium Fe isotope fractionation (Dideriksen et al., 2008), but also the isotopic exchange of Fe bearing minerals (Fe-sulfides as well as Fe-oxyhydroxides) with Fe rich solutions will produce equilibrium isotope effects (Skulan et al., 2002; Welch et al., 2003).

1.4.2 Kinetic isotope fractionation

In cases of fast, incomplete or unidirectional reactions, such as evaporation, diffusion, dissociation reactions, and biological reactions, kinetic isotope effects occur (White, 2005). As shown above, molecules containing the heavy isotope have higher dissociation energies and are thus more stable than those containing the light isotope. This implies that bonds involving the light isotopes can be broken more easily and are hence the first to be broken during a reaction. In other words, the heavy isotope reacts more slowly, which is also expressed by its kinetic energy, given by:

\[ E_{\text{kinetic}} = \frac{1}{2} m v^2 \]  

(Equation 1.10)

where \( m \) corresponds to the mass of a molecule or atom and \( v \) to its velocity. The velocity of a molecule or atom is also affected by its mass and differs according to:

\[ m_{\text{light}} / m_{\text{heavy}} = v_{\text{heavy}}^2 / v_{\text{light}}^2 \]  

(Equation 1.11)
Consequently, when reactions are incomplete and hence do not achieve equilibrium, the lighter isotope is usually expected to be preferentially concentrated in the reaction products. A typical example for kinetic isotope fractionation relevant to this study is the enrichment of the light Fe isotopes in Fe-sulfides rapidly precipitating from a hydrothermal vent fluid upon mixing with seawater (Butler et al., 2005; Rouxel et al., 2008). This nicely highlights how the same chemical reaction (precipitation of a solid phase from solution) may result in very different isotope effects as a function of reaction kinetics.

1.4.3 Stable Fe isotopes

Iron has four stable isotopes ($^{54}$Fe, $^{56}$Fe, $^{57}$Fe and $^{58}$Fe) that occur with different natural abundances ($^{54}$Fe: 5.8%, $^{56}$Fe: 91.72, $^{57}$Fe: 2.2%, $^{58}$Fe: 0.28% (Anders and Grevesse, 1989)). As a result of the rather small variations in Fe isotope abundances in nature, the Fe isotopic composition is expressed in δ-notation relative to the IRMM-14 certified isotope reference material as follows:

\[
\delta^{56}\text{Fe} = \left(\frac{^{56}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{sample}} - \left(\frac{^{56}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{standard}} - 1
\]

(Equation 1.12)

Since the development of multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) in the late 1990s, Fe isotope measurements with analytical precisions of around ± 0.05‰ (2 standard deviation, 2 SD) with respect to $\delta^{56}$Fe can now be routinely obtained (Arnold et al., 2003; Belshaw et al., 2000; Schoenberg and von Blanckenburg, 2005; Weyer and Schwieters, 2003).

Variations in the Fe stable isotope composition can be either the result of biotic and abiotic redox processes or can arise from non-redox processes (Bennett et al., 2009). The largest Fe isotope effects are expected to occur in low temperature environments because equilibrium isotope fractionation decreases with increasing temperature (Schauble, 2004). Accordingly, only limited Fe isotope variation was observed amongst meteorites, lunar rocks and igneous rocks from Earth’s high temperature settings (Beard et al., 2003; Poitrasson and Freydier, 2005; Schoenberg and Blanckenburg, 2006; Weyer et al., 2005; Zhu et al., 2001), while biologically mediated processes operating at low temperature in Earth’s surface environments were shown to significantly fractionate Fe isotopes (Balci et al., 2006; Beard et al., 1999; Crosby et al., 2007; Guelke and von...
Blanckenburg, 2007; Johnson et al., 2005). Low-temperature redox conversions seem to generate the largest isotopic fractionations, resulting in an Fe(II) pool enriched in the light Fe isotopes and an Fe(III) pool enriched in heavy isotopes (Johnson et al., 2008). Accordingly, there is large potential for Fe isotope fractionation in hydrothermal systems and plumes due to kinetic isotope effects during rapid Fe-sulfide precipitation, or alternatively, upon (partial) oxidation of Fe(II)\textsubscript{aq} to Fe(III)\textsubscript{aq} and subsequent precipitation of Fe-oxyhydroxides. The magnitude of these processes will determine how strongly the original Fe isotopic composition is fractionated.

Because of the low Fe concentration in the modern oceans, the residence time of Fe in seawater is limited to 70-200 yrs (Johnson et al., 1997). As a result, the Fe isotopic composition of seawater can be subjected to rapid changes if either the relative fluxes of Fe with distinctive Fe isotopic compositions change, or upon variation in the Fe isotopic composition of the Fe delivered to the oceans (Beard et al., 2003b).

1.5 Iron isotopes in the marine system

Although in theory every significant Fe source can either change its flux or its Fe isotopic composition, some are more likely to create significant shifts in the Fe isotopic composition of seawater than others. This is either because of the magnitude of their flux into the ocean or due to a particularly distinctive isotopic signature and is discussed in the following paragraphs. A schematic overview is also presented in figure 1.5.

The Fe isotopic composition of a broad range of sedimentary rocks of different ages, loess, modern marine sediments, the suspended load from rivers as well as soil and modern aerosols define a very limited range of $\delta^{56}$Fe values (average $\delta^{56}$Fe = +0.02‰ ± 0.07‰, (Beard et al., 2003b)), which overlaps with the suggested $\delta^{56}$Fe for the Bulk Silicate Earth of $\delta^{56}$Fe = +0.09‰ ± 0.08‰ (Beard et al., 2003). This limits the potential influence of weathering, transport and diagenesis on seawater $\delta^{56}$Fe, as well as the feasibility of resolving riverine from atmospheric inputs to the marine dFe inventory on the basis of mass balance calculations. Since most of the riverine particulate matter is assumed to be stored on the continental shelves, forming massive layers of sediment, its contribution could in fact be negligible (Beard et al., 2003b). However, the chemical reduction of poorly soluble Fe(III) to highly soluble Fe(II) in these thick continental
margin sediment layers mobilizes a considerable flux of isotopically light dissolved Fe to the ocean which may be distinguished from ‘unfractionated’ atmospheric deposition (Homoky et al., 2013). Besides reductive dissolution, ‘non-reductive’ dissolution of continental margin sediments was shown to produce a smaller and isotopically heavier flux of dFe to seawater (Homoky et al., 2013).

Atmospheric deposition was previously mentioned as one major source of Fe (section 1.2.2). Although it is unfractionated and lacks a distinct isotopic signature, it contributes roughly $30 \times 10^{10}$ mol Fe/yr to the marine Fe pool (Duce and Tindale, 1991; Jickells and Spokes, 2001). Fluctuations in Fe load and/or changes in the $\delta^{56}$Fe of dust would impact on the seawater Fe isotopic composition by changing oceanic mass balance. Mead et al. (2013) discovered an isotopically distinct non-soil-dust Fe source in the $<2.5 \ \mu m$ size fraction of size-segregated Bermuda aerosol samples that was suggested to originate from biomass burning (Mead et al., 2013).

Another clearly distinct impact is expected from hydrothermal discharge, contributing Fe with negative $\delta^{56}$Fe in the range of $-0.69\%$ to $-0.12\%$ (Beard et al., 2003b; Mackey et al., 2002; Rouxel et al., 2008; Severmann et al., 2004; Sharma et al., 2001) with a recently estimated annual flux of four gigamoles per year (Bennett et al., 2008; Fitzsimmons et al., 2014; Resing et al., 2015; Tagliabue et al., 2010). Accordingly, resolving between the relative influence of atmospheric and hydrothermal input appears feasible.

However, significantly increased $\delta^{56}$Fe values (ranging from $+0.3$ to $+0.7\%$) have been detected in surface mixed layers thought to be dominated by dust deposition, and were attributed to fractionation of bulk aerosol ($\delta^{56}$Fe $\approx 0\%$, (Beard et al., 2003b; Mead et al., 2013; Waeles et al., 2007) during dissolution (Conway and John, 2014). Similarly, fractionation of the original vent $\delta^{56}$Fe was proposed to occur in the plumes above most hydrothermal systems (Bennett et al., 2009; Severmann et al., 2004), highlighting the potential for alteration of the original isotopic signatures assigned to specific Fe sources upon their introduction to the marine environment, with consequences for mass balance approaches such as those published by Beard et al. (2003b) or Conway and John (2014).
Figure 1.5
Schematic review of the oceanic iron isotope cycle adapted from Radic et al. (2011). The main Fe sources to seawater and their respective isotopic signatures are indicated (see references a-f) as well as estimates of the isotopic fractionations ($\Delta^{56}$Fe) associated with biological uptake and Fe removal in the water column, although caution is advised.

References are:
a Bergquist and Boyle (2006b); De Jong et al. (2007); Escoube et al. (2009); b Beard et al. (2003b); Bergquist and Boyle (2006b); Ingri et al. (2006); Escoube et al. (2009); c Severmann et al. (2006); Homoky et al. (2009); Severmann et al. (2010). $\delta^{56}$Fe as observed in sediment pore waters and benthic chambers in reducing environments; d Sharma et al. (2001); Beard et al. (2003b); Rouxel et al. (2008); e Beard et al. (2003b); Waeles et al. (2007); Mead et al. (2013) f Radic et al. (2011)

1.5.1 Iron isotopic composition of seawater
Despite the uncertainties involved with the isotopic characterization of the various Fe sources, early predictions based on mass balance calculations by Beard et al. (2003b) agree well with direct measurements of seawater dissolved $\delta^{56}$Fe utilizing state of the art seawater preconcentration protocols and double spiking techniques (Conway et al., 2013; John and Adkins, 2010; Lacan et al., 2010; Radic et al., 2011).

Specifically, Beard et al. (2003b) calculated the expected average Fe isotopic composition for seawater in different ocean basins with varying proportions of atmospheric deposition and mid-ocean ridge hydrothermal discharge, whereby the northern oceans received predominantly atmospheric input yielding $\delta^{56}$Fe close to zero (e.g. dissolved $\delta^{56}$Fe $\approx$ -0.1‰ for the North Atlantic) while the southern oceans received greater proportions of hydrothermal input resulting in more negative $\delta^{56}$Fe values (e.g.
dissolved $\delta^{56}\text{Fe} \approx -0.35\%$ for the South Atlantic). In these calculations, the relative ridge-axis length was used to define the proportions of hydrothermal influx to the different ocean basins.

Directly measured dissolved Fe isotope compositions by Lacan et al. (2008; 2010), ranging from $-0.49 \pm 0.08\%$ to $+0.23 \pm 0.08\%$ generally reproduced the negative $\delta^{56}\text{Fe}$ values proposed for the southern Atlantic by Beard et al. (2003b), while data from the North Atlantic reveal significantly more positive $\delta^{56}\text{Fe}$ values ($+0.3 \pm 0.07\%$ to $+0.8 \pm 0.07\%$) (Conway and John, 2014; John and Adkins, 2010; Lacan et al., 2010) than suggested from the earlier mass balance calculations. Furthermore, positive $\delta^{56}\text{Fe}$ values ranging from ca. $+0.01$ to $+0.58\%$ were reported from the tropical South Pacific (Papua New Guinea area) by Radic et al. (2011) but may represent a more local trend, since this area’s Fe inventory is mostly influenced by sedimentary inputs.

In general, the density of $\delta^{56}\text{Fe}$ data points and coverage of the world’s oceans remains very poor. However, to a first approximation, the general suggestions made by Beard et al. (2003b) appear realistic. Further studies have proposed that the Fe budget of the Southern Ocean is predominantly controlled by hydrothermal input (e.g. Tagliabue et al. (2010)).

Increased utility of iron isotope datasets will enable better constraints to be placed on oceanic Fe budgets and will thus improve understanding of the effects of changing Fe input on the oceanic Fe cycle, which will also allow for better climate model parameterization (Resing and Barrett, 2014). The first $\delta^{56}\text{Fe}$ section across an ocean basin covering the North Atlantic was produced as part of the international GEOTRACES program by Conway and John (2014) and allowed for ‘fingerprinting’ and quantification of dissolved Fe from different sources. According to their model, wind-borne Saharan dust was found to be the largest Fe source to the North Atlantic, followed by the non-reductive release of Fe from North American continental margin sediments and reductive sedimentary dissolution on the African margin (Conway and John, 2014). Hydrothermal venting was identified as a smaller but steady Fe source to the deep Atlantic, potentially influencing surface productivity. However questions remain about the processes and mechanisms that fractionate Fe isotopes upon influx to the ocean and cycling between the dissolved and particulate phases (Conway and John, 2014; Resing and Barrett, 2014).
1.6 Objectives

The previous sections introduced Fe as a key element in the marine system and the ongoing debate about its sources. In particular, the significant role of hydrothermal discharge as a source of oceanic Fe has seen a change of paradigm. Additional studies are required to constrain the biogeochemical cycling of this Fe source, especially those considering the density and special character of hydrothermal activity in the Southwest Pacific. With Fe isotopes emerging as a robust tracer of the biogeochemical processes at work, combined with the advent of the direct analysis of Fe isotopes in dissolved seawater, the opportunity arises to study the direct impact of hydrothermally derived dissolved Fe on water column processes in the southwest Pacific. This area has been the focus of only a few studies investigating the biogeochemistry of Fe and particularly the cycling of Fe in hydrothermal systems. Since no major river systems drain into the Southwest Pacific delivering large volumes of sediments, and as the impact of aerosol deposition is likely reduced, the relative contribution of hydrothermal Fe to the oceanic Fe inventory may be significantly higher than elsewhere. Furthermore, hydrothermal activity occurs at shallower depths compared to mid-ocean ridge settings and often in enclosed marine basins in the southwest Pacific Ocean. The biogeochemistry of Fe in such enclosed basins is consequently expected to be more strongly controlled by hydrothermal Fe fluxes in this region than elsewhere, with fewer outside influences acting to potentially obscure the effects on seawater dissolved $\delta^{56}$Fe.

The aim of this thesis is to better constrain Fe isotope fractionation behavior in submarine hydrothermal systems from island arc and back-arc settings. For this purpose, this study comprises three main aspects:

1. Establishment of instrumental parameters for the Fe isotope analysis of low concentrations of iron, utilizing double spiking techniques and MC-ICPMS
2. Development of ion-exchange preconcentration and separation protocols enabling the direct analysis of seawater dissolved Fe isotopic compositions
3. Investigation of Fe isotope variations in high temperature and diffuse venting hydrothermal systems during mineral precipitation and along dispersing particle plumes
1.7 Chapter outline

This thesis is divided into the following chapters as follows:

**Chapter 2** describes the analytical techniques developed to determine the isotopic composition of Fe in various samples.

**Chapter 3** investigates Fe isotope fractionation in a back-arc hydrothermal system in Vanuatu.

**Chapter 4** examines how plume processes modify the original hydrothermal isotopic signature upon dispersal of hydrothermally derived Fe.

**Chapter 5** provides a summary of the research findings and arising implications for future research.
Chapter II

Analytical Methods
This chapter describes the theoretical background of multiple-collector inductively
coupled plasma mass spectrometry (MC-ICPMS) and the development of the
instrumental parameters, the double spiking technique and chemical preconcentration
and separation protocols.

The candidate was responsible for the method development in close collaboration with
postdoctoral fellow Dr. Melanie Gault-Ringold, including data acquisition, interpretation
and discussion of Fe isotope data.

Establishment of chemical preconcentration and separation protocols intended to be
utilized for seawater multi-element extraction was also achieved in joint collaboration
with PhD candidate John Rolison.
2.1 Introduction

Fundamental to accurate determination of trace metal (such as Fe, Cu, Zn or Cd) concentrations in the oceans, is a rigorous observance of certain working practices to avoid sample contamination. With concentrations of dissolved iron down to 0.05 nM in open ocean surface waters, samples show analyte concentrations well below their usual concentrations in the environment and are therefore prone to contamination. This is even more crucial when analyzing the isotopic composition of trace metals in the ocean, since contamination may not just increase the blank but may also alter the isotopic composition.

Therefore, approved trace metal clean techniques (Bruland et al., 1979) were used during sample collection and preparation. In this study, a continuous trace metal clean working environment was ensured at all times. All chemical and sample preparation was carried out in an ISO Class 4 laminar flow bench in an ISO Class 5 clean lab at the Center for Trace Element Analysis at the University of Otago. All equipment was acid cleaned prior to use and only trace metal clean reagents were used for chemical and sample preparation.

The very low iron concentrations in open ocean surface waters, contrasted by high concentrations of matrix elements (Na, Cl, Ca, Mg) also imply increased analytical difficulties, as these elements may cause spectral and/ or non-spectral interferences with Fe (see sections 2.2.5 and 2.2.6). To obtain sufficient quantity of iron, large volumes of sample need to be processed, isolated and purified from the large quantity of such matrix elements.

Advancements in iron isotope analysis, using double spiking techniques and multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS), have led to an enhanced ability to precisely measure the isotopic composition of iron and resolve even very small levels (typically in the range of a few per mil) of isotopic fractionation (Millet et al., 2012; Schoenberg and von Blanckenburg, 2005; Weyer and Schwieters, 2003). In addition to improvements in instrumental analysis, new techniques allow for the quantitative extraction of trace metals from seawater and separation of matrix at the same time (Conway et al., 2013; John and Adkins, 2010; Lacan et al., 2008; Sohrin and
Bruland, 2011). This preconcentration step is followed by a purification step to ensure sample purity while keeping blanks low.

As discussed previously, this study represents one of only a few studies so far, that have investigated isotope fractionation of dissolved iron in seawater and hydrothermal fluids. The pioneering study by Lacan et al (2008) used a two-stage ion exchange separation protocol to preconcentrate and purify seawater samples for iron isotope analysis was developed. In this study, an alternative preconcentration procedure was devised by adapting a protocol reported in Biller and Bruland (2012), which uses the newly available Nobias-chelate PA1 chelating resin to preconcentrate seawater samples. Subsequent purification of seawater samples used procedures modified from Millet et al (2012). This second-stage method was used for the purification of geological samples, such as sulfide minerals and rock samples, as well. An alternative purification protocol was adapted from Conway et al. (2013), which seemed to work better for seawater samples. Subsequent isotope analysis was carried out by MC-ICPMS using a double spike technique to correct for instrumental mass fractionation. All techniques used in this study will be described in detail in the following sections.

2.2 Mass Spectrometry Theory

In isotope ratio mass spectrometry, different isotopes across a limited mass range (typically spanning the masses of one element) are detected according to their mass over charge ratio (m/z); it is one of the most sensitive analytical methods today. To be able to separate the different isotopes according to their mass, all atoms need to become ionized first, in order to facilitate acceleration by an electric field and injection into the analyzer for mass-separation and subsequent detection. Hence, all mass spectrometers can be subdivided into ion source, analyzer and detector/s, but there are variable mechanisms of operation for each of those segments.

Traditionally, thermal ionization mass spectrometry (TIMS) has been used to perform precise and accurate isotope ratio measurements on solid samples, while in IRMS (isotope ratio mass spectrometry) samples are introduced as gases (and ionized by electron impact). During the last few years however, inductively coupled plasma mass spectrometry (ICPMS) has become much more prominent in isotope ratio determination
as well, as it features several advantages over TIMS and IRMS (see following sections). While each technique differs in its type of ion source, mass-separation of the different isotopes is always achieved with a magnetic sector mass analyzer (instrumentation is further detailed in the next two sections). The instrumentation of a magnetic sector mass spectrometer allows for comparatively high transmission and enables multiple collection which features striking advantages in isotope ratio analysis as pointed out in the following paragraph (Belshaw et al., 2000). For certain applications, TIMS or IRMS will remain the method of choice, but ICPMS is capable of a broad range of applications.

2.2.1 ICPMS

Plasma source mass spectrometry or inductively coupled plasma mass spectrometry (ICPMS) dates back to the 1970’s and is the most widely used form of ionization in inorganic mass spectrometry today. It benefits from the high ionization efficiency of the plasma source, even allowing ionization of elements with particularly high ionization potentials, like iron. The sample can be introduced in liquid (dilute acid solution) or solid state (e.g. laser ablation), and at atmospheric pressure, which allows for convenient handling and higher sample throughput compared to TIMS with its time-consuming sample preparation (Halliday et al., 1998a; Rehkamper et al., 2001). Sample solutions are either pumped into the plasma as a “wet” aerosol or are introduced by a self-aspirating desolvating sample introduction system, either utilizing a membrane system (DSN) or a Peltier cooled condenser (Apex) to remove the solvent and form a “dry” aerosol. Using either aspiration method, the aerosol is injected into the plasma via a nebulizer, similar to the wet aerosol. The wet plasma suffers from higher oxide formation and lower ionization efficiency, both of which are hindering, especially when measuring iron.

The Argon plasma of an ICP is created with a quartz torch, placed in an induction coil (also called load coil). The quartz torch consists of three concentric tubes and argon flow through all of them is optimized in a way to prevent the torch from melting while giving the plasma its characteristic tear-drop shape. The centrally located injector tube also carries the gas flow from the nebulizer -therefore often called nebulizer gas flow- and by doing so introduces the sample aerosol into the plasma. When argon gas is passed through the torch, to which a radio frequency (RF) power of for example 1300 W is
applied, an alternating current oscillates within the field, forming electrical and magnetic fields at the top of the torch (Nelms, 2005). Via a Tesla coil, a spark is applied to the argon gas, leading to electrons being stripped from some argon atoms and subsequently trapped in the magnetic field, where they are accelerated in closed circular paths (Nelms, 2005). This process is known as inductive coupling, and the thereby formed plasma as inductively coupled plasma (ICP). The rapidly circulating electrons collide with further, neutrally charged argon atoms, stripping some of their electrons and hence a chain reaction is established. Respectively, the plasma is a combination of neutral argon atoms, positively charged argon atoms and electrons, and will exist as long as RF power is applied. The constant collisions are also producing the high temperatures of 6000 to 10000 K, depending on the region within the plasma. The nebulizer gas flow impacts on the centre of the annular fireball and -assuming the flow rate is sufficient- creates a channel (annulus) through the centre of the plasma (torus), where the sample will pass through (Nelms, 2005). At those temperatures a sample aerosol, containing virtually all elements, is readily desolvated, vaporized, atomized and subsequently ionized to a high extent, which is the main advantage over TIMS.

2.2.2 MC-ICPMS

Originally paired with a quadrupole mass analyzer, the precision of isotope ratio measurements (sequential detection) was insufficient. Somewhat better results were obtained by ICP time-of-flight mass spectrometers and in particularly with single-collector double-focusing sector-field ICPMS instruments. However, none of these designs were able to keep up with TIMS in providing the most precise and accurate isotope ratio measurements (Belshaw et al., 1998; Halliday et al., 1998b; Halliday et al., 1998a; Halliday et al., 1995; Rehkamper et al., 2001). This is due to the instability of the plasma (plasma flicker) and the poor focusing properties of the quadrupole mass analyzer, severely limiting the precision of measurements when measuring sequentially with a single-collector set-up (Halliday et al., 1998a). MC-ICPMS instruments were designed to overcome this limitation, combining the ionization capabilities of the ICP source, with the magnetic analyzer and the multiple-Faraday cup array of TIMS (see figure 2.1 for a schematic), making virtually all elements of the periodic table accessible to isotopic analysis (Rehkamper et al., 2001). The double focusing sector-field mass
analyzer with its strong focusing properties achieves the flat-top peaks necessary for high-precision isotope ratio measurements and permits multiple-collection. The Faraday cup array realizes multiple-collection by allowing simultaneous measurement of all relevant ion beams over a restricted mass range (Halliday et al., 1998a) and thereby cancels out the effect of a “noisy” signal, resulting from the plasma flicker (Rehkamper et al., 2001), as signal noise is equal on all ion beams collected at the same time and therefore cancels out when one ion beam is reported as a ratio against another. Another significant advantage of MC-ICPMS is that instrumental mass discrimination, although particularly large, is relatively stable over time (unlike TIMS, where it changes over time) and thus it is potentially easier dealt with (Archer and Vance, 2004; Belshaw et al., 1998; Halliday et al., 1998b). MC-ICPMS has found application in a growing number of laboratories, due to its high precision and immense versatility (Rehkamper et al., 2001).

Figure 2.1
Schematic diagram of the Nu Instruments Nu Plasma MC-ICPMS (adopted from Rehkamper et al. 2001)

Immediately behind the plasma source follows the sampling interface, intended to extract the ions produced in the center of the plasma and to transfer them into the mass separating part of the instrument. Sample extraction involves transporting the analyte ions from the high temperature (~7500 K), atmospheric pressure environment of the ICP source, through the sample interface consisting of sample- and skimmer cone, and
through a set of electromagnetic lenses into the mass analyzer (the set-up is schematically illustrated in figure 2.2), which operates at room temperature (~300 K) and under reduced pressure ($10^{-5}$ to $10^{-9}$ mbar). This requires tremendous pressure change (factor $10^8$ to $10^{12}$) and is more easily achieved with an intervening space in between the two cones (expansion chamber), which can be pumped down to an intermediate pressure (Nelms, 2005). The reduced pressure behind the sample cone results in a significant portion of the plasma being drawn through the aperture into the expansion chamber, where the particle cloud quickly increases in speed and expands. This is where much of the ion loss occurs and where the very large mass discrimination is encountered. From the cloud of gas atoms, molecules, ions and electrons entering the expansion chamber, typically <1% is transmitted through the skimmer cone into the mass spectrometer. This large ion loss during transfer from atmospheric pressure to the high vacuum generates the low transmission efficiency characteristic to MC-ICPMS, one of its main weaknesses.

The smaller, lighter isotopes are more easily deflected from the ion beam axis during collisions with larger, heavier isotopes or when repelled by equally charged ions of the heavier isotopes (called space-charge effect). The low mass ions are therefore more readily ejected to the rims (fringes) of the ion beam or lost all together, while the heavier ions are transmitted more efficiently. Significant instrumental mass fractionation is thus observed during MC-ICPMS, about 10-100 times higher than naturally occurring isotope fractionation (in the range of 0.5 to 1.5%/atomic mass unit (amu) for high-mass elements such as U and even higher for low-mass elements such as B (15 to 40%/amu)) and approximately one order of magnitude higher than observed for TIMS (Rehkamper et al., 2001; Rehkämper et al., 2004). As mentioned before, instrumental mass fractionation although relatively large in magnitude is also relatively stable over time and large mass ranges as well as between elements (Rehkämper et al., 2004) and is therefore potentially easier to deal with (see section 2.2.3. for characterization and correction of instrumental mass fractionation).

As the majority of elements form positive ions more efficiently than negatively charged ions in the ICP, a negative voltage is applied to extract the cations from the gas cloud and to accelerate them into the ion optics, where beam shape is optimized for highest sensitivity through a stack of electromagnetic lenses. The magnitude or polarity of the
voltage applied to each of them is adjusted independently to alter the beam shape in different dimensions. Also, beam shape is deliberately changed from circular to rectangular, as this allows focusing the ion beams through the rectangular entrance slit. Since the slit width controls mass resolution, reshaping the beam is essential in order to be able to perform isotope measurements in high resolution mode.

![Diagram of ion optics and energy focusing](image)

**Figure 2.2**
Nu Plasma sampling interface and ion optics (Nu Instruments, 2005)

When passing through the entrance slit, the ion beam enters the analyzer where separation according to mass/charge occurs. In practice, a magnet sector mass analyzer separates ions by their momentum and thus not only by mass since ion trajectories are dependent on velocity (kinetic energies) as well. Accordingly, for successful mass separation in the magnetic sector analyzer, all ions entering the magnet must have uniform kinetic energy. Otherwise, ions of identical mass but with different kinetic energies would disturb the ion optical image produced by the analyzer. This is less of an issue with TIMS, where the energy spread of ions is small, but in ICPMS, plasma ionization produces ions that display a large spread of kinetic energies (~20-30 V) (Rehkamper et al., 2001). To improve the resolution capabilities, most modern instruments are double-focusing, consisting of an energy focusing electrostatic
analyzer (ESA) and the mass focusing magnet. The ESA compensates the energy dispersion by applying an electrostatic field, which will only allow ions of a certain kinetic energy to pass through. This is crucial in order to achieve the flat-topped peaks necessary for high-precision isotope ratio measurements (Rehkamper et al., 2001). Only when the measured ion beam intensity is constant over a small mass range precision will not be compromised by small errors in mass calibration. For multiple-collection, only a so-called Nier-Johnson geometry (ESA first, followed by the magnetic sector) is possible.

The following magnetic sector analyzer consists of the flight tube, located between the poles of an electromagnet. By passing through the magnet, the ion beam is spatially separated according to mass, allowing each mass (isotope) to hit a different collector. A second slit, the so-called exit- or collector slit sits behind the magnet and can be used for high-resolution applications as well, by cutting certain fractions of the ion beam. The Nu Instruments Nu Plasma used at Otago University only features this option on a limited number of collectors. The Nu Plasma is fitted with a fixed array of 12 Faraday cups for signals from ~10mV to 50V and three ion counters for small ion beams of 1 to $10^8$ counts per second (cps). Ion beams are directed into the respective collector by a set of zoom lenses located behind the magnet. An alternative set-up as featured by the Neptune Plus used at the ANU consists of an array of moveable Faraday cups. Motorized detector carriers allow reorientation of 8 of the 9 cups (4 on each side of the fixed center cup) independently to match with the trajectories of individual ion beams.

Both instruments feature capability to measure in high mass resolution mode, necessary to allow for separation of analyte and interference peaks (e.g. $^{56}\text{Fe}$ of $^{40}\text{Ar}^{16}\text{O}^+\)$. High mass resolution is achieved with two mechanical slits, one between the ion optics and mass analyzer and one between the analyzer and detector. Increasing mass resolution to high resolution mode results in a significant loss of ion transmission efficiency and hence intensity and does not permit flat-topped peaks due to spatial limitations of the instruments (triangular peak shapes). Since flat-top peaks are a necessary requirement, pseudo high resolution mode is used instead. In this operational mode, only the source slit width is changed (the Nu plasma additionally features the so-called alpha slits), while the entrance slit remains unchanged. Consequently interferences are not fully resolved, but flat-top peaks are maintained. Since the relevant interferences are mainly present on
the higher mass side of a peak of interest, interference separation in pseudo high resolution mode is still adequate to ensure high precision isotope ratio measurements. Mass resolution describes the capability to differentiate between masses and is defined (for pseudo high resolution) as: \[ R = \frac{m}{\Delta m} \] (Equation 2.1)

with \( m \) being the mass the magnet is set to, and \( \Delta m \) as the difference between the masses, where analyte intensities reach 95% and 5% of the maximum signal intensity respectively.

2.2.3 Instrumental mass fractionation

The instrumentally induced mass fractionation, also often referred to as mass discrimination or simply mass bias is particularly high in plasma source mass spectrometry when compared to other mass spectrometers and needs to be carefully controlled and accounted for. Mass discrimination originates from the preferential transmission of heavier isotopes and is attributed mainly to space-charge effects (Douglas and Tanner, 1998; Jarvis et al., 1992), as discussed above (section 2.2.2), although this remains controversial (e.g. Maréchal et al. (1999)). In contrast to TIMS, instrumental mass fractionation in plasma source mass spectrometry is not primarily a time-dependent process, but instead appears to be a relatively simple function of mass (Rehkamper et al., 2001). However, there can be other second-order-mass-independent effects that are not easily accounted for. Mass discrimination also depends on the matrix, as more ions (in addition to the analyte of interest) are steered down the flight path, some of which are more likely to form doubly charged ions. Even subtle differences in the matrix content change the characteristics of the plasma and the way in which ions are extracted.

To describe this instrumental mass fractionation, three different fractionation laws are used in the literature, described by the linear-, power- and exponential law (Albarède and Beard, 2004; Maréchal et al., 1999).

1. The linear law is probably the most intuitive of all the mass fractionation laws (Albarède and Beard, 2004). It assumes, that the linear fractionation \( \alpha=r/R \) is expressed as a function of the mass difference \( \Delta M=M_2-M_1 \) (Maréchal et al., 1999). The common form of the linear law is given as:
In this expression, $r$ and $R$ stand for the measured and true isotopic ratio respectively, $(R=M_2/M_1)$. Unfortunately, the linear law is not consistent: if two ratios fractionate according to the linear law, the ratio of these ratios does not (Albarède and Beard, 2004). Therefore, two other mass fractionation laws are generally considered, the power law and the exponential law.

2. The power law assumes, that the logarithmic fraction $\beta = \ln(r/R)$ is expressed as a function of the mass difference $\Delta M = M_2 - M_1$ (Maréchal et al., 1999) and its common form is:

$$r = R \times (1 + \beta)^{\Delta M}$$  \hspace{1cm} \text{Equation 2.3}

3. The exponential law assumes, that the logarithmic fraction $\beta = \ln(r/R)$ is expressed as a function of the mass log-difference $\Delta (\ln M) = \ln M_2 / \ln M_1$ (Maréchal et al., 1999) and its common form is:

$$r = R \times \left(\frac{M_2}{M_1}\right)^{\beta}$$  \hspace{1cm} \text{Equation 2.4}

Both the power law and the exponential law are consistent. Furthermore, they share another remarkable property: linear alignments are achieved, when one measured isotopic ratio is plotted against another in a log-log plot (Albarède and Beard, 2004). Power law and exponential law are in relationship to each other, which is best understood as particular cases (expressed by the variable exponent $n$) of a more generalized mass fractionation law, called the general power law.

$$r = R \times \beta(M_2^n - M_1^n)$$  \hspace{1cm} \text{Equation 2.5}

The variable forms of the general power law resulting from different values of the exponent $n$ are shown in table 2.1.
Table 2.1 Forms of the generalized power law for different values of n

<table>
<thead>
<tr>
<th>n</th>
<th>Mathematical form</th>
<th>Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2</td>
<td>$r = R^* \beta (1/M_2^2 - 1/M_1^2)$</td>
<td>Minus squared</td>
</tr>
<tr>
<td>-1</td>
<td>$r = R^* \beta (1/M_2 - 1/M_1)$</td>
<td>Inverse</td>
</tr>
<tr>
<td>-1/2</td>
<td>$r = R^* \beta (1/\sqrt{M_2} - 1/\sqrt{M_1})$</td>
<td>Minus square-root</td>
</tr>
<tr>
<td>0</td>
<td>$r = R^* (M_2/M_1)^\beta$</td>
<td>Exponential</td>
</tr>
<tr>
<td>1/2</td>
<td>$r = R^* \beta (\sqrt{M_2} - \sqrt{M_1})$</td>
<td>Plus square-root</td>
</tr>
<tr>
<td>1</td>
<td>$r = R^* \beta (M_2 - M_1)$</td>
<td>Power</td>
</tr>
<tr>
<td>2</td>
<td>$r = R^* \beta (M_2^2 - M_1^2)$</td>
<td>Plus squared</td>
</tr>
</tbody>
</table>

Several MC-ICPMS studies have shown the exponential and power law models to be superior to the linear model in terms of accuracy; the linear model however is sufficiently accurate for quadrupole applications. The exponential law seems to characterize mass bias best for most metal isotope systems and was therefore used in this study (Habfast, 1998; Halliday et al., 1995; Maréchal et al., 1999; Rehkamper et al., 2001; Russell et al., 1978).

### 2.2.4 Instrumental mass fractionation correction

To ensure that instrumental mass fractionation does not dominate the measured isotopic signatures and obscure the natural isotope fractionation, it needs to be carefully monitored and corrected for. Different strategies have been developed to compensate for instrumental mass bias, with each of them having certain advantages and disadvantages. The four most used strategies are standard-sample bracketing, internal normalization, external normalization and double spiking.

1. **Internal normalization (internal as being within the sample):** This method uses the natural stable isotopes present in the sample to correct for instrumental mass fractionation. It is the routine procedure used for the elimination of instrumental mass discrimination where stable isotope fractionation is not of interest (since all mass-
dependent fractionation is eliminated), e.g., for the isotope systems used in the Earth Sciences that involve radiogenic isotopes, such as the Nd or Sr isotope systems (Archer and Vance, 2004). Since instrumental mass fractionation appears to a first order to be mass-dependant in plasma source mass spectrometry, the mass discrimination for a certain isotope ratio in the first approximation can be calculated from a different isotope ratio close to the target one (Nelms, 2005; Rehkamper et al., 2001). In practice another isotope ratio of the same element with a constant universal value is used. In the case of an isotope system involving radiogenic isotopes that means, that an invariant, stable isotope ratio of the same element is measured as well to determine a fractionation factor which is subsequently applied to the measured radiogenic isotope ratio to correct for instrumental mass fractionation.

2. **External standardization (external as being outside the sample):** This is the most practical and most frequently used method that offers sufficient accuracy. It benefits from the steady-state operation of the ICP source resulting in mass discrimination primarily not being a time-dependant process (Archer and Vance, 2004; Rehkamper et al., 2001). The instrumental mass fractionation factor is determined from analysis of a certified reference standard of known isotopic composition and is then applied to the measured isotope ratio of a sample. To account for any temporal drift of instrumental fractionation throughout the measurement cycle and variability between individual measurements, the reference standard is repeatedly analyzed, before and after every sample measurement, and the average value is used to calculate the fractionation factor applicable to the bracketed sample analysis. Since every sample is bracketed with two standard measurements, this procedure is commonly referred to as standard sample bracketing (SSB) method. A second requirement beside non time-dependency is similar mass bias behavior of sample and bracketing standard. Ideally standards are therefore matrix matched with the sample since matrix effects may cause instrumental fractionation. However, it is rather difficult to exactly match a sample’s residual matrix artificially as the matrix of natural samples can be quite complex and may differ significantly between individual samples of the same sample type. Furthermore, correlation has been observed between the concentration of Fe analyte solutions and instrumental mass bias (Malinovsky et al., 2003; Schoenberg
and von Blanckenburg, 2005) and consequently inaccurate stable Fe isotope determinations may arise from poorly matched concentrations between samples and bracketing IRMM-14 Fe standard.

3. **External normalization:** Since mass bias appears to be in first order a mass-dependent phenomenon and not dependent on the chemical nature, elements with overlapping mass ranges show a nearly identical mass bias. Therefore, as long as two elements display overlapping mass ranges and similar mass bias behavior, it is possible to use the mass discrimination observed for one element of known isotopic composition to determine the unknown isotopic composition of a second element and correct for mass bias (Archer and Vance, 2004; Rehkamper et al., 2001). This procedure is also referred to as: *external correction, interelement normalization, element doping or spiking.* In practice, the sample and the bracketing standards are doped with an isotope standard of a different element, usually a neighbor in the periodic table (e.g. Zn for Cu, Cu or Ni for Fe, Ag for Cd). This was first suggested for and is still commonly applied to lead (Pb) isotope analysis with thallium (Tl) used as reference element (Rehkämper and Halliday, 1998).

However, using Zn-normalization for Cu isotope measurements and vice versa, Marechal et al. (1999) proved that mass bias is not exactly the same for the analyte and dopant. If the instrumental mass bias were to follow perfectly the exponential mass fractionation law, the measured isotope ratios of Zn and Cu should display a linear relationship in a ln-ln plot. Although they do show a linear relationship, there was significant deviation of the measured slope from the theoretical slope due to the very subtle differences in the mass bias behavior of the two elements. Despite these differences in mass discrimination between the two elements, external normalization was validated to be accurate (Maréchal et al., 1999) and represents with few exceptions the best method for mass bias correction for isotope systems with less than four stable isotopes, particularly when combined with SSB.

The mass dispersion of the Nu Plasma is insufficient to allow for simultaneous collection of Fe isotopes and the doped element (Ni or Cu) and applying this technique to Fe requires sequential analysis and changing of the mass range. For elements with at least four stable isotopes, double spiking represents a robust alternative.
4. **Double spiking:** This is increasingly becoming a well established technique in isotope ratio mass spectrometry to correct for instrumental mass fractionation and it is applicable to any element that has four or more naturally occurring or artificially produced stable isotopes, as in the case for uranium stable isotope measurements for example (Chen and Wasserburg, 1981; Dodson, 1963; Stirling et al., 2005; Stirling et al., 2006). It is a form of internal normalization and is thought to be the most accurate method to correct for instrumental mass bias, provided that isotopic anomalies other than mass-dependent fractionation are absent (Lacan et al., 2008; Siebert et al., 2001). Other than SSB, it allows for natural and instrumental mass fractionation to be resolved from each other in the very same sample measurement, thereby eliminating any possible temporal changes. It further needs only a single run, using the same element as that of interest (other than external normalization) and therefore reduces analysis time and the amount of sample needed. A spike is a solution enriched in a certain naturally occurring, or artificial, isotope of an element that is less abundant in natural samples, and by combination of two single spikes enriched in different isotopes, a double spike is created. Since the spiked isotopes are isotopes of the same element as the sample, there is certainty that the sample and spike behave similarly during analysis and follow the same mass fractionation law (Lacan et al., 2008; Millet et al., 2012; Rudge et al., 2009; Siebert et al., 2001), provided the sample and spike have been ‘chemically equilibrated’ prior to chemical processing. An additional advantage associated with double spiking is its ability to account for mass fractionation during instrumental analysis as well as during chemical processing and resolve it from naturally occurring fractionation. Furthermore, provided the double spike and sample are equilibrated prior to chemical separation, any isotope fractionation occurring during ion-exchange chemistry can also be reliably compensated for. This greatly simplifies sample processing since it is not necessary to achieve quantitative yields and the highest purity sample separation, because the double spike will also account for changes in instrumental mass fractionation arising from differing residual sample matrix in the plasma (Rudge et al., 2009). The double spike technique therefore perfectly suits the analysis of samples that have low analyte concentrations in high ion-strength solutions, such as, for example, transition metal isotopes in seawater (Albarède and Beard, 2004).
In addition, the double spike technique also allows for determination of elemental concentrations using the isotopic dilution method (see section 2.7.2 for information about this technique). However, the limitation of this method is the necessity of at least four naturally occurring stable isotopes, which restricts its application. Also, using a Fe double spike makes monitoring for isobaric interferences in a three isotope plot impossible (John and Adkins, 2010). The double spike technique is described in more detail in section 2.3.1.

2.2.5 Spectral interferences

The term ‘interference’ in isotope ratio mass spectrometry refers either to isobaric atomic ions, multiply charged ions, polyatomic ions or intense adjacent signals overlapping with the signal of the isotope of interest, and are described in more detail below. These spectral interferences tend to create mass-independent fractionation and show an unpredictable behavior. While normally the occurrence of mass-independent fractionation during an analytical session can be revealed from a three-isotope plot (where all measurements should plot on the mass fractionation line), this is not possible when using a double spike. Also, even small interferences on only one of the four masses used for the double spike correction can dramatically alter the calculated ‘true’ isotope value. This is problematic and therefore interferences need to be carefully monitored. Depending on the nature of the occurring interference and the achievable mass resolution, they can either be resolved or their relative abundances can be monitored and corrected for. Interferences can occur on all four isotopes of iron ($^{54}$Fe, $^{56}$Fe, $^{57}$Fe and $^{58}$Fe).

Isobaric interferences are caused by isotopes of different elements with masses equal to those of the analyte (e.g. $^{54}$Cr and $^{54}$Fe; $^{58}$Fe and $^{58}$Ni). Mass differences between isotopes of the same nominal mass are usually too small to resolve with magnetic sector ICPMS, but can be predicted. Based on measurements of one of the interfering element’s other isotopes, either in the same analysis cycle (if mass dispersion of the instrument permits) or during a second cycle, mathematical correction is possible, considering the known natural isotope abundances for each individual element (e.g. measurement of $^{53}$Cr in order to constrain natural $^{54}$Cr, adopting a ‘true’ $^{54}$Cr/$^{53}$Cr ratio of 0.2489), as long as the interference is not too large.
When interferences are multiply-charged the following relationship applies: ions mass = the nominal mass/charge (e.g. $^{112}\text{Cd}^{2+}$ interferes on $^{56}\text{Fe}^+$). These ions are less likely to form in ICPMS, as the second and higher ionization potentials are higher than the first ionization potential and not generally reached in the plasma source; normally the vast majority of produced ions are only singly charged species. The required mass resolution is well within the capabilities of magnetic sector mass spectrometry (Nelms, 2005).

Molecular or polyatomic interferences derive from matrix elements, atoms of the solvent and/or the plasma gas (e.g. $^{40}\text{Ca}^{14}\text{N}$ or $^{27}\text{Al}_2^+$ on $^{54}\text{Fe}$, $^{40}\text{Ca}^{16}\text{O}$ on $^{56}\text{Fe}$ or $^{40}\text{Ca}^{16}\text{O}^1\text{H}$ on $^{57}\text{Fe}$). The plasma gas (argon) contributes a significant amount of argide molecular interferences, such as $^{40}\text{Ar}^{14}\text{N}$ on $^{54}\text{Fe}$, $^{40}\text{Ar}^{16}\text{O}$ on $^{56}\text{Fe}$ and $^{40}\text{Ar}^{16}\text{O}^1\text{H}$ on $^{57}\text{Fe}$. The necessary mass resolution required for separating polyatomic species from the isotope of interest (typically 2300 on $^{54}\text{Fe}$, 2500 on $^{56}\text{Fe}$ and 2100 on $^{57}\text{Fe}$) is well within the possible range of modern high resolution MC-ICPMS (Belshaw et al., 2000; Millet et al., 2012; Schoenberg and von Blanckenburg, 2005; Weyer and Schwieters, 2003).

Very high signal intensities can significantly interfere on adjacent peaks with lower intensities (e.g. $^{40}\text{Ar}^{16}\text{O}$ next to $^{56}\text{Fe}$), in the form of a ‘tailing’ from the dominant signal, found on its low mass side. Collisions behind the magnetic mass filter, reflections on the tube wall or space charge effects are the reason for the presence of such off-peak ions that follow divergent trajectories. As a result, the ions differ in their energies from the main ion beam, and alter the apparent peak baseline in a continuous way (Albarède and Beard, 2004). The parameter quantifying the instruments ability to measure low signals adjacent to very high signals is called ‘abundance sensitivity’; low abundance sensitivity refers to low ability of dealing with a neighboring peak’s contribution. For a nuclide of mass $M$, abundance sensitivity is defined as the ratio between the signal at mass $M$ (larger signal) and the signal at mass $M+1$ (smaller signal) arising from the same species (Albarède and Beard, 2004). Applying high mass resolution can offer some improvement in abundance sensitivity. Also, as routinely done for uranium series measurements, a second stage energy filter can be used to filter out the tail. Particularly high abundance sensitivity is required for uranium series measurements because of the very large measured atomic ratios (in the $10^5$-$10^6$ range).
Table 2.2 Isobaric and molecular interferences affecting Fe isotope analysis. Values are % abundance

<table>
<thead>
<tr>
<th>Mass</th>
<th>52</th>
<th>53</th>
<th>54</th>
<th>55</th>
<th>56</th>
<th>57</th>
<th>58</th>
<th>59</th>
<th>60</th>
<th>61</th>
<th>62</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td></td>
<td></td>
<td>5.8</td>
<td></td>
<td>91.7</td>
<td>2.2</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Isobaric interferences*

Cr | 83.8 | 9.5 | 2.4 |
Ni | 68.3 | 26.1 | 1.1 | 3.6 |

*Polyatomic interferences*

Argides $^{40}\text{Ar}^{14}\text{N}$ $^{40}\text{Ar}^{16}\text{O}^+$ $^{40}\text{Ar}^{16}\text{O}^+\text{H}^+$ $^{40}\text{Ar}^{18}\text{O}^+$

Oxides $^{37}\text{Cl}^{16}\text{O}^+\text{H}^+$ $^{40}\text{Ca}^{16}\text{O}^+$ $^{40}\text{Ca}^{16}\text{O}^+\text{H}^+$

### 2.2.6 Non-spectral interferences

Non-spectral interferences or matrix effects are caused by residual matrix elements in the sample solution. Remaining matrix elements or compounds can create changes in the plasma, influencing ionization and transmission efficiency of the ions produced, which in turn affects the instrumental response to the analyte. The signal intensities for a sample solution of a certain concentration can be reduced in the presence of residual matrix compounds compared to an equally concentrated solution containing no residual matrix elements. Even instrumental mass bias behavior can be affected due to matrix effects, with mass-dependent and mass-independent fractionation occurring simultaneously that cannot be reliably corrected for. Matrix effects are beyond control or predictability and cannot be monitored. Thus it is crucial to evaluate which matrix compounds might still be present in samples following purification. Once the residual matrix composition can be routinely identified, different options exist to ensure these effects do not compromise the reliability of the measurements. For example, doping tests where standards are spiked with realistic amounts of various matrix compounds are one way to assess whether the residual matrix actually causes the measured ratio to deviate from the true ratio. However, since matrix effects are not reliable enough to allow for prediction, such tests only help to identify such effects, but are by no means a way to correct for these effects. One approach to minimize matrix effects is to matrix-match
bracketing standards with the samples to ensure that all potential matrix effects equally affect the sample and standard analyses. However, it is rather difficult to exactly match a sample’s residual matrix artificially as the matrix of natural samples can be quite complex and may differ significantly between individual samples of the same sample type. Thus it is also important to characterize natural samples of well known isotopic composition; isotopic reference materials such as rock (e.g. BCR-2, BHVO-2) or seawater standards (e.g. NASS-6) that resemble the (‘unknown’) samples matrix and were processed and analyzed identically. The other, and generally preferred, option is to completely remove matrix elements from the sample with effective purification procedures such as ion-exchange chromatography or precipitation reactions. Using a double spike for mass bias correction offers some security since the isotopes from the spike will be similarly affected by matrix-induced fractionation processes as the sample isotopes, and therefore instrumental mass fractionation can be accounted for.

2.3 Fe Double Spike

2.3.1 Double spike theory

The double spike technique is now a commonly used method for mass bias correction and has been applied to a wide range of stable isotope systems (Bermin et al., 2006; Bizzarro et al., 2011; Conway et al., 2013; Galer, 1999; Gopalan et al., 2006; John, 2012; Ripperger and Rehkämper, 2007; Rudge et al., 2009; Schoenberg et al., 2008; Siebert et al., 2001). It is applicable to isotope systems with four or more stable isotopes and relies on mixing together a sample, with an isotope ratio close to the natural abundance, and a spike, a solution enriched in two isotopes, which displays an isotopic composition very different from natural systems. Measurements of the four isotopes in the sample-spike mixture by MC-ICPMS are used to determine three independent isotope ratios (e.g. $^{54}\text{Fe}/^{56}\text{Fe}$, $^{57}\text{Fe}/^{56}\text{Fe}$, $^{58}\text{Fe}/^{56}\text{Fe}$). In this study, these three isotope ratios are used to calculate three unknown quantities, using iterative equation solving techniques described by Siebert et al. (2001) as follows: (1) the exact ratio between the concentrations of spike and sample ($C_{\text{spike}}/C_{\text{nat}}$), (2) amount of isotopic fractionation due to instrumental and/or methodological mass bias and (3) isotopic fractionation of the sample compared to a standard (John and Adkins, 2010). Point (1) allows as a
byproduct the highly accurate determination of the sample concentration using isotope dilution methods, provided, that the amount of double spike added is well known.

The geometry of the double spike technique is simple and best illustrated by figure 2.3. It is based on the property, that the mass bias line going through a given isotope composition has a direction that varies with the value of this composition. Therefore, different sample-spike ratios will produce mass bias lines with different directions, as well as a natural sample produces a line with a distinctive direction. All natural samples must lie on this natural fractionation line \( f_n \) (Albarède and Beard, 2004), as much as all mixtures sharing the same sample-spike ratio will plot onto one mass discrimination line \( f_m \). Mass fractionation lines are curved as mass bias does not follow linear behavior.

From the very well known composition of the spike, an infinite number of straight lines can be drawn in 3-dimensional isotope space, intersecting with all possible fractionated mixtures that share the same sample-spike ratio and hence lie on \( f_m \) (Albarède and Beard, 2004). One of these lines, which is to be determined from the calculations, is the sample-spike mixing line and in 3-dimensional isotope space, the spike (S), the corrected sample (N) and the corrected mixture (M) must all plot on that line (Galer, 1999).

With all the lines connecting the true spike composition with various points on \( f_m \), a

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**Figure 2.3**

Schematic illustration of the double spike technique.

Originating from the spike composition, an infinite number of straight lines connects to all possible fractionated mixtures with the same sample-spike ratio, thereby spanning a surface in 3-dimensional isotope space. The stippled line represents the sample-spike mixing line, which connects the spike composition with the true composition of the mixture and the sample. Intersection with the natural fractionation line marks the true isotopic composition of the sample. Iterative equation solving techniques allow calculating this position in 3-dimensional isotope space, as well as the proportions of sample and spike in the mixture.
surface is formed in 3-dimensional isotope space, containing spike (S), corrected mixture (M) and measured mixture (m); surface M-m-S. The intersection of the pure samples mass fractionation line with this surface produces the unfractionated composition of the sample (and represents the mixing line) and by additional measurement of a standard/reference material, a value for the natural mass fractionation is obtained. For a well defined mixing line, the angle of intersection (θ) should be close to 90°; it is dependent on the isotopic composition of the spike as well as the ratio of sample and spike in the mixture as both of them change the orientation of surface M-m-S in 3-dimensional isotope space.

2.3.2 Double spike design

As previously discussed, three isotope ratios of four isotopes are needed to solve the equations of the double spike reduction scheme; they share one common nuclide as their denominator. Two isotopes of the analyte must be artificially enriched in the double spike. Since the precision of the technique depends on the choices of double spike composition and mixing ratio of sample and double spike (Rudge et al., 2009), the double spike design should be chosen carefully.

Iron has four stable isotopes (\(^{54}\)Fe, \(^{56}\)Fe, \(^{57}\)Fe, \(^{58}\)Fe) with \(^{56}\)Fe being the most abundant. As pointed out in 2.2.5, all isotopes of Fe are somewhat affected by isobaric and polyatomic interferences, and consequently there is no obvious choice of isotopes to be selected for the double spike. However, \(^{57}\)Fe and \(^{58}\)Fe display only very low abundances (2.2 and 0.28 % respectively), which could justify enrichment of those two isotopes in order to increase signal strength on the respective collectors.

Following the work of Millet et al. (2012), \(^{57}\)Fe and \(^{58}\)Fe were selected for the double spike composition, with a ratio of \(^{57}\)Fe: \(^{58}\)Fe \(\sim 1:1\) and the spike to sample ratio \(C_{\text{spike}}/C_{\text{nat}}\) was kept close to \(\sim 1:1\). This is in accordance with recommendations from Rudge et al. (2009) and John (2012) whose research suggests this configuration to result in minimal error. In practice, it was attempted to over- rather than underspike samples since addition of larger quantities of spike than needed results in further improvement of analytical errors by improving counting statistics, as long as detector limits are not exceeded and provided the spike composition is sufficiently well constrained (John,
Fe was chosen as the common denominator resulting in $^{54}\text{Fe}/^{56}\text{Fe}$, $^{57}\text{Fe}/^{56}\text{Fe}$ and $^{58}\text{Fe}/^{56}\text{Fe}$ as the three isotope ratios defining three-dimensional isotope space. Although attempts were made to keep $C_{\text{spike}}/C_{\text{nat}}$ consistent in all samples by initial quantitative analysis of samples by quadrupole ICPMS to obtain a preliminary Fe concentration for the sample and inform the double spike addition, the exact $C_{\text{spike}}/C_{\text{nat}}$ could vary significantly due to inaccuracy in the preliminary Fe concentration measurements of seawater samples, given their extremely low Fe concentrations. Therefore, it is important to test the reliability of the double spike reduction for a range of $C_{\text{spike}}/C_{\text{nat}}$. For this purpose, aliquots of the IRMM-14 Fe isotopic standard were spiked with different $C_{\text{spike}}/C_{\text{nat}}$ ranging from 0.25 to 4. Results (figure 2.4) prove that the double spike reduction gives accurate $\delta^{56/54}\text{Fe}$ results for at least $C_{\text{spike}}/C_{\text{nat}}$ values ranging from 0.5 to 4. However, a $C_{\text{spike}}/C_{\text{nat}}$ of 0.25 results in a measured $\delta^{56/54}\text{Fe}$ deviating from the average composition ($\delta^{56/54}\text{Fe} = 0.02 \pm 0.03 \, \%$, determined with $C_{\text{spike}}/C_{\text{nat}}$ of 1 (solid blue line)), and external reproducibility (blue shaded band is 0.03 2STDV).

![Figure 2.4](image)

Fe isotope data for IRMM-14 with various spike-sample ratios $C_{\text{spike}}/C_{\text{nat}}$ compared to the average isotopic composition obtained for $C_{\text{spike}}/C_{\text{nat}}$ of 1 ($\delta^{56/54}\text{Fe} = 0.02 \, \%$), represented by the solid blue line. The shaded blue band indicates external reproducibility ± 0.03 \% (2SD).

### 2.3.3 Double spike preparation

For the preparation of the Fe double spike, individual $^{57}\text{Fe}$ and $^{58}\text{Fe}$ isotope spikes were purchased in oxide ($^{57}\text{FeO}$) and metallic ($^{58}\text{Fe}$) form from Oak Ridge National Laboratory (USA) and Isoflex (USA) respectively. Both individual spikes were separately dissolved in concentrated high-purity quartz-distilled (q-) HNO$_3$ acid in 15 ml Teflon vials (Savillex...
Ltd, U.S.A.) and combined after dissolution over several days. The combined $^{57}$Fe-$^{58}$Fe double spike was then cleaned of potential impurities that may form isobaric or polyatomic interferences with Fe, Zn or Cd isotopes (eventually all three elements shall be extracted from a single water sample) using Fe purification ion exchange procedures. This Fe separation procedure follows the protocol developed by Millet et al. (2012), and is described in more detail in 2.5.4. After the purification step, the highly concentrated double spike was diluted with 1M qHNO$_3$ to 1L in a Teflon bottle, allowed to equilibrate, and subsequently analyzed for its Fe concentration and potential traces of interfering elements by quadrupole ICPMS. A second dilution for very low-Fe samples was made up as well from the original double spike and named L-Spike (‘L’ for ‘low’ as opposed to H-Spike for ‘high’).

2.3.4 Double spike characterization
To determine the exact Fe isotopic composition of the $^{57}$Fe-$^{58}$Fe double spike, repeated measurements of the pure Fe double spike and a series of different mixtures of double spike and the isotopic standard IRMM-14 (see figure 2.4 for the analyzed ratios and results of those mixtures) were performed using MC-ICPMS. The numbers obtained for the pure double spike were manipulated within analytical uncertainty to achieve reproducible Fe isotope compositions for the measured spike-standard mixtures. Once the double spike composition had been constrained, a set of certified reference materials (CRMs), combined with the double spike, were analyzed to test the accuracy obtained with the chosen spike numbers (see table 2.3 for the Fe isotopic composition of the double spike). For the original double spike, the concentrations of $^{57}$Fe and $^{58}$Fe were determined to be 3973 ppb ± 36 ppb and 5429 ppb ± 45 ppb (4 measurements) respectively. The lower concentrated L double spike represents a 100 fold dilution of the original double spike.

| Table 2.3 Isotopic composition of the $^{57}$Fe-$^{58}$Fe double spike |
|-----------------|-----------------|-----------------|
| Fe double spike | $^{54}$Fe/$^{56}$Fe ± 2SD | $^{57}$Fe/$^{56}$Fe ± 2SD | $^{58}$Fe/$^{56}$Fe ± 2SD |
| $^{57}$Fe-$^{58}$Fe | (0.01610 ± 0.00034) | (14.46 ± 0.10) | (18.74 ± 0.13) |
|                  | (0.016102 ± 0.00002) | (14.4589 ± 0.0046) | (18.7430 ± 0.0062) |
2.4 Fe isotopic standards

2.4.1 IRMM-14
Results for Fe isotope analyses are reported in δ-notation (see 1.4.3) relative to the composition of the Fe isotopic standard IRMM-14. This standard is the internationally used isotopic reference standard for all Fe isotope data and its isotopic composition is defined as $\delta^{56}\text{Fe} = 0$ ‰. At the beginning of every analytical session, instrumental performance was characterized by repeated measurements of IRMM-14, which then was further measured between every sample to monitor instrumental drift over the course of an analytical session (SSB). External reproducibility as well as internal precision for all IRMM-14 measurements performed in one analytical session is demonstrated in figure 2.5.

![Graph showing variability of IRMM-14 measurements](image)

**Figure 2.5**
Variability of IRMM-14 measurements during one analytical session. Internal precision (within-run precision) was typically ± 0.03. Average Fe isotopic composition for this day is 0.00 ‰ (solid blue line); external reproducibility is ± 0.04 ‰ (2 SD; blue shaded band).

2.4.2 Certified reference materials
In order to validate accuracy and precision of the Fe isotopic results obtained with the analytical instrumentation as well as sample processing procedures, certified reference materials (CRMs) were double spiked and chemically processed using the same methods are used for the unknown samples and repeatedly measured within each
analytical session. Commonly used CRMs included BCR-2 (Columbia River basalt, USGS), BHVO-2 (Hawaiian Volcanic Observatory basalt, USGS) and NOD-A1, a ferromanganese nodule from the Atlantic Ocean, Blake Plateau. These rock standards (see table 2.4 for isotopic compositions of CRMs) were purified using the same chemical separation protocol (see 2.5.4) applied to all sample materials for the effective and quantitative separation of Fe form matrix elements. Repeated Fe isotopic analysis of CRMs also validated analytical performance as the obtained results agreed well with published reference values.

Also, NASS-6 (North Atlantic Surface Seawater), a seawater reference material from the National Research Council of Canada was purchased in order to test the seawater preconcentration protocols in terms of metal recoveries. Additionally, its Fe isotopic composition was determined, however to date there are no literature values available for this CRM for comparative purposes.

### Table 2.4 Fe isotopic compositions of certified reference materials analyzed in this study

<table>
<thead>
<tr>
<th>CRM</th>
<th>Material</th>
<th>$\delta^{56/54}$Fe ± a, b, c</th>
<th>δ$^{56/54}$Fe ± 2SD (2SE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCR-2</td>
<td>Basalt</td>
<td>0.091 ± 0.011 a, d</td>
<td>0.09 ± 0.11 (0.05)</td>
</tr>
<tr>
<td>BHVO-2</td>
<td>Basalt</td>
<td>0.114 ± 0.011 a, d</td>
<td>0.10 ± 0.07 (0.05)</td>
</tr>
<tr>
<td>NOD-A1</td>
<td>Ferromanganese nodule</td>
<td>-0.42 ± 0.07 b, e (0.06) c</td>
<td>-0.42 ± 0.07 (0.05)</td>
</tr>
<tr>
<td>NASS-6#1</td>
<td>Seawater</td>
<td>-</td>
<td>-0.09 ± (0.07)</td>
</tr>
<tr>
<td>NASS-6#2</td>
<td>Seawater</td>
<td>-</td>
<td>-0.1 ± (0.07)</td>
</tr>
</tbody>
</table>

- a) 95% confidence interval
- b) 2*standard deviation (2SD)
- c) 2*standard error (2SE)
- d) Craddock and Dauphas (2011)
- e) Dideriksen et al. (2006)

# Two individually processed replicates

### 2.5 Sample preparation

#### 2.5.1 Reagents

To ensure samples are not contaminated during preparation, all reagents used were of ultra-high purity and equipment was acid cleaned before use. Ultrapure water was generated by a Millipore Milli-Q Element H$_2$O purification system, while all acids were purified (from reagent grade acids) by single sub-boiling distillation in a quartz still
(named q-HNO₃, q-HCl hereafter for quartz-distilled HNO₃ and HCl, respectively). Acid concentrations were regularly checked by titration (with NaOH). High purity hydrogen peroxide (H₂O₂) was purchased from Fisher Scientific. Trace metal clean ammonia (NH₄OH) was produced by bubbling gaseous ammonia (NH₃) into Milli-Q water. The saturated solution was titrated (with 1 M HCl) to a concentration of ~14 M and was diluted by 50% to ~7 M as this concentration was considered to be less prone to degradation during storage and resulting volumes were easier to pipette. A solution of 5 M ammonium acetate (NH₄Ac), as needed for the preconcentration procedure, was made up from quartz distilled acetic acid (q-HAc) and the 7 M ammonia stock solution to ensure highest purity. A 0.02 M NH₄Ac rinse/conditioning solution for ion exchange column rinsing and conditioning was made by diluting the 5 M NH₄Ac stock solution with Milli-Q H₂O. All reagents were made in acid washed Teflon bottles (Savillex Ltd, U.S.A.). A compilation of cleaning protocols is found in the appendix.

2.5.2 Digestion
In order to be able to chemically separate and purify Fe from matrix elements, samples need to be brought into acid solution.

Silicates were processed as bulk samples. After breaking and crushing, silicates were thoroughly washed, dried and ground with a mortar and pestle in a laminar flow bench. Grinding the rocks assists the subsequent acid digestion and also helps to homogenize the sample. Rock pieces showing strong signs of alteration were removed beforehand. A defined amount of sample to yield a sufficient amount of Fe for isotope analysis was then weighed into 60 ml vials and digested in a mixture of concentrated q-HF and concentrated q-HNO₃ in a ratio of 10:1 (HF:HNO₃) at 120° C over the course of three days first, followed by roughly 12 hrs in 7 M q-HNO₃ only, in order to digest all components, fully oxidize the sample and drive off any remaining HF. Another 12 hrs in 6 M q-HCl dissolved what had been left undigested and converted all sample material to chloride form. The sample was evaporated in between steps.

Sulfide samples were crushed and minerals were separated by hand picking. The separated minerals were digested in aqua regia (made up from concentrated q-HNO₃ and concentrated q-HCl in a ratio of 1:3 (HNO₃:HCl) at 120° C until fully dissolved. After evaporation, samples were refluxed in concentrated (12 M) q-HCl and taken to dryness
again in order to remove any remaining nitrate and convert all sample material to chloride form.

Hydrothermal fluids, although already in liquid state, were also digested. This is because of the very high metal content, which cannot be kept in solution when the fluid samples cool. Between sampling from the vent orifice and sample recovery on board the ship, fine precipitates (polymetallic sulfides) may form in some samples. These precipitates sometimes re-dissolve when samples are acidified after subsampling but also persist in many cases. Even in acidified samples, precipitation can occur in the sample container during storage. As precipitation can potentially affect the Fe isotopic composition of the remaining dissolved phase, any precipitates that formed after sampling needed to be re-digested to release any Fe they may have incorporated back into the aqueous form.

Fluid samples showing evidence of precipitation, were decanted and solids digested with aqua regia until fully dissolved, followed by an additional step with concentrated (12 M) q-HCl only (as for the sulfides), and re-homogenized with the decanted liquid phase afterwards.

While seawater samples did not require digestion, the marine particles, captured from plume- and seawater samples, needed to be digested. Particles had been separated from the bulk samples by filtration and were brought back into solution by digesting the whole filter membrane in concentrated (14 M) q-HNO₃ at 120° C for several days.

Aliquots were taken from all sample materials after digestion to determine analyte concentrations by quadrupole ICPMS. Seawater samples were analyzed with a flow injection analysis (FIA)-fluorescence method, since the low analyte concentrations and a high ion-strength matrix cause severe complications with ICPMS. Using this method, following a preconcentration step utilizing Nobias-chelate PA1 resin, Fe was directly eluted from the column into a reagent stream containing luminol a luminescence-producing reagent in the presence of Fe (e.g. Rijkenberg et al. (2014)). Luminol coordinates with Fe and was carried to a fluorescence spectrophotometer for detection.

The detailed protocols of the individual digestion procedures are described in the respective chapters.
2.5.3 Double spiking
As discussed in section 2.2.4, one of the key features of the double spike technique is the ability to account for isotope mass fractionation that occurs during chemical preparation of the sample, provided the double spike is added prior to sample processing. For hydrothermal fluids, sulfide minerals, rock powders, and other geological materials, defined aliquots of each sample were weighed into 15 ml Savillex Teflon beakers based on the preliminary concentration data, and an appropriate amount of double spike was weighed into the same beaker to obtain a $C_{\text{spike}}/C_{\text{nat}}$ of 1. The spike and sample were subsequently dried down together to promote sample-spike equilibration and redissolved in ~5 ml 6 M q-HCl + 0.001% H$_2$O$_2$ to help convert all Fe (comprising a mix of Fe(II) and Fe(III)) to Fe (III) and thus homogenizes two Fe pools with potentially different isotopic composition.

The seawater samples were weighed, then an appropriate amount of double spike was weighed into a 15 ml Savillex beaker and added to the already acidified sample. Spiked seawater samples were allowed to equilibrate for 3 days before Fe extraction by ion exchange chromatography was started.

2.5.4 Preconcentration
As mentioned previously (section 2.1), the combination of low analyte concentrations and a high ion-strength matrix impose tremendous difficulties for the analysis of Fe isotopes in seawater. Iron concentrations in seawater are within the lower nM range, while matrix ions (e.g. Na, Mg, Ca and Cl) that are likely to interfere with Fe isotope analysis occur at the permil level. Accordingly, a preconcentration step is necessary in order to transform a large volume with low analyte concentrations into a highly concentrated aliquot that contains sufficient Fe for isotope analysis, while removing a large proportion of matrix elements from the sample.

2.5.4.1 Development of preconcentration protocols
Numerous extraction/preconcentration techniques have been developed for the selective extraction of various dissolved transition metals from a seawater matrix, including organic solvent extraction (e.g. Bruland et al. (1979)), co-precipitation with, for example, magnesium hydroxide Mg(OH)$_2$ (Wu and Boyle, 1997) and solid-phase extraction utilizing various chelating resins (Biller and Bruland, 2012; Milne et al., 2010; Sohrin et
al., 2008). Trace metal extraction using a chelating resin benefits from high sample throughput, easy handling and low blanks. The latest, most promising approach has been with the Nobias-chelate PA1 resin. This resin has both ethylenediaminetriacetic acid (EDTriA) and iminodiacetic acid (IDA) functional groups and provides strong binding capabilities for transition metals while only minor amounts of Na, K, Mg and Ca (the major matrix elements in seawater) are captured at a pH below 7 (Biller and Bruland, 2012; Sohrin et al., 2008). With this technique simultaneous extraction of a wide variety of trace metals and even REE can be achieved.

Previous research groups have either used the Nobias-chelate resin in columns (Milne et al., 2010; Sohrin et al., 2008) or as batch extraction (Conway et al., 2013; Lee et al., 2011). In this study the utilization of a column was favored, as it was considered to simplify handling and therefore to be cleaner. It was also found that, once set up, the columns could be re-used day after day with the whole assembly staying in place, provided sufficient cleaning in between samples was carried out. For sample volumes from 1 L up to 10 L, a resin volume of 2.5 ml was chosen, packed into acid washed polypropylene columns purchased from BioRad (USA), and immobilized in the columns with porous polypropylene frits (at the bottom and on top). The resin was initially cleaned and conditioned with 1 M q-HNO₃ (the elution acid), Milli-Q H₂O and 0.02 M NH₄Ac, the

![Figure 2.6](image)

**Figure 2.6**
This figure illustrates the pH dependency of trace metal extraction. Aliquots of a homogenized bulk seawater sample were adjusted to different pHs with a combination of ammonium acetate (NH₄Ac) and ammonia (NH₄OH). In addition to the deliberately chosen pH values (4.5 to 6 in 0.5 increments) results from tests where deviating pHs were obtained are plotted as well. While the true trace metal content of the bulk sample is not known, and thus assessment of true % trace metal recoveries is not possible, the results are presented as % of expected metal contents (expected from numerous replicate analyses) and demonstrate that extraction efficiency of Fe, Cu, Zn and Cd from seawater is similar across the pH range.
only reagents it would come into contact with and was repeatedly cleaned with 1 M q-HNO₃ after the columns had been packed.

Extraction efficiency with the Nobias-chelate PA1 varies with sample pH as has been shown by Sohrin et al. (2008) and Biller and Bruland (2012). While some elements, like Fe, elute with high yields even at low sample pH, others, like Mn, Zn or Cd need higher pH. If pH is too high, however, matrix elements are retained in higher quantity on the resin as well. Fine tuning tests of method protocols (see figure 2.6) showed a pH range of 4.5 to 6 to be ideal for extraction of a broad range of trace metals, and particularly Fe, Zn and Cd at the highest possible yields. Since all seawater samples are acidified to a pH <2 after sampling in order to break down organic complexes, sample pH needs to be raised again for trace metal extraction. This process is significantly simplified when pH adjustments don’t need to be exact, as proved by the experiments.

For these tests, a bulk seawater sample was divided into subsamples and each aliquot (in replicates) was adjusted to a different pH ranging between 4.5 and 6 (with 0.5 increments) and loaded onto the Nobias resin. Seawater volumes were carefully controlled by weighing every sample so that extracted trace metal amounts could be related to the volume loaded. Although no trace metal concentrations for the bulk sample were known, the experiments would nevertheless reveal relative differences in extraction yields between aliquots and hence extraction pHs. The same experiment was repeated with aliquots where trace amounts of HF (0.6 mM HF in the sample) had been added prior to pH adjustment as it was hypothesized that HF could improve the yields of Fe, in particular, by minimizing adsorption of Fe onto the bottle walls. However, experiments did not reveal any obvious improvements due to HF addition. Moreover, it became apparent, that Fe yields show notable fluctuations that could not be related to pH or other parameters and thus seem to occur randomly, possibly resulting from incomplete breakdown of organic complexes. Although Fe extraction with lower than ideal yields is not desirable, it does not influence the accuracy of Fe isotopic analysis as non-quantitative recoveries are accounted for by the double spike. The effects of various pH values on element recoveries for the Nobias-chelate PA1 have also been investigated by Kagaya et al. (2013) and produced similar results.

The pH of all samples were adjusted with a combination of NH₄Ac and NH₄OH in accordance with the work of Biller and Bruland (2012). These reagents are easily
produced with high purity in the clean laboratory and do not interfere with the analysis of the target elements Fe, Zn and Cd. The respective concentrations of 5 M for NH₄Ac and 7 M for NH₄OH were adopted, as the resulting pipette volumes are manageable and the necessary amounts of reagents are kept to low volumes, minimizing the blank contribution. Addition of NH₄Ac, to obtain a final concentration of ~0.02 M NH₄Ac in the sample, buffers the sample and prevents accidental ‘overshooting’ when raising the pH further with NH₄OH. Since the pK value of acetic acid (HAc) is ~4.75, it was relatively straightforward to yield a pH between 4.5 and 5 by adding small volumes of NH₄OH, with little risk of ‘overshooting’. Above ~pH 5.2 however, addition of equally small volumes of NH₄OH will increase pH in larger increments. In some cases (depending on actual sample pH) addition of the buffer only proved to be sufficient, while additional NH₄OH was needed in other cases. The pH was checked again after allowing for equilibration of sample and buffer.

Adjustment of sample pH needs to be completed prior to sample loading. Thereby, the time span between buffer addition and sample loading needs to be sufficiently long to allow for complete equilibration of the sample and buffer. However, at higher pH, some metals are prone to adsorb onto the walls of high- and low-density polyethylene (HDPE/LDPE) bottles. This is particularly a problem for larger sample volumes, stored in a single container (5 L/10 L cubitainers), as the whole sample is pH adjusted at the same time but extraction will only complete after several hours. Accordingly the pH adjusted sample spends significant time in the sample container. In order to investigate if the prolonged time in the container at raised pH influences trace metal recoveries, aliquots of a bulk seawater sample were adjusted to a pH of ca. 5 and stored for up to 6 days before extraction started (figure 2.7). Aliquots were processed in replicates, and, again, were processed with HF as well to investigate if this might improve extraction efficiency. However, no obvious improvements could be related to the presence of HF in the sample. Also, although Fe yields varied between samples, no correlation between extracted trace metal quantities and storage time were identified. Despite this evidence, samples were always loaded as soon as possible after pH adjustment. All samples processed for this study had maximum volumes of three liters; all stored in individual 1 L bottles. As described in the following paragraph, the column set-up allows for the loading of 1 L of seawater at a time. Each bottle was therefore pH-adjusted separately and only
Figure 2.7
Trace metal extraction after different equilibration times. Another set of aliquots from the bulk seawater sample used for the pH tests already (figure 2.6) was pH adjusted to identical pH (roughly pH 5) at once, but allowed to equilibrate for different time spans. The first set of samples was loaded onto the Nobias resin after 24 hrs equilibration time, the remaining samples after three and six days, in order to identify potential effects of trace metal adsorption onto reservoirs and bottle walls at extraction pH. Since the preconcentration of large volume seawater samples can take several hours to days it was considered important to rule out any potential interaction between dissolved trace metals and the LDPE/HDPE materials. As illustrated, no such relationships were revealed; a similar percentage of trace metals was extracted from the aliquots regardless of equilibration time at increased pH. Since the true trace metal content of the bulk sample is not known, the data only represents the percentage extracted relative to expected metal contents inferred from numerous replicate analyses.

shortly before loading of the respective liter. Since addition of HF didn’t reveal any advantages, it was no longer performed.

For sample volumes between one and five liters, which are sampled in 1 L LDPE or HDPE bottles, large reservoirs were designed from 1 L HDPE bottles with holes cut in their bottoms. The reservoir sits on top of the column and is connected via a Teflon connector placed within the bottle lid that had been cut as well (see figure 2.8 for an illustration). This assembly allows for loading 1 L of sample at a time. Six of these units fit onto a specially designed rack enabling the simultaneous processing of up to six samples, each consisting of several liters of seawater.
2.5.4.2 Sample processing

Following weighing and addition of the double spike (as mentioned in 2.5.2), seawater samples were prepared for the preconcentration technique. As discussed in detail in the previous paragraph, sample pH needs to be adjusted to give an approximate pH of 5 before loading the sample onto the column. The desired final concentration of 0.02 M NH₄Ac in a 1 L sample was obtained by addition of 4 ml of the 5 M NH₄Ac stock solution. The pH was raised to achieve close to the target pH (as checked on small aliquots) and thus no further fine adjustment of pH with NH₄OH was necessary.
While the sample and buffer were equilibrating, the resin was cleaned with one full column volume (equal to 5 resin volumes) of 1 M q-HNO₃ then conditioned with one column volume of 0.02 M NH₄Ac. The sample was then poured into the reservoir and slowly pumped across the resin with a peristaltic pump connected to the waste line. Due to the low affinity of the Nobias resin for the major seawater matrix elements, mostly trace metals bind to the functional groups of the resin, resulting in trace metal preconcentration and matrix removal being obtained in one step (> 95% of the initial matrix ions are removed during this ion exchange procedure).

When sample loading was complete, reservoirs were removed (columns easily come off the Teflon connectors) and the columns were filled to the top with 0.02 M NH₄Ac. Remaining salts were thereby removed from the column walls and matrix elements bound to the resin were further rinsed off, minimizing the amount of residual seawater matrix remaining on the column prior to loading of the next sample onto the same column at a later stage. For trace metal elution, waste lines were disconnected and 15 ml Savillex PFA beakers were placed beneath the columns instead. Transition metals are then eluted in 12.5 ml 1 M q-HNO₃, which is equivalent to 5 resin volumes (see figure 2.9 for elution curves). After extraction, the collected trace metal concentrate is evaporated to dryness and re-dissolved in 6 M q-HCl + 0.001% H₂O₂ in preparation for second-stage ion-exchange chromatography in order to purified Fe for subsequent Fe isotope analysis. The reservoirs are rinsed with Milli-Q H₂O and then cleaned in two stages of q-HCl, each for ~24 hrs. Columns are generously rinsed with further q-HNO₃ and can be re-used for another sample immediately after.

Iron yields, determined by pre-concentrating 3 L of seawater with known Fe contents, were variable using this technique, but were typically in the range of 70-95%. However, yields were also measured by preconcentrating the NASS-6 seawater standard, resulting in significantly higher recoveries of >95%. This may either be a result of the better constrained initial Fe concentrations of NASS-6 as compared to other seawater samples (due to the difficulties in measuring Fe in seawater), or is related to the gamma radiation that NASS-6 (but not the other sample) was exposed to. This raises the question if organic complexes that can bind Fe were sufficiently broken down with the addition of acid.
2.5.5 Chromatographic purification

For reliable, high precision isotope analysis using MC-ICPMS, the specific element of interest must be separated from all other elements occurring in the sample matrix which can interfere during analysis. Chemical purification of Fe is based on its affinity for chloride complexes and their high partition coefficients on anion exchange resins (Millet et al., 2012; Strelow, 1980) and is reasonably straightforward for most sample types. For anion exchange chromatography, 500 µl of the BioRad® AG1-X4 resin were packed into homemade heat shrinkable Teflon columns. This resin is commonly used to purify Fe for isotopic analysis; the detailed sequence of reagents is highlighted in table 2.5. To summarize, the sample is loaded in 6 M q-HCl + 0.001% H₂O₂. In HCl, Fe generally forms chloro-complexes, while peroxide guarantees all Fe is fully oxidized. When loaded, the Fe chloro-complexes bind to the resin, while other metals are flushed through. Additional 6 M q-HCl + 0.001% H₂O₂ rinses off remaining matrix elements, which do not form complexes with chlorine and hence are not retained on the resin. When chlorine is reduced by addition of 4 ml of 0.05 M q-HCl, chloro-complexes break down and Fe elutes from the column. Elements like Zn or Cd remain on the resin and are only eluted by addition of HNO₃. To ensure full separation, the purification protocol was repeated a second time, after the resin had been cleaned with HNO₃. The collected Fe fraction was evaporated to dryness, converted to nitric form and re-dissolved in 2% q-HNO₃ for subsequent Fe isotope analysis with MC-ICPMS.
Fe purification with the AG1-X4 is commonly used and well established. Recoveries for Fe are very good with reliably high yields, and matrix elements are generally reduced to trace amounts. However, there are some restrictions that are of increased significance when ion exchange separation and preconcentration chemical protocols are combined to process seawater samples. Millet et al. (2012) draw attention to the poor separation efficiency of the AG1-X4 resin for Zn. Although Zn does not directly interfere with Fe isotope measurements, it has been demonstrated by Millet et al. (2012) that the presence of Zn at 20% of the Fe concentration causes isotopic shifts towards higher $\delta^{56/54}$Fe. This observation was reproduced during tests with IRMM-14 doped with different concentrations of Zn. While most geological samples, except Zn-rich sulfides, display Zn/Fe ratios below 5%, where no effect was observed on Fe isotopic composition (Millet et al., 2012), Zn/Fe ratios can be significantly higher in the concentrates produced with the Nobias preconcentration technique. Since a broad range of elements is eluted together from the Nobias resin, the following separation chemistry needs to be highly capable and efficient in purifying Fe. Besides Zn, Ni, U and Mo are efficiently concentrated with the Nobias resin as well. All three elute together with Fe but are not adequately removed with the AG1-X4. Particularly U is difficult to separate from Fe. As with the Zn, most geological samples display very low Ni/Fe, U/Fe and Mo/Fe ratios and hence the AG1-X4 is very well applicable for Fe purification from geological samples. For chemical separation of preconcentrated seawater however, another resin proved more suitable. The BioRad® AG-MP1 resin (see table 2.6 for separation protocol) has successfully been applied to separate Fe from Cd and particularly from Zn (Conway et al., 2013). Samples of seawater cast 30CTD (see
Chapter II

Chapter 4. For details) were re-processed with the AG-MP1 resin after anomalous Fe isotope values were obtained ($\delta^{56}$Fe values as low as -2.9‰). Originally processed with the AG1-X4, a screening later revealed increased U, Mo and Zn concentrations relative to Fe as well as traces of Ni remaining. The complete removal of Ni is particularly crucial, since its most abundant isotope $^{58}$Ni interferes with $^{58}$Fe. Re-processing with the AG-MP1 removed remaining traces of Ni while significantly reducing Zn, Mo and U.

Table 2.6 Fe separation chemistry

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 µl BioRad® AG-MP1 resin in custom made Teflon columns</td>
<td></td>
</tr>
<tr>
<td>6 ml 1 M q-HCl</td>
<td>Resin cleaning</td>
</tr>
<tr>
<td>6 ml 6M q-HCl + 0.001 % H$_2$O$_2$</td>
<td>Resin conditioning</td>
</tr>
<tr>
<td>Load sample in 6M q-HCl + 0.001 % H$_2$O$_2$</td>
<td></td>
</tr>
<tr>
<td>6 ml 6M q-HCl + 0.001 % H$_2$O$_2$</td>
<td>Elute matrix</td>
</tr>
<tr>
<td>4 ml 1 q-HCl</td>
<td>Collect Fe</td>
</tr>
</tbody>
</table>

2.5.6 Blanks

Blank contributions associated with the preconcentration technique and chemical separation protocols were addressed. To this end, 3L of Milli-Q water was acidified and buffered in the same manner as the samples, and were chemically processed using the preconcentration method in parallel with ‘unknown’ samples. Since the same columns were used to process multiple samples, albeit with thorough cleaning in between, this blank procedure was repeated in order to address potential carry over between sample batches. No more than 3-5 ng of Fe was recovered during these blank tests. This corresponds to less than 2% of the total natural Fe present in the lowest preconcentrated sample (~250 ng natural Fe) and less than 1% of the total natural Fe present in the average seawater sample processed over the course of this study (>400 ng natural Fe).

Contributions arising from the ion exchange chemical separation procedures are less than 1 ng Fe. These contributions were not considered high enough to influence Fe isotopic compositions and hence no blank corrections were applied.
2.6 Fe isotopic analysis by MC-ICPMS

Iron isotopic measurements of vent fluid samples were performed on a Thermo Neptune Plus at the Australian National University (ANU) in Canberra, Australia in collaboration with Dr. Michael Ellwood. More detailed descriptions about the Neptune Plus and measurement protocols are given in the respective chapter (chapter 3). Sample digestion and chemical purification of vent fluid samples was carried out at the Centre for Trace Element Analysis in the Department of Chemistry at the University of Otago.

The remaining samples, including seawater samples, particle filters, sulfides and rock samples were analyzed on a Nu Instruments Nu Plasma MC-ICPMS at the Centre for Trace Element Analysis at the University of Otago. A Nu Instruments DSN-100 fitted with a PFA 80 µl/min self-aspirating nebulizer was used for sample introduction; samples were introduced in 2% HNO₃. In between samples, the DSN was rinsed for a total of 4 min, comprising 2 min with 5% HNO₃ followed by another 2 min with 2% HNO₃. Measurements were carried out in pseudo-high resolution mode so that it is possible to resolve analyte and interference peaks. On the Nu Plasma, this operational mode is set up by narrowing the source slit to 0.03 mm and closing the alpha slits until signal intensity halves. In this set-up it is only possible to partially resolve Fe peaks from Ar-based interference peaks as they form a ‘shoulder’ on the lower mass side of the argide peak (see figure 2.10). Accordingly, instead of measuring in the centre of a flat-top peak, magnet positions for Fe isotope analysis were set to the flat shoulder plateaus. Analysis positions were carefully chosen to be close to the shoulder edge in order to avoid any possible contribution from tailing originating from the interference peaks. Particularly when sample Fe is limited and thus analysis is performed with low Fe intensities, tailing from the large polyatomic interference peaks of $^{40}\text{Ar}^{16}\text{O}^+$ and $^{40}\text{Ar}^{14}\text{N}^+$ can be significant below the relatively small Fe shoulder peak. The tail contribution is therefore smallest the further away from the argide peak the analysis is performed. However, if too close to the edge of the flat-top shoulder region, even small fluctuations in magnet calibration could compromise precision as signal intensity is only constant over a very limited mass range. Typically, the magnet position was offset by 0.005 amu from the edge of the shoulder towards higher mass. Once the magnet position was set, background signal intensities were monitored on blank acid to confirm the absence of potential argide
As these polyatomic interferences and their tailing effects can vary slightly throughout the analytical session, it is important to carefully monitor and account for these on a regular basis. On-peak background intensities in blank acid (on-peak zeros) were therefore continuously monitored. Before every sample, on-peak zeros were measured for 60 sec in 2% HNO₃ (from a separate vessel than the rinse solution, containing the acid used for sample preparation). These characterize the instrumental baseline as well as the above-mentioned spectral interferences arising from argide species (ArN, ArO, etc., but also blank contributions from the reagent) and are subtracted from analyte intensities. Moreover, the standard-sample bracketing technique is a useful approach to monitor conditions throughout an analytical session. Performing on-peak zeros revealed significant formation of plasma based interferences on masses 52 and 54 that were thought to originate from $^{38}\text{Ar}^{14}\text{N}$ and $^{40}\text{Ar}^{14}\text{N}$ respectively. Although in the same mass range, contamination with chromium (Cr) was ruled out by examination of the mass spectrum.
Even minor interference contributions on one of the four Fe isotopes severely influence the double spike technique and alter the obtained isotope values. As $^{54}\text{Fe}$ is by far the smallest Fe ion beam ($^{57}\text{Fe}$ and $^{58}\text{Fe}$ reach equal intensities as $^{56}\text{Fe}$ due to double spiking), effects of an interference signal on this ion beam would be even more pronounced. In an attempt to increase the Fe/argide ratio, the interface pressure was increased from ~0.96 mbar to 1.4 mbar as previously described by Millet et al. (2012). However, increasing interface pressure further reduces transmission and hence instrument sensitivity. Operating at pseudo-high resolution already significantly reduces the sensitivity of the instrument and therefore necessitates higher sample concentrations (roughly 450 ppb Fe in order to achieve 9V signal intensity). Given the low-Fe concentrations of the majority of samples processed here, an alternative approach was sought. It was found that increasing RF power (usually at 1300 W) effectively reduced argide formation while sensitivity was not compromised. At an increased RF power of 1400 W, intensities of interfering species were significantly reduced from ~30 mV to only about 4 mV. Operational conditions are summarized in table 2.7.

Table 2.7 Typical instrument settings on the Nu Plasma MC-ICPMS and DSN-100 during the course of this study

<table>
<thead>
<tr>
<th>Nu Plasma parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>RF power</td>
<td>1400 W</td>
</tr>
<tr>
<td>Coolant gas flow</td>
<td>13 L/min</td>
</tr>
<tr>
<td>Auxillary gas flow</td>
<td>0.9 L/min</td>
</tr>
<tr>
<td>High Voltage</td>
<td>6000 V</td>
</tr>
<tr>
<td>Interface pressure</td>
<td>0.96 mbar</td>
</tr>
<tr>
<td>Slit width</td>
<td>0.03 mm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DSN-100 parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane temperature</td>
<td>116°C</td>
</tr>
<tr>
<td>Membrane gas flow</td>
<td>2.8-3.5 L/min</td>
</tr>
<tr>
<td>Hot gas flow</td>
<td>13-25 PSI</td>
</tr>
<tr>
<td>Spray chamber temperature</td>
<td>110°C</td>
</tr>
<tr>
<td>Sample uptake rate</td>
<td>~80 µl/min</td>
</tr>
<tr>
<td>Nebulizer pressure</td>
<td>29.7 PSI</td>
</tr>
</tbody>
</table>

Upon sample introduction, a transfer time of 90 sec was allowed for the signal to stabilize before starting analysis. All Fe isotopes, $^{54}\text{Fe}$, $^{56}\text{Fe}$, $^{57}\text{Fe}$ and $^{58}\text{Fe}$, were measured in Faraday collectors configured with $10^{11}$ Ohm resistors (see table 2.8 for the collector configuration) during one run consisting of 60 five-second integrations, measured in three blocks. Peaks were centered before each block. Including the four minute wash, transfer time and 60 sec on-peak zero, analysis of one sample takes approximately 15 min. However, the sample was only introduced for around eight minutes, consuming roughly 290
ng Fe (at an uptake rate of ~80 µl/min) to achieve around 26 V total beam intensity (with roughly 9 V for each of $^{56}$Fe and $^{58}$Fe). Multiple analyses of IRMM-14 routinely yielded an external reproducibility for $\delta^{56/54}$Fe of $\pm 0.04$ to $0.12 \%$. Internal precision was usually $\pm 0.02$ to $\pm 0.05 \%$ for samples as low as 80 ng natural Fe. Samples were screened for Cr and Ni prior to analysis and therefore no particular interference run was necessary.

### Table 2.8 Collector configuration

<table>
<thead>
<tr>
<th>Collector</th>
<th>H6</th>
<th>H5</th>
<th>H4</th>
<th>H3</th>
<th>H2</th>
<th>H1</th>
<th>Ax</th>
<th>L1</th>
<th>L2</th>
<th>L3</th>
<th>L4</th>
<th>L5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotope</td>
<td>58</td>
<td>57</td>
<td>56</td>
<td>56</td>
<td>54</td>
<td>54</td>
<td>54</td>
<td>54</td>
<td>54</td>
<td>54</td>
<td>54</td>
<td>54</td>
</tr>
</tbody>
</table>

#### 2.7 Data reduction

All data obtained from MC-ICPMS analyses were reduced offline in an Excel-based spreadsheet to correct for instrumental mass fractionation using the double spike method and determine the $\delta^{56}$Fe isotopic composition of each sample as well as the Fe concentrations of a selected number of samples by isotope dilution.

#### 2.7.1 Double spike reduction

All data were processed at the cycle level for all 60 five-second integrations. This procedure is much more rigorous than processing data from average values. The spike reduction method used to deduce the mass bias corrected Fe isotope ratios from the measured raw data was based on iterative equation solving techniques published by Siebert et al. (2001). Assuming an exponential mass fractionation law (Habfast, 1998; Maréchal et al., 1999; Russell et al., 1978), a series of equations (as can be found in Siebert et al. (2001)) were used to derive the following quantities from the three measured Fe isotope ratios: (1) the exact ratio between the concentrations of spike and sample ($C_{\text{spike}}/C_{\text{nat}}$), (2) the amount of Fe isotopic fractionation due to instrumental and/or methodological mass bias and (3) the Fe isotopic fractionation of the sample compared to a standard (see also 2.3.1).

To simplify the iteration, an Excel Visual Basic macro was used, allowing the entire reduction to be completed offline at cycle level in one spreadsheet.
2.7.2 Isotope dilution technique

As discussed previously, accurate determination of dissolved Fe concentrations in seawater is a labor intense task. It requires removal of the high ion-strength matrix, while carefully ensuring quantitative Fe recovery, and subsequent concentration measurements by sector field ICP-MS, since the analyte concentrations are very low. Alternatively, dissolved Fe (dFe) concentrations can be obtained by flow injection, but the accuracy of these results is limited. The isotope dilution technique is an ultra precise method for determination of analyte concentrations in combination with mass spectrometry and is readily implemented in the double spike technique. Provided the sample is sufficiently equilibrated with the double spike, and provided that sample and spike amounts are carefully determined, Fe concentrations can easily be calculated retrospectively from the mass bias corrected data obtained during Fe isotopic analysis by MC-ICPMS, regardless of preconcentration factors and yields. Calculations are based on the proportion of spike to sample and therefore the relative abundances of $^{56}\text{Fe}$ and $^{58}\text{Fe}$ in each must be known, additionally to their respective amounts. Information about the isotope dilution technique can be found in de Jong et al. (2008).

2.8 Conclusions

The techniques described in this chapter demonstrate how precise determination of Fe concentrations and isotopic compositions can be achieved, despite all difficulties. The methods developed over the course of this study, utilizing seawater preconcentration protocols and double spike techniques, enable acquisition of high quality Fe concentration and isotopic data for all areas of the world’s oceans even where Fe concentrations are below the 1 nM level. The methods further provide a good foundation for similar protocols to be established for other transition metals in seawater.

However, there are aspects to improve, such as the varying and in parts very low Fe recoveries. For future tests and sample treatments more rigorous sample acidification is advised, and even UV radiation may be considered.

Furthermore anomalous shifts of measured isotopic composition were related to remaining traces of Zn and/ or Ni in samples even after chemical purification and highlight the urgent need for rigorous Fe separation protocols. Even though the majority
of seawater matrix elements are removed during the preconcentration step, two cycles of the purification chemistry are advised in order to fully separate Fe and Zn and to remove all Ni. This is of particular importance as an isobaric Ni interference was demonstrated to cause severe shifts towards more negative isotope values. Since using a Fe double spike makes monitoring for isobaric interferences in a three isotope plot impossible (John and Adkins, 2010), these Ni interferences remain undetected during isotope analysis. While earlier research already highlighted the poor separation efficiency of the AG1-X4 resin for Zn as a weakness (Millet et al., 2012), the insufficient separation of Ni is likely only a result of the single cycle purification chemistry. Nevertheless it is recommended to rather utilize the AG-MP1 resin for separation of seawater trace metal concentrates (because of the demonstrated excellent separation of Fe and Zn) into Fe and Zn aliquots followed by an additional purification of Fe with either the same or the AG1-X4 resin and to rigorously scan for impurities prior to isotope analysis.
Chapter III
Iron isotope study of the Nifonea vent field, Vanuatu
Chapter III

Manuscript: Iron isotope study of the Nifonea vent field, Vanuatu

Philipp Nasemann\textsuperscript{1,2}, Melanie Gault-Ringold\textsuperscript{1,2,8}, Claudine Stirling\textsuperscript{2}, Michael Ellwood\textsuperscript{3}, Katja Schmidt\textsuperscript{4}, Andrea Koschinsky\textsuperscript{4}, Dieter Garbe-Schönberg\textsuperscript{5}, Florian Häckel\textsuperscript{6}, Sylvia Sander\textsuperscript{1,7}, \textit{in preparation}.

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\textsuperscript{7} NIWA/University of Otago Research Centre for Oceanography, University of Otago, Dunedin 9054, New Zealand
\textsuperscript{8} Now at: Antarctic Climate & Ecosystems Cooperative Research Centre (ACE CRC), University of Tasmania, Australia

The author was solely responsible for collection of hydrothermal fluid and plume samples for Fe isotope analysis. Unprocessed whole rock samples were provided by Prof. Karsten Haase, Friedrich-Alexander University Erlangen-Nürnberg. Mineral (sulfide) separates from hydrothermal chimney fragments were kindly provided by Florian Häckel, Federal Institute for Geosciences and Natural Resources, Hannover, Germany.

Sample preparation of hydrothermal fluid, plume and sulfide samples as well as volcanic rock samples was performed solely by the candidate at the Centre for Trace Element Analysis, Department of Chemistry, University of Otago, Dunedin, New Zealand, with support from Dr. Melanie Gault-Ringold and Assoc. Prof. Claudine Stirling. Acquisition of Fe isotope data of fluid and plume samples was performed by the candidate under guidance of Dr. Michael Ellwood in the analytical facilities of the Research School of Earth Sciences, ANU, Canberra, Australia, whereas Fe isotope data of sulfide and rock samples was independently collected by the candidate at the Centre for Trace Element Analysis.

Concentration data of hydrothermal fluids was provided by Katja Schmidt (Research group of Andrea Koschinsky, Jacobs University Bremen, Earth and Space Sciences, Bremen, Germany) and Dieter Garbe-Schönberg (University of Kiel, Institute of Geosciences, Kiel, Germany) as part of a status report available for the whole science party of research cruise SO229. Analyses to acquire concentration data of plume and sulfide samples were performed by Dave Barr from the Centre for Trace Element Analysis. Interpretation of the data was mainly performed by the candidate with discussions with Andrea Koschinsky, Katja Schmidt, Dieter Garbe-Schönberg and Charlotte Kleint.
Iron isotope study of the Nifonea vent field, Vanuatu

Abstract

In the present study, we constrain the iron (Fe) isotope systematics of hydrothermal fluids and precipitates from the newly discovered Nifonea vent field in Vanuatu. Located in a young back-arc basin, Nifonea provides a unique opportunity to study processes affecting Fe isotope fractionation, represented by δ\(^{56}\)Fe, in environments characterized by short-lived heat pulses and relatively low water depths, and to better constrain Fe isotope effects resulting from subsurface sulfide precipitation and phase separation. The results indicate a complex interplay of sulfide formation and phase separation producing large spatial variability of fluid Fe isotopic compositions with generally low δ\(^{56}\)Fe. High temperatures from recent volcanic events are interpreted to facilitate slow precipitation of chalcopyrite with systematically higher δ\(^{56}\)Fe compared to hydrothermal fluid causing considerable Fe isotope effects. In addition, phase separation at relatively low pressure conditions produces low-Cl vapor phases and appears to strongly partition the Fe isotopes between vapor and liquid phases. For the first time, we demonstrate fractionation of Fe isotopes during phase separation in the field with similar isotope effects as suggested from recent experimental studies.
3.1 Introduction

Hydrothermal activity at oceanic spreading centers is one of the key processes controlling energy and mass transfer between seawater and oceanic crust (Edmond et al., 1979; Elderfield and Schultz, 1996). Previous studies have highlighted the complexity and diversity of these environments and demonstrated that the chemistry of hydrothermal fluids is not only dependent on the host-rock composition, but is furthermore controlled by a range of additional processes, including phase separation, water-rock ratios and the extent to which metal sulfides are precipitated from vent fluids in the subsurface (Edmond et al., 1995; Fouquet, 1997; Hannington et al., 1995; Janecky and Shanks, 1988; Tivey, 1995).

Stable isotope studies, especially of the transition metals, have proven useful for unraveling the competing effects of the above processes, providing valuable insights on the processes at work that cannot be robustly constrained on the basis of elemental distributions alone (John et al., 2008; Rouxel et al., 2003; Rouxel et al., 2004a; Rouxel et al., 2004b; Rouxel et al., 2008). However, despite these efforts, the systematics of the transition metal isotope systems, including Fe, in submarine hydrothermal systems remain poorly constrained. This is, in large part, because knowledge to date of the behavior of the Fe isotope system in hydrothermal settings is limited.

Significant differences between the Fe isotopic composition of source rocks and hydrothermal fluids have been demonstrated, suggesting preferential mobilization of the light isotopes from the source rock during hydrothermal activity (Rouxel et al., 2003; Rouxel et al., 2008). In nature, isotopic fractionation of Fe is largely controlled by both biotic and abiotic redox processes during the Fe(II)-Fe(III) transition, together with other reactions operating under kinetic and/or equilibrium conditions (see chapter 1) that are not related to Fe redox chemistry, such as precipitation (Johnson et al., 2004; Welch et al., 2003). Accordingly, Fe isotope shifts resulting from phase separation are expected (Syverson et al., 2014), but have not yet been documented in natural hydrothermal systems. In particular, the influence of kinetic and equilibrium isotope effects have been highlighted as a means to generate large $\delta^{56}$Fe shifts through incomplete conversion of the reactant to the product (Butler et al., 2005; Polyakov et al., 2007; Rouxel et al.,
2008). By implication, subsurface sulfide precipitation has huge potential to influence the Fe isotope composition of the vent fluid sources. These hydrothermal processes may result in varying Fe isotope compositions depending on precipitation rates that are, in turn, dependent on specific geological or physicochemical conditions.

In this study, we investigate the Fe isotope systematics of hydrothermal fluids and precipitates from the newly discovered Nifonea vent field in Vanuatu. The Nifonea vent field is located in the back-arc of the New Hebrides Island arc located in the southwest Pacific. While previous studies have investigated the Fe isotope systematics of submarine hydrothermal systems focused on the Mid-Atlantic ridge and spreading centers in the eastern Pacific, this is the first study to investigate Fe isotope variations in vent fluids from an island arc - back-arc system.

3.2 Geological Setting

3.2.1 Geology

Commencing between the late Oligocene (28 to 23 Ma) and the middle Miocene (15.9 to 11.6 Ma), subduction of the Pacific Plate underneath the Australian Plate lead to the formation of the New Hebrides Island arc (Schellart et al., 2006). In the southern segment of this island arc, subsequent rifting produced the three volcanically and hydrothermally active basins of the Coriolis Troughs. These three extensional basins of the Vate, Erromango and Futuna Troughs are located some 30 to 50 km east of the volcanic front of the New Hebrides Island arc and vary in width from 10 km to 30 km while being about 75 km long (see also figure 3.1). The southern part of Vate Trough is dominated by the Nifonea volcano, rising about 1000 m from the floor of the basin to depths of about 1850 m. This volcano is crescent-shaped with a large, 4.5 km diameter caldera open towards the SE where it grades into a volcanic rift zone. Lavas from the caldera are the youngest products of the Nifonea volcano. Abundant hydrothermal activity was found within the caldera, characterized by diffuse and focused venting of high-temperature fluids emanating from black smoker chimneys and along fractures and interstitials in recent basaltic to trachyandesitic lava flows (McConachy et al., 2005).
3.2.2 Nifonea vent field

The Nifonea vent field is about 1 km² in size and located at about 1875 to 1885 m water depth. The greater part of hydrothermal activity thereby appears to be focused at the transition between jumbled and collapsed sheet flows and low mounds of inflated pillow lavas. Areas of more intense venting are pooled in the eastern part of the vent field where isolated chimney structures emanating high-temperature black smoker fluids (up to 378°C) can be found at the base and on the slopes of broken pillow or sheet flow talus or on fresh pillow mounds. Outside these areas, the seafloor is rather dominated by jumbled sheet flows, as well as fractured and drained lobes that are unable to focus hydrothermal fluid flow. In particular, the western area of Nifonea, located approximately 500 m west of the central black smoker field hosts large areas of diffuse venting (<20°C), but also in the eastern part of the field, diffuse venting occurs between zones of focused high-temperature fluid flow. These diffuse fluids resemble milky white clouds.
hanging between pillow basalt structures with emanation sites that are not always identifiable. Large volumes of similar murky white fluids are emitted by some inter-pillow vents, although these typically lack focused discharge. The widespread occurrence of this type of venting suggests that the majority of hydrothermal activity at Nifonea is of a diffuse nature and likely the source of the persistent particle plume hanging above much of the caldera.

Several small chimneys (60-01, 66-06) were observed to be venting significantly hotter (up to 345°C), clear fluids with almost no smoke, despite high sulfur contents. These fluids are characterized by low metal contents resulting from precipitation of metals in the chimneys or in the sub-seafloor.

One striking observation is the absence of any older, inactive chimneys or sulfide talus, suggesting relatively young activity for the vent field. The very high fluid temperatures of 378°C, the hottest vent temperature measured in an arc setting in the western Pacific (Mottl et al., 2011), and the Cu-rich nature of the chimneys further suggests that hydrothermal activity may result from a short-lived pulse of heat following a recent eruption. This possibly occurred within the last decade, as these systems are short-lived and only active as long as volcanic products provide sufficient heat. Fresh mounds of pillow lavas deliver the heat necessary to drive the system and are porous enough to facilitate fluid flow. At the same time, the large areas of diffuse fluid flow indicate that much of the sub-seafloor permeability has not yet been sealed properly to allow for more focused fluid discharge. Sustained high-temperature fluid flow could eventually seal the subsurface substrate but it is unlikely that the high heat flow can be sustained in this style of volcanism. Once the lava has cooled down, activity will cease until the next magmatic event reinstalls hydrothermal activity. The absence of old sulfide chimneys or mounds suggests that past hydrothermal events were short-lived as well.

The overall fluid chemistry (Schmidt et al., in prep) is consistent with this interpretation of a young, post-eruptive and high temperature hydrothermal system, with a shallow reaction zone. Low Li contents and Li/Cl indicate that water-rock interaction occurs at high water-rock ratios without significant leaching from rocks. Two-phase venting (see section 3.2.3) was observed at nearly all investigated chimneys, indicating phase separation near the seafloor, which is also reflected by the distinct low chlorinity.
Consequently, Nifonea vents resemble characteristics similar to very high temperature venting at Brandon vent (21°S on the EPR), where a shallow heat source was inferred from the distribution of venting and silica contents of the fluids. At Brandon, phase separation and segregation were interpreted to be occurring in ‘real time’ within the sulfide structure itself (Von Damm et al., 2003). The small change in pressure occurring within the height of the chimney was sufficient to cause phase separation. While at Nifonea the two phases are venting simultaneously from a single conduit, vapor and brine emanated from separate orifices at Brandon.

3.2.3 Phase separation at Nifonea

Phase separation is a common process associated with high-temperature hydrothermal vent systems causing seawater-derived fluids to separate into vapor and liquid (‘brine’) phases at relevant temperature and pressure conditions, strongly influencing fluid chemistry (Syverson et al., 2014). However, although phase separation and subsequent segregation are assumed to be widespread, rarely have both phases been sampled from the same chimney, and if so, then mostly at times widely apart. At Brandon vent (EPR 21°S), vapor and brine were found to be emanating simultaneously, but generally time-displaced venting of both individual phases is assumed, usually requiring storage of the brine phase within the oceanic crust (Von Damm et al., 2003).

The Nifonea vent field features fluids with strongly reduced chlorinity (Schmidt et al., in prep) indicating that phase separation has occurred. Moreover, almost all investigated chimneys showed two-phase venting evident from “flames” of water vapor visible at the vent orifices. This behavior indicates that fluids were boiling at the seafloor (due to adiabatic decompression), which requires a temperature of at least 363°C for seawater at 188 bars. A maximum temperature of 378°C was measured at vent 77-10, placing Nifonea fluids near the two-phase boundary of seawater and even partially within the field of coexisting vapor + liquid (Schmidt et al., in prep); see figure 3.2.

During phase separation at p-T conditions below the critical point of seawater (cp) the fluid separates into a low chlorinity vapor phase and high chlorinity brine, whereby the chloride content of the vapor phase is controlled by dominating p-T conditions. Given the pressure of 188 bars, a temperature of ~363°C is needed to intersect the two-phase boundary and drive the separation of one single fluid into vapor and brine. The resulting
chloride content at these conditions is estimated to be about 3 mM Cl (Driesner, 2007; Driesner and Heinrich, 2007), significantly lower than the actual end-member chloride contents determined for Nifonea fluids (26-89 mM Cl). The lowest Cl content (26 mM) belongs to vent 77-10, with a temperature of 378°C clearly within the two-phase region of NaCl-H2O. The higher than expected Cl content (26 mM instead of calculated 3 mM) could indicate mixing of the vapor phase with another high-Cl, but Mg-free hydrothermal fluid phase prior to venting, possibly the Cl-enriched and not fully separated brine or non-phase separated ‘evolved’ seawater (Schmidt et al., in prep).

Considering that phase separation is likely occurring just below the vent site or maybe even within the sulfide structure, it seems possible that phase separation may be associated with non-complete segregation of vapor and brine resulting in emanation of a constant mixture of both phases (Schmidt et al., in prep).

3.3 Analytical Methods

Samples were collected during RV Sonne cruise 229 in 2013. The ROV “Kiel 6000” was used as a platform for detailed geological mapping and sampling of geological and hydrothermal materials, including vent fluids and samples from the buoyant plume.

3.3.1 Sampling and analysis of volcanic source rocks and chimney fragments

Volcanic rocks were sampled from various locations all over Nifonea vent field, generally within the vicinity of active vents. Samples were collected from the surface using the robotic arm of the ROV. In the laboratory at Otago University, rock samples were broken
down, crushed and washed after existing surface coatings had been removed. Fragments of unaltered volcanic rock corresponding to ~0.5 g were powdered in a laminar flow bench in order to obtain a representative sample for bulk rock Fe isotope analysis. For each sample, a defined amount of rock powder (based on Fe content) was digested in a 60 ml Teflon vial (Savillex, USA) with a mixture of high-purity, concentrated Teflon-distilled HF and concentrated q-HNO₃ in a ratio of 10:1 (HF:HNO₃) at 120° over the course of three days, followed by roughly 12 hrs in 7 M q-HNO₃, in order to digest all components, fully oxidize the sample and drive off any remaining HF. This was followed by another 12 hrs of digestion in 6 M q-HCl to dissolve remaining undigested material and converted the digest to the chloride form. The sample was evaporated in between steps.

Chimney fragments were collected similarly to rock samples from selected chimneys where fluids were taken as well. The recovered fragments were broken down and crushed for mineral separation by hand picking. Sulfide grains, corresponding to a weight of 25 to 50 mg were picked in order to obtain a representative sulfide component. Digestion of sulfide grains required a maximum of three days at 120°C in closed 15 ml Teflon vials utilizing aqua regia, a combined reagent of three parts concentrated q-HCl and one part concentrated q-HNO₃. After an evaporation step, any remaining nitrate was removed by addition of concentrated q-HCl and further evaporation to dryness.

Concentrations of Fe, Cu, Zn, Ca and Pb in volcanic rocks and chimney fragments were determined by quadrupole ICP-MS using an Agilent 7500 cs/ce instrument (Agilent Technologies, USA) equipped with a dual hydrogen reaction/helium collision cell to reduce/eliminate interferences such as ⁴⁰Ar¹⁶O on ⁵⁶Fe or ⁴⁰Ar¹⁶O¹H on ⁵⁷Fe. The results allowed the purity of the mineral separates to be assessed, and assisted in ensuring the addition of appropriate amounts of a ⁵⁷Fe-⁵⁸Fe double spike (yielding sample-spike ratios of ~ 1:1) for precise determination of instrumental mass fractionation, internally and at the cycle level, during Fe isotope analysis by MC-ICPMS.

Fe isotope analysis was performed on a Nu Plasma-HR MC-ICPMS (Nu Instruments, UK) at the University of Otago after Fe extraction and purification by ion exchange chromatography. The chemical separation procedure followed established protocols adapted from Millet et al. (2012) utilizing BioRad AG1-X4 resin (see chapter 2). The Nu plasma features high resolution capabilities in order to separate interferences from
analyte peaks. A fixed array of 12 Faraday collectors enables simultaneous collection of $^{54}\text{Fe}$, $^{56}\text{Fe}$, $^{57}\text{Fe}$ and $^{58}\text{Fe}$ ion beams. Every sample analysis contained three blocks, each of twenty measurements, with signal integration times of five seconds. Ion beam ‘peaks’ were centered before each block, and on-peak zeros in 2% q-HNO$_3$ were quantified before every sample analysis to monitor minor background signals caused by memory effects, fluctuations in gas flows or reagent blanks. A $^{57}\text{Fe}$-$^{58}\text{Fe}$ double spike was used for instrumental mass fractionation correction in combination with standard-sample bracketing.

Fe isotope compositions are reported in delta notation relative to the Fe isotope standard IRMM-14 and expressed in per mill [‰] as described in equation 3.1 below.

$$\delta^{56}\text{Fe} = \left(\frac{^{56}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{Sample}} / \left(\frac{^{56}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{Standard}} - 1$$  \hfill (Equation 3.1)

**3.3.2 Sampling and analysis of vent fluids and diffuse/buoyant plume liquids**

End-member fluids were sampled using a pumped flow-through system (Kiel Pumping System, KIPS) in combination with ROV Kiel 6000. KIPS is entirely made of inert materials (perfluoralkoxy (PFA), polytetrafluorethylene (PTFE), and high purity titanium), and allows sampling directly from vent orifices or diffuse venting sites utilizing a titanium nozzle (Garbe-Schönberg et al., 2006). The nozzle was inserted into the vent orifice by the robotic arm and the sample was pumped through PFA tubing. After flushing the lines and sampling flasks for several minutes, the valves were closed and samples were retained within the PFA flasks. An online temperature probe mounted parallel to the titanium nozzle monitored in-situ fluid temperatures.

Samples of diffuse fluids and the buoyant plume (1-3 m above selected vent outlets) were collected with a rack of three metal-free and acid cleaned Niskin bottles, mounted onto the front of the ROV. These Niskin bottles were maneuvered into the buoyant plume or an area of diffuse venting and closure was triggered using the robotic arm.

All fluid samples were sub-sampled onboard under a class 100 laminar-flow clean hood (Slee, Germany) for various analyses of major, minor and trace element concentrations. Each sample was homogenized (by shaking) prior to subsampling. Aliquots were either directly acidified (without filtration) until all precipitates had dissolved or filtered (under pressurized N$_2$) through 0.4 µm filters (Whatman polycarbonate 47 mm), followed by
acidification with concentrated q-HCl (1 ml per liter of filtered sample, roughly yielding a pH of 1.8). For Fe isotope analysis, an aliquot of the original vent fluid was transferred into an acid cleaned polyethylene bottle (60 ml) for shore-based analysis. Samples were acidified with ultrapure concentrated HCl (TraceSELECT®Ultra, Sigma-Aldrich (Fluka)) until all precipitate had dissolved. For some fluid samples, the precipitates were instead dissolved in the Centre for Trace Element Analysis, University of Otago by pressure digestion with aqua regia at 120°C followed by re-homogenization. Niskin samples were pressure filtered onboard, collected in 1 L acid cleaned low-density polyethylene (LDPE) bottles and immediately acidified with 1 ml HCl. Iron from both sample types was purified by ion exchange chromatography (BioRad AG1-X4) utilizing established protocols (e.g. Millet et al. (2012); Chapter 2).

Major, minor and trace elements were determined at Jacobs University, Bremen on filtered aliquots and non-filtered aliquots (following pressure-digestion with HCl, HNO₃, and HF at 160°C and subsequently re-homogenization with the sample) utilizing ICP-OES and ICP-MS, respectively. The accuracy and reproducibility of the analytical results was validated by repeated measurements of the seawater standards NASS-5 and IAPSO, as well as an in-house reference hydrothermal fluid (JUB). Details about analytical procedures and the reference materials mentioned are presented in (Schmidt et al., in prep).

Unlike for the sulfide and rock samples, Fe isotope analysis of vent fluid samples was performed on a Thermo Neptune Plus MC-ICPMS (Thermo Scientific, Germany) at the Australian National University (ANU) in Canberra, Australia in collaboration with Dr. Michael Ellwood. Like the Nu Plasma the Neptune is a sector field plasma source mass spectrometer allowing for multiple collection on nine Faraday collectors. For Fe isotope analysis, signals of $^{54}$Fe, $^{56}$Fe, and $^{57}$Fe were detected simultaneously, as well as $^{53}$Cr in order to correct for possible isobaric interferences of $^{54}$Cr on $^{54}$Fe. In this case the instrumental mass bias was monitored and corrected for using the standard-sample bracketing approach in addition to inter-element normalization with a doped certified $^{60}$Ni/$^{61}$Ni standard. Utilizing $^{60}$Ni/$^{61}$Ni normalization benefits from reduced analysis time since both Ni isotopes can be collected simultaneously with Fe and $^{53}$Cr using the Neptune instrument, but precision is slightly lower compared to the double spiking technique (as evident from slightly larger 2SE of these samples).
Acid blank on-peak zeros were performed prior to each standard-sample block. Analyses were performed in high-resolution mode allowing for full separation of iron analyte peaks from major polyatomic interferences $^{40}\text{Ar}^{14}\text{N}$, $^{40}\text{Ar}^{16}\text{O}$ and $^{40}\text{Ar}^{16}\text{OH}$ on $^{54}\text{Fe}$, $^{56}\text{Fe}$ and $^{57}\text{Fe}$ respectively. Fe isotope compositions are reported in delta notation as described in equation 3.1.

3.4 Results

3.4.1 Elemental composition of chimney sulfides

The chimneys sampled at NF1, NF4 and NF6 were rather isolated structures located on top of broken pillow or sheet flow talus. Vent site NF1 is a single chimney, about 2.5 m high and characterized by several orifices venting black smoke. Macroscopic investigations of the mineralogical composition revealed abundant anhydrite forming the central conduit, while the chimney walls are composed of alternating zones of sulfides (dominated by pyrite (FeS$_2$), minor chalcopyrite (CuFeS$_2$)) and sulfates such as anhydrite (CaSO$_4$) and barite (BaSO$_4$). Pyrite and chalcopyrite were separated for Fe isotopic analysis (table 3.1). Site NF4, on the other hand, was one of a group of six chimneys located at the base, and on the edge, of a shallow pillow mound venting black to dark grey smoke. Fluid (66-03) and sulfide (66-04) samples were taken from this black smoker which macroscopically revealed a distinct lining of chalcopyrite in the interior of the conduit, indicating high fluid temperatures (>$300^\circ\text{C}$). Microscopic investigations identified chalcopyrite and pyrite phases, both of which were separated for analysis. Site NF6 was discovered in the area of a lava field mainly consisting of jumbled sheet flows. The sampled vent was about 50 cm high and emanating black smoke (77-06). The identified mineral assemblage was dominated by chalcopyrite amongst pyrite and anhydrite; only chalcopyrite was separated. Generally, the mineral assemblages of all three chimneys were identified to comprise sphalerite (ZnS), chalcopyrite, pyrite and marcasite (both FeS$_2$), often characterized by dense intergrowth of the main sulfides. The common mineralogy suggests formation at similarly high temperatures. Fine grained sulfides are often dispersed in a matrix of anhydrite that builds up the main chimney framework. Chalcopyrite is particularly abundant in the innermost zones of (high temperature) chimneys forming a distinct lining.
along the conduit. Sporadic replacement of sphalerite by chalcopyrite suggests changes in fluid chemistry and/or temperature. While Cu defines a group of elements precipitating at high fluid temperatures, Zn represents lower formation temperatures. Pyrite dominates the area between the central conduit and outer wall of the chimney, which in turn is dominated by sphalerite and marcasite.

Table 3.1 Chemical and Fe isotopic composition of sulfide mineral separates from chimneys

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Vent-Site</th>
<th>Minerals</th>
<th>Ca [wt%]</th>
<th>Fe [wt%]</th>
<th>Cu [wt%]</th>
<th>Zn [wt%]</th>
<th>Pb [wt%]</th>
<th>δ56Fe [‰]</th>
<th>2SE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>27-10 NF1</td>
<td>py</td>
<td>0.06</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.75</td>
<td>0.04</td>
</tr>
<tr>
<td>27-10 NF1</td>
<td>cpy</td>
<td>0.76</td>
<td>27.62</td>
<td>30.00</td>
<td>0.83</td>
<td>0.00</td>
<td>-0.43</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>66-04 NF4</td>
<td>py</td>
<td>3.10</td>
<td>34.74</td>
<td>0.50</td>
<td>0.88</td>
<td>0.04</td>
<td>-0.97</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>66-04 NF4</td>
<td>cpy</td>
<td>0.72</td>
<td>28.04</td>
<td>29.83</td>
<td>0.20</td>
<td>0.00</td>
<td>-0.42</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>77-09 NF6</td>
<td>cpy</td>
<td>0.18</td>
<td>28.04</td>
<td>28.13</td>
<td>0.11</td>
<td>0.01</td>
<td>-0.23</td>
<td>0.05</td>
<td></td>
</tr>
</tbody>
</table>

* py: pyrite; cpy: chalcopyrite

Based on the contents of Ca, Fe, Cu, Zn and Pb in the mineral separates, their modal mineralogy, and hence purity, was determined quantitatively. Chalcopyrite (CuFeS₂) separates generally represent highly pure phases (>97 mol%) with only minor addition of sphalerite (ZnS; maximum 1.4 mol% in 27-10 cpy) and anhydrite (CaSO₄; maximum 1.28 mol% in 27-10 py). The purity of the pyrite separates is also high (97 mol% in 27-10 py), but impurities of ZnS are increased compared to the chalcopyrite separates (up to 2.25 mol% in 66-04 py) as a result of the dense intergrowth of the minerals. Also, anhydrite is contained in greater quantity than in chalcopyrite separates although it is only present in 66-04 py (7.9 mol%). Mineral separation from chalcopyrite, on the contrary, is adequate as the two minerals are intergrown to a much lesser extent. Pb concentrations indicate no galena (PbS) was present.

3.4.2 Elemental composition of vent fluids

Elemental compositions of vent fluids sampled during SO229 are summarized in table 3.2. A more detailed interpretation of the vent fluid data can be found in Schmidt et al. (in prep).

The collected vent fluids display a large range of temperatures (107 to 378°C), and include the highest temperature recorded so far in the south-western Pacific. Elemental concentrations varied significantly as well between individual chimneys with large spreads in metal and chlorine concentrations as well as H₂S contents. In fact the
measured Cl concentrations were amongst the lowest measured in hydrothermal fluids so far. Copper was only above detection limit (0.01 µM) in fluids from five out of seven vents and only in non-filtered sample aliquots where particles had been digested, indicating immediate and complete removal of Cu from the dissolved fraction upon mixing with seawater. Similarly, Zn was only detected in non-filtered aliquots. Both elements are commonly incorporated into polymetallic sulfides (CuS, CuFeS₂, ZnS) when hydrothermal fluids are abruptly cooled down at the vent orifice. Metal contents are highest in sample 77-06 with Zn well above average concentrations (Bennett et al., 2008; James et al., 2014; John et al., 2008; Rouxel et al., 2008) but in good agreement with data from other back-arc hydrothermal systems (James et al., 2014).

Previous research investigating Fe isotope fractionation in hydrothermal systems has repeatedly highlighted the importance of Fe/H₂S ratios in vent fluids (Bennett et al., 2009; Rouxel et al., 2008; Severmann et al., 2004). Sulfide precipitation in the subsurface is suspected to be the main process controlling the Fe isotopic composition

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<tbody>
<tr>
<td>27-14B</td>
<td>NF1</td>
<td>250*</td>
<td>77</td>
<td>12.3</td>
<td>173</td>
<td>901</td>
<td>518</td>
<td>1</td>
<td>30.1</td>
<td>6200</td>
<td>0.1</td>
<td>-0.65</td>
<td>0.05</td>
</tr>
<tr>
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<td>NF1</td>
<td>250*</td>
<td>72</td>
<td>15.1</td>
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<td>793</td>
<td>464</td>
<td>1</td>
<td>26.1</td>
<td>6200</td>
<td>0.1</td>
<td>-0.61</td>
<td>0.06</td>
</tr>
<tr>
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<td>~0</td>
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<td>560</td>
<td>2.86</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-0.66</td>
<td>0.05</td>
</tr>
<tr>
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<td>NF1</td>
<td>-</td>
<td>-</td>
<td>54</td>
<td>560</td>
<td>2.07</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-0.64</td>
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<tr>
<td>60-01B</td>
<td>NF2</td>
<td>345*</td>
<td>53</td>
<td>25.4</td>
<td>296</td>
<td>92.6</td>
<td>223</td>
<td>-</td>
<td>12.3</td>
<td>7800</td>
<td>0.1</td>
<td>-0.57</td>
<td>0.05</td>
</tr>
<tr>
<td>60-01C</td>
<td>NF2</td>
<td>345*</td>
<td>21</td>
<td>42.5</td>
<td>462</td>
<td>43.9</td>
<td>124</td>
<td>-</td>
<td>8.6</td>
<td>3400</td>
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<td>-0.41</td>
<td>0.05</td>
</tr>
<tr>
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<td>NF2</td>
<td>-</td>
<td>~0</td>
<td>54</td>
<td>560</td>
<td>0.85</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-0.29</td>
<td>-0.55</td>
<td>0.06</td>
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<tr>
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<td>-</td>
<td>49</td>
<td>27.6</td>
<td>311</td>
<td>670</td>
<td>317</td>
<td>2</td>
<td>15.7</td>
<td>7800</td>
<td>0.1</td>
<td>-0.55</td>
<td>0.06</td>
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<tr>
<td>66-03</td>
<td>NF4</td>
<td>-</td>
<td>40.2</td>
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<td>484</td>
<td>1040</td>
<td>382</td>
<td>6</td>
<td>16.5</td>
<td>1600</td>
<td>0.7</td>
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<td>174</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-0.37</td>
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<td>14.9</td>
<td>340</td>
<td>6110</td>
<td>1810</td>
<td>45</td>
<td>157</td>
<td>4700</td>
<td>1.3</td>
<td>-0.50</td>
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<td>NF7</td>
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<td>3.9</td>
<td>62.7</td>
<td>544</td>
<td>106</td>
<td>19</td>
<td>88</td>
<td>6200</td>
<td>0.1</td>
<td>-0.53</td>
<td>0.05</td>
</tr>
<tr>
<td>27-11</td>
<td>NF8</td>
<td>nd</td>
<td>~0</td>
<td>55</td>
<td>566</td>
<td>0.27</td>
<td>0.19</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>0.01</td>
<td>-0.61</td>
<td>0.04</td>
</tr>
</tbody>
</table>

*a Venting black smoke; ⁵ Venting milky white to grey fluids; ⁶ Buoyant plume sample; ⁷ Diffuse fluid sampled with Niskin bottle
⁸ Calculated fluid fraction in the collected sample, calculations are based on Mg content with assumed zero Mg for pure fluids
⁹ Isotopic composition of original fluid sample
* Temperatures represent the minimum temperature inferred from observations as the online probe failed and hence no detection of in-situ temperatures was possible

All element concentrations and isotopic compositions were determined on non-filtered samples
of vent fluids (Rouxel et al., 2008) and is, in turn, controlled by the ratio of \( \text{Fe}/\text{H}_2\text{S} \), as well as the Fe isotopic composition of the overlying hydrothermal plume (Bennett et al., 2009; Severmann et al., 2004). In the present study, in all but one case (77-06), the ratio of Fe to \( \text{H}_2\text{S} \) is <1, indicating excess \( \text{H}_2\text{S} \) over Fe. Diffuse fluids (27-11), and fluids sampled at vents 60-01 and 66-06 (both small chimneys venting higher temperature milky fluids), display the lowest \( \text{Fe}/\text{H}_2\text{S} \) ratios of \( \leq 0.02 \), followed by fluids 27-14, 66-01 and 77-10 with intermediate \( \text{Fe}/\text{H}_2\text{S} \) ratios of ca. 0.1. Higher \( \text{Fe}/\text{H}_2\text{S} \) ratios are only revealed by fluids at vents 66-03 (0.7) and 77-06 (1.3). These two samples also display the highest Fe concentrations, possibly a result of reduced subsurface Fe-sulfide precipitation. In all cases, similarity in \( \text{Fe}/\text{H}_2\text{S} \) also reflects similar chemical behavior, as samples with the lowest \( \text{Fe}/\text{H}_2\text{S} \) ratios, 27-11, 60-01 and 66-06, all vented clear to milky fluids, while samples 27-14, 66-01 and 77-10 with intermediate \( \text{Fe}/\text{H}_2\text{S} \) ratios were all black smokers. Although a very low \( \text{Fe}/\text{H}_2\text{S} \) ratio suggests rapid removal of Fe from the dissolved phase, only minor formation of FeS was observed in samples 27-11, 60-01 and 66-06. This is interpreted to result from sub-seafloor metal sulfide precipitation and the resulting low Fe contents of the fluids (0.27 to 92.6 \( \mu \text{M} \)).

The relatively high Mg contents (3.9 to 43.3 mM, table 3.2) in all fluid samples reflect, in part, significant entrainment of seawater during sampling. During circulation of hydrothermal fluids within oceanic crust Mg is widely assumed to be almost quantitatively removed from the fluid due to formation of Mg-OH-Si minerals. Consequently, hydrothermal fluid end-members before seawater entrainment are considered essentially Mg free (Mottl and Holland,)}
Based on this assumption of zero Mg end-member fluids, sample concentrations of a range of elements were extrapolated to a hypothetical hydrothermal end-member containing no Mg (Mg = 0 mM). This is a common procedure described in literature (e.g. Douville et al. (2002) or Schmidt et al. (2007)) and is also exemplified in figure 3.3. The proportion of original vent fluid in the sampled fluid-seawater mixture was calculated using principles of mass balance, assuming zero Mg in the pure fluid end-member and 55 mM Mg in the pure seawater end-member. The corresponding proportion of the fluid component in the collected samples varies between 20 and 93%. The presence of a non-zero Mg fluid component cannot be ruled out and will be addressed through measurements of the Sr isotopic composition of vent fluids in the near future (based on Ravizza et al. (2001)).

From the calculated fluid end-member Fe concentrations (defined as 100%) the fraction of Fe remaining in the dissolved phase was calculated for each replicate sample. For example, this calculation yields fluid proportions of 52% and 24.5% for the exemplified samples 60-01B (92.6 μM Fe) and 60-01C (43.9 μM Fe) shown in figure 3.3, respectively. Upon cooling and contact with oxygenated seawater, the Fe from hydrothermal fluids typically precipitates quickly to form both polymetallic sulfide and oxyhydroxide phases that settle out of the rising plume (Rudnicki and Elderfield, 1993). Previous studies have highlighted the strong influence of kinetic isotope effects during the precipitation of Fe-sulfides and Fe-oxyhydroxides on the fluid δ^{56}Fe (Bennett et al., 2009; Rouxel et al., 2008; Severmann et al., 2004). Accordingly, Fe isotope fractionation upon mixing with seawater and during early ascent of the buoyant plume is controlled by precipitation induced kinetic isotope effects (Bennett et al., 2009; Severmann et al., 2004). These Fe isotope systematics are best modeled using a Rayleigh fractionation equation (3.2) that describes kinetic isotope fractionation in an open system (where the product is irreversibly separated from the reactant and thus lost from the system) during a one directional reaction where the reactant A (e.g. aqueous Fe^{2+}) and product B are separated instantaneously, precluding any back-reaction (such as evaporation or precipitation):

\[ R = R_i \times f^{(\alpha_{B-A} \times \text{t})} \]  

(Equation 3.2)
where R is the measured isotope ratio (e.g. $^{56}\text{Fe}/^{54}\text{Fe}$) and $R_i$ corresponds to the initial ratio, while $f$ represents the fraction of A remaining. The fractionation factor $\alpha$ ($R_{\text{Product}}/R_{\text{Reactant}}$; see also chapter 1, section 1.4) describes the fractionation of isotopes between reactant (A) and product (B).

If the fraction of Fe remaining in the dissolved phase is plotted against the Fe isotopic composition of dissolved Fe determined for the respective sample, the value of $\alpha$ can be modified in order to find the best matching curve to fit the data points and determine the approximate end-member $\delta^{56}\text{Fe}$ (see figure 3.4). Elemental and isotopic end-member compositions are listed in table 3.3.

**Table 3.3 Elemental and Fe isotopic end-member compositions for the initial vent fluid**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Vent Site</th>
<th>T [°C]</th>
<th>Cl [mM]</th>
<th>Na [mM]</th>
<th>Fe [µM]</th>
<th>Mn [µM]</th>
<th>Cu [µM]</th>
<th>Zn [µM]</th>
<th>Fe/Mn</th>
<th>$\delta^{56}\text{Fe}$c [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>27-14a</td>
<td>NF1</td>
<td>64.4</td>
<td>39.2</td>
<td>1145.3</td>
<td>663.7</td>
<td>1.3</td>
<td>38</td>
<td>1.73</td>
<td>-0.66</td>
<td></td>
</tr>
<tr>
<td>60-01a</td>
<td>NF2</td>
<td>88.9</td>
<td>56</td>
<td>178.9</td>
<td>433.4</td>
<td>-</td>
<td>23.9</td>
<td>0.41</td>
<td>-0.74</td>
<td></td>
</tr>
<tr>
<td>66-03a</td>
<td>NF4</td>
<td>313</td>
<td>117</td>
<td>5718</td>
<td>2101</td>
<td>-</td>
<td>90</td>
<td>2.72</td>
<td>-0.5</td>
<td></td>
</tr>
<tr>
<td>77-06b</td>
<td>NF6</td>
<td>268</td>
<td>169</td>
<td>8512</td>
<td>2521</td>
<td>63</td>
<td>219</td>
<td>3.38</td>
<td>-0.5*</td>
<td></td>
</tr>
<tr>
<td>77-10b</td>
<td>NF7</td>
<td>378</td>
<td>26</td>
<td>19.9</td>
<td>587</td>
<td>114</td>
<td>20.5</td>
<td>95</td>
<td>5.15</td>
<td>-0.53*</td>
</tr>
</tbody>
</table>

* End-member calculated for one individual chimney
b End-member composition based on a single analysis
c Determined by modeling based on Rayleigh fractionation equations (* uncorrected value since single analysis, but reflects high proportion of fluid component; * uncorrected value since sample reflects 93% fluid component)
In addition to end-member calculations for each individual chimney, the elemental concentration data further allows the elemental composition of their common end-member to be determined, since all samples plot on a common mixing line with Mg, except 77-06, which deviated from this mixing line (Schmidt et al., in prep). Three of such plots are listed below as examples (figure 3.5).

![Figure 3.5](image)

Common mixing lines with Mg [mM] for Cl [mM], Li [µM] and Fe [mM]. Lithium was selected to represent the elements generally behaving conservatively upon mixing with seawater (e.g. Li, Na, K, Ca, Sr, U, etc., data from Schmidt et al. (in prep)) while Fe contents depend on a range of other parameters too. Sample 77-06 (shown as red square) clearly deviates from the common mixing lines, suggesting a separate end-member composition for this fluid.

### 3.4.3 Fe isotopic composition

Iron isotopic compositions of vent fluids span a broad range (ca. -0.65‰ to -0.39‰, table 3.2), similar to previously published data (Bennett et al., 2009; Rouxel et al., 2008; Severmann et al., 2004), but reflect a high degree of seawater dilution. Based on a modeling approach and Rayleigh fractionation equations (equation 3.2), individual end-member δ^{56}Fe were determined for chimneys NF1, NF2, NF4, NF6 and NF7 (figure 3.4, table 3.3), yielding end-member δ^{56}Fe of as low as -0.74‰ (NF2) and -0.66‰ (NF1). These values are in accordance with the previously suggested δ^{56}Fe range of -0.2 to -0.7‰ for hydrothermal fluids (compared with the 0.09‰ average of the bulk silicate Earth, (Rouxel et al., 2008)). However, compared with other investigated vent fields, taken together, Nifonea fluids display relatively negative end-member δ^{56}Fe (figure 3.6).

Of the Nifonea samples, the high-Fe fluids (>5000 µM Fe) neither feature extremely light nor heavy Fe isotopic compositions (both end-member δ^{56}Fe = -0.5‰), while the low-Fe fluids (587 to 1145 µM Fe) display the largest variations in δ^{56}Fe (-0.74‰ to -0.54‰).
Diffuse fluids with seawater Mg levels, such as 27-11, reveal very light Fe isotopic compositions ($\delta^{56}\text{Fe} = -0.61\%$), suggesting distinctly low $\delta^{56}\text{Fe}$ for the plume layer above the caldera. Since the elemental compositions indicate a common end-member (section 3.4.2) it is suggested that the varying end-member Fe isotopic compositions of each individual chimney were modified from the common source fluid by a range of processes, such as water-rock interaction, phase separation, or sulfide precipitation, which will be discussed in detail in sections 3.5.1 to 3.5.4.

Chalcopyrite from NF1 displays an Fe isotopic composition of $\delta^{56}\text{Fe} = -0.43\% \pm 0.05\%$ (2SE, table 3.1), which is heavier by $0.23 \pm 0.05\%$ relative to the end-member composition of the associated vent fluid of $-0.66 \pm 0.05\%$. Similarly, the $\delta^{56}\text{Fe}$ of chalcopyrite from NF6 is heavier compared with the corresponding vent fluid by $0.27 \pm 0.04\%$, while at NF4 no significant difference between the fluid and chalcopyrite is evident ($\Delta^{56}\text{Fe}_{\text{Fluid-Chalcopyrite}} = -0.08 \pm 0.05\%$; $\Delta_{A-B}$ is defined as $\delta_A - \delta_B$, see also chapter 1, section 1.4). The observation of generally positive Fe isotope fractionation between chalcopyrite and its associated vent fluids is consistent with observations from the Lucky Strike, Rainbow and Logatchev as well as the EPR 9-10°N vent fields (Rouxel et al., 2008). Rouxel et al. (2008) found chalcopyrite $\delta^{56}\text{Fe}$ in samples from EPR 9-10°N to be on average, slightly higher by $0.14 \pm 0.09\%$ ($\Delta^{56}\text{Fe}_{\text{Fluid-Chalcopyrite}}$) relative to the composition of associated vent fluids. This $\Delta^{56}\text{Fe}$ is barely resolvable and thus $\Delta^{56}\text{Fe}_{\text{Fluid-Chalcopyrite}}$ is seen as comparatively high at NF1 and NF6.
The $\delta^{56}$Fe values of coexisting pyrite tend to be systematically lighter than the signatures of chalcopyrite (Rouxel et al., 2004b; Rouxel et al., 2008). Iron isotope differences between chalcopyrite and pyrite ($\Delta^{56}$Fe$_{\text{Chalcopyrite-Pyrite}}$) was calculated to be $0.32 \pm 0.09\%_\circ$ and $0.55 \pm 0.10\%_\circ$ for NF1 and NF4 respectively. This is significantly smaller than previously reported values, such as $0.94 \pm 0.13\%_\circ$ for $\Delta^{56}$Fe$_{\text{Chalcopyrite-Pyrite}}$ in samples from EPR 9-10°N (Rouxel et al., 2008). In contrast, Fe isotope fractionation between pyrite and the aqueous Fe$_{\text{aq}}^{2+}$ of the associated vent fluids was very different between NF1 and NF4 (no coexisting pyrite minerals were separated from NF6). In pyrite separated from NF1, $\delta^{56}$Fe (see table 3.1) is almost identical to the calculated end-member vent fluid composition, giving rise to a $\Delta^{56}$Fe$_{\text{Fluid-Pyrite}}$ of $0.09 \pm 0.04\%_\circ$, while $\delta^{56}$Fe fractionation between Fe$_{\text{aq}}^{2+}$ and FeS$_2$ in samples from NF4 yielded a $\Delta^{56}$Fe$_{\text{Fluid-Pyrite}}$ of $0.47 \pm 0.05\%_\circ$, which is within the previously reported range (Rouxel et al., 2008). However, it should be noted, that all calculations were based on mineral separates from single chimney fragments and may not represent the whole chimney. Furthermore, pyrite minerals contain impurities of sphalerite and, in part, chalcopyrite (see 3.4.1), particularly at NF4. Both minerals preferentially incorporate heavy Fe (Rouxel et al., 2008) and accordingly, the $\delta^{56}$Fe of pyrite may be shifted towards anomalously heavy values if Fe containing impurities are present.

All volcanic rocks processed for Fe isotope analysis were basaltic aphyric lavas from the Nifonea caldera showing minor evidence of alteration only, except 27-09. Sample 27-09, taken from a mound of broken pillow lavas hosting chimney NF1, displayed strong signs of hydrothermal alteration. Iron isotopic compositions for the volcanic rock samples ranged from $\delta^{56}$Fe = $0.10 \pm 0.04\%_\circ$ to $0.23 \pm 0.05\%_\circ$ (2SE) (table 3.4). Accordingly, with the exception of 27-09, the $\delta^{56}$Fe of all samples are identical, within the range of their analytical uncertainties. The results agree well with the Fe isotopic composition of Bulk Silicate Earth (BSE) determined as $0.09\%_\circ \pm 0.05\%_\circ$ (Beard et al., 2003) and are consistent with the composition of the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rock type</th>
<th>$\delta^{56}$Fe [%]</th>
<th>2SE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>27-01</td>
<td>basaltic aphyric lava</td>
<td>0.15</td>
<td>0.05</td>
</tr>
<tr>
<td>27-09</td>
<td>basaltic aphyric lava</td>
<td>0.23</td>
<td>0.04</td>
</tr>
<tr>
<td>60-09</td>
<td>basaltic aphyric lava</td>
<td>0.16</td>
<td>0.05</td>
</tr>
<tr>
<td>60-13</td>
<td>basaltic aphyric lava</td>
<td>0.14</td>
<td>0.05</td>
</tr>
<tr>
<td>66-10</td>
<td>basaltic aphyric lava</td>
<td>0.10</td>
<td>0.04</td>
</tr>
<tr>
<td>77-03</td>
<td>basaltic aphyric lava</td>
<td>0.10</td>
<td>0.04</td>
</tr>
</tbody>
</table>
BHVO-2 (Hawaiian Volcanic Observatory basalt, USGS) reference material as well, which produces a $\delta^{56}\text{Fe}$ of 0.10% $\pm$ 0.07 (2SD). Sample 27-09, however, is significantly enriched in heavy Fe compared with other samples and BSE, probably reflecting preferential leaching of isotopically light Fe during hydrothermal alteration.

3.5 Discussion

The Fe isotope results from the Nifonea vent field are yet another data set providing evidence that $\delta^{56}\text{Fe}$ of hydrothermal fluids and sulfides are generally isotopically light compared with the composition of BSE, determined as 0.09‰ (Beard et al., 2003b; Bennett et al., 2009; Dauphas and Rouxel, 2006; Rouxel et al., 2008; Severmann et al., 2004; Sharma et al., 2001). Fluid $\delta^{56}\text{Fe}$ values as low as -0.74‰ were calculated for end-member fluids (see section 3.4.3 and table 3.3) thereby expanding the range of $\delta^{56}\text{Fe}$ observed in hydrothermal vent fluids along the Mid-Atlantic Ridge and East Pacific Rise and to slightly lighter compositions than previously observed. Several processes are potentially important for controlling the Fe isotope variability in hydrothermal fluids, including high-temperature basalt alteration, phase separation and subsurface mixing and precipitation processes. These are discussed in turn below.

3.5.1 Influence of the source rock on the Fe isotopic composition of vent fluids

Volcanic rocks recovered from the Nifonea vent field define a small range of $\delta^{56}\text{Fe}$ centered about 0.14 ± 0.05‰ that are identical, within error, to BSE, although some compositions were significantly heavier and up to 0.23‰. Preferential leaching of light Fe is suggested to occur during low-temperature as well as high-temperature hydrothermal alteration, leaving altered basaltic rocks behind with increased $\delta^{56}\text{Fe}$ relative to fresh rocks (e.g. Rouxel et al. (2003); Rouxel et al. (2008)). Hydrothermal activity at Nifonea is assumed to be very young and fluid chemistry suggests high water-rock ratios without significant leaching from rocks. Thus, only limited Fe mobilization from the volcanic rock can be suspected, and with light Fe being preferentially leached, this process may account for the comparably light $\delta^{56}\text{Fe}$ of end-member fluids at Nifonea (table 3.3). Considerable enrichment of heavy Fe isotopes in hydrothermally altered basalts (most likely in form of secondary Fe-bearing minerals), resulting from the
preferential removal of light Fe isotopes, is evident from a high $\delta^{56}$Fe value in the one collected rock sample featuring the highest degree of alteration (27-09, table 3.4).

3.5.2 Iron isotope systematics during phase separation

Phase separation has been identified as one of the fundamental processes controlling mid-ocean ridge vent fluid chemistry (Von Damm, 1995). However, no direct influence of phase separation on the Fe isotopic composition of vent fluids has been demonstrated so far. Several observations suggest only limited Fe isotope fractionation during this process. For example, Beard et al. (2003b) compared the $\delta^{56}$Fe of both the vapor and brine phases emanating from Brandon Vent at EPR 21.5°S (see 3.2.2) yielding no more than a 0.15‰ difference in compositions. Furthermore, at EPR 9-10°N (although not spatially related to each other) the $\delta^{56}$Fe of high salinity fluids did not differ significantly from the $\delta^{56}$Fe of lower salinity, vapor-rich fluids (Rouxel et al., 2008). In addition to these observations, experimental work by Syverson et al. (2014) demonstrated that Fe isotope fractionation during phase separation in the NaCl-H$_2$O system yields a maximum fractionation factor $\Delta^{56}$Fe$_{vapor\text{-}liquid}$ of 0.15 ± 0.05‰. This result is consistent with the observations from Brandon vent. According to Syverson et al. (2014), with proceeding phase separation, a separating vapor phase becomes progressively enriched in the heavy Fe isotopes relative to the coexisting NaCl-rich liquid and the non-separated single phase fluid. Their observed Fe isotope fractionation was interpreted to reflect differences in the abundance and coordination chemistry between Fe chloro- and aquo-complexes and their partitioning between vapor and coexisting liquid as suggested by theoretical calculations (Hill and Schauble, 2008; Hill et al., 2009; Hill et al., 2010; Schauble et al., 2001). Specifically, the type and number of coordinated ligands, such as Cl$^-$ or H$_2$O, complexed to Fe can vary significantly as a function of P, T and solution composition of the vapor and liquid (Syverson et al., 2014). At high temperatures, for example, the neutrally charged Fe$^{2+}$-aquo-chloro complex $[\text{FeCl}_2(\text{H}_2\text{O})_2]^0$ and Fe$^{2+}$-chloro complexes like $[\text{FeCl}_4]^{2-}$ are both potential Fe species with their relative abundances being controlled by dissolved chloride concentrations. Syverson et al. (2014) infer that the chloride-rich liquid phase is dominated by $[\text{FeCl}_4]^{2-}$, whereas the more volatile H$_2$O-rich $[\text{FeCl}_2(\text{H}_2\text{O})_2]^0$ primarily partitions into the vapor phase. Because metal-bearing complexes rich in water provide more potential for bonds (O bonds), the
heavy isotopes of Fe are enriched relative to \([\text{FeCl}_4]^{2-}\) (Black et al., 2011) as is evident from their experimental data. However, the vapor phase is susceptible to changes in the relative abundance of both species with progressing phase separation. Although conducted in a different P-T region (of 424-420°C and 352-315 bar), these theoretical and experimental suggestions are consistent with observations from Nifonea. Individual end-member fluids display a negative correlation between \(\delta^{56}\text{Fe}\) and Cl content, suggesting the preferential incorporation of the heavy isotopes into the vapor phase and progressive enrichment of the light isotopes with increasing Cl content (figure 3.7). As discussed earlier, all fluids are interpreted to reflect mixtures of vapor and brine, resulting from non-complete segregation following phase separation just beneath the vent site. Phase separation results in the partitioning of \([\text{FeCl}_2(\text{H}_2\text{O})_2]^0\) and thus heavy Fe into the vapor phase, while \([\text{FeCl}_4]^{2-}\) is partitioned into the liquid phase accompanied by enrichment of the light Fe isotopes. Subsequent mixing of both phases (and potentially non-phase separated ‘evolved’ seawater) to different degrees is likely to have produced the observed fractionation trends. With only 26 mM Cl (table 3.3) fluids taken from NF7 represent the mixture with the highest vapor proportion. It is thus expected that the pure vapor phase, calculated to have only 3 mM of Cl at given P-T conditions and dominated by Fe\(^{2+}\)-aquo-chloro complexes such as \([\text{FeCl}_2(\text{H}_2\text{O})_2]^0\), would display an even heavier \(\delta^{56}\text{Fe}\), inferred to be around \(-0.45\permil\) based on extrapolation of the indicated trend. This theoretical pure vapor makes up only 11.5% of sample 77-10, and accordingly, through mass balance considerations, the remaining

![Figure 3.7](image)

\(\delta^{56}\text{Fe}\) vs. Cl concentrations of individual fluid end-members (27-14, 60-01, 77-06 and 77-10) from Nifonea vent field (data compiled in table 3.3). All end-member fluids have chlorine contents below seawater level (indicated by the dashed grey bar). Samples 27-14, 60-01 and 77-10 show perfect correlation of \(\delta^{56}\text{Fe}\) and Cl, while 77-06 (green diamond) on the contrary, significantly deviates from this trend. Altogether sample 77-06 shows very distinct geochemical characteristics that preclude integration into a common end-member (Schmidt et al., in prep).
88.5% must be isotopically light, having a $\delta^{56}\text{Fe}$ of -0.54‰ to result in sample 77-10 displaying a net $\delta^{56}\text{Fe}_{\text{vapor-liquid}}$ of ~0.09‰. This corresponds to an isotope fractionation between the vapor and liquid phases of $\Delta^{56}\text{Fe}_{\text{vapor-liquid}}$ ~0.09‰. However, to yield the low $\delta^{56}\text{Fe}$ of sample 60-01 (-0.74‰), where the theoretical vapor represents only 3.4% of the sample, the admixed liquid phase would need to be fractionated relative to the vapor phase with a $\Delta^{56}\text{Fe}_{\text{vapor-liquid}}$ of ~0.3‰, which is well above experimentally predicted values. Syverson et al. (2014) report that the vapor phase is susceptible to changes in the relative abundance of $[\text{FeCl}_2(\text{H}_2\text{O})_2]^0$ and $[\text{FeCl}_4]^{2-}$. Since the Cl concentrations of vapor phase fluids highly depend on pressure conditions and thus depth (Driesner and Heinrich, 2007), vapor fluids formed in back-arc settings (with their generally lower water depths compared with mid-ocean ridge settings) may generally feature considerably lower Cl contents. Formation of complexes with Fe may therefore be dominated by $[\text{FeCl}_2(\text{H}_2\text{O})_2]^0$ or even $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, resulting in more pronounced Fe isotope fractionation between the vapor and liquid phases and possibly lower Fe concentrations in vapor phases in general. Interestingly, although Fe contents in hydrothermal fluids are largely controlled by the concentration of complex building chlorine, Fe contents determined in the present study do not correlate with Cl content. Despite having a higher Cl content than 77-10 and 27-14, sample 60-01 displays the lowest Fe content amongst the individual end-members plotted (table 3.3), suggesting that each of these three samples experienced variable degrees of Fe loss through precipitation of Fe-sulfides. The effects of phase separation and subsurface sulfide precipitation on the Fe isotopic composition are likely to obscure each other to varying degrees. Precipitation of Fe-sulfides in the subsurface can alter the fluid $\delta^{56}\text{Fe}$ in either direction (as discussed in the next paragraph) thus acting to either negate or reinforce the effects of phase separation on fluid $\delta^{56}\text{Fe}$. Consequently phase separation at the seafloor (producing the two-phase venting observed at some of the vent sites) may overprint the isotope effects associated with precipitation of Fe-sulfides deeper in the crust (and thus prior to phase separation). Contrarily, formation of Fe-sulfides within the chimney stockwork root zone may overprint Fe isotope fractionation produced by phase separation at sites where the separation occurs at greater depths (not all vent sites displayed signs of near-surface phase separation). This complex interplay with variable chronologies and degrees of sulfide precipitation and phase separation rather complicates attempts to deconvolve the
Fe isotope effects associated with each process. A model schematically illustrating the possible variations in the interplay of phase separation and subsurface sulfide precipitation between vent sites is presented in the conclusions section.

As can be seen in figure 3.7, sample 77-06 deviates significantly from the observed trend of increasingly heavy $\delta^{56}\text{Fe}$ with decreasing Cl content described by samples 27-14, 60-01 and 77-10. It is suggested that a lower degree of subsurface Fe-sulfide precipitation at greater depth may have caused the non-separated fluid sourcing vent site NF6 to have a heavier Fe isotopic composition even before this fluid underwent phase separation. Phase separation would then produce even heavier $\delta^{56}\text{Fe}$ in the vapor phase. This would explain the relatively high $\delta^{56}\text{Fe}$ displayed by sample 77-06, despite its high Cl content.

3.5.3 Control of subsurface sulfide formation on the Fe isotopic composition of vent fluids

Precipitation of Fe-sulfides in the subsurface has large potential for generating sizeable Fe isotope fractionation (Rouxel et al., 2004b). Conductive cooling or entrainment of minor amounts of seawater may cause the formation of Fe-sulfides prior to venting resulting in significant Fe isotope effects. The modifications necessary to produce the distinct fluid properties, observed at some of the various venting sites, from a single common source fluid require subsurface precipitation (Schmidt et al., in prep). In particular, the transition metal contents of these fluids are controlled by precipitation and dissolution processes, suggesting that low-Fe fluids may be most affected by subsurface precipitation. As pointed out in section 3.4.3, low-Fe fluids (587 to 1145 µM Fe) display also the largest variations in $\delta^{56}\text{Fe}$ (-0.74‰ to -0.54‰, table 3.3) further suggesting that subsurface precipitation also modifies the Fe isotopic composition of those fluids. Accordingly, variable influence from subsurface precipitation could also explain the spread of Fe isotopic compositions between individual chimney end-members.

One good indicator to test for the influence of subsurface Fe-sulfide precipitation on the $\delta^{56}\text{Fe}$ of vent fluids is the relationship between $\delta^{56}\text{Fe}$ and the ratio of Fe to Mn (Rouxel et al., 2008). Subsurface precipitation will produce significant depletion of Fe in
hydrothermal fluids, while Mn, which tends to behave conservatively, is less affected, leading to a fractionated Fe/Mn that is a good indicator of Fe-sulfide precipitation in the subsurface environment (Seewald and Seyfried Jr, 1990). Other than Fe/Mn, the ratio of Fe to Cl, while largely controlled by phase separation, can be affected by Fe-sulfide precipitation as well. Both ratios show a positive correlation with each other for individual end-members (except 77-10), indicating that Fe contents in relation to chloride are a result of Fe-sulfide precipitation, rather than phase separation (figure 3.8a). Sample 77-10 has been most affected by phase separation, as is evident from its very low Cl content (section 3.5.2, table 3.3 and figure 3.7). This suggests that its low Fe content is a consequence of phase separation rather than sulfide precipitation. The fact that sample 77-10 deviates from the main trend (figure 3.8a), is interpreted as indication that Fe-sulfide precipitation is the more substantial cause of low Fe contents and variations of $\delta^{56}$Fe in the remaining samples.

A positive correlation between Fe/Mn and $\delta^{56}$Fe in the affected samples (with an $R^2$ of 0.98) further suggests that the observed Fe isotope systematics are related to Fe-sulfide precipitation (figure 3.8b). Although the $\delta^{56}$Fe and Fe/Mn values of 77-10 do not follow this

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**Figure 3.8**

Fe/Mn vs. Fe/Cl (a) and $\delta^{56}$Fe vs. Fe/Mn (b) of individual fluid end-members (data compiled in table 3.3). 60-01, 27-14 and 77-06 show perfect correlation indicating significant influence of Fe/Mn on $\delta^{56}$Fe. Increased sulfide precipitation corresponds to more negative $\delta^{56}$Fe of the associated fluids, which are offset by -0.2 and -0.1‰ relative to the least affected sample (77-06). Solely 77-10 appears to be unaffected by this trend.
linear trend, a precipitation-induced Fe isotope effect prior to phase separation cannot be ruled out for this sample.

Subsurface precipitation of metal sulfides can cause Fe isotope effects of opposing directions, depending on the kinetics of precipitation. While positive fractionation factors are calculated (Polyakov et al., 2007; Schauble et al., 2001) and observed (Rouxel et al., 2004b) for the formation of chalcopyrite and pyrite from hydrothermal fluids under equilibrium conditions, studies by Butler et al. (2005) and Rouxel et al. (2008) highlight the importance of kinetic Fe isotope fractionation during rapid precipitation of FeS, which give rise to a negative fractionation factor, followed by the rapid formation of pyrite or quantitative conversion of the FeS precursors to pyrite, preserving negative fractionation factors during FeS precipitation.

As is evident from figure 3.8b, progressive Fe depletion, monitored as lower Fe/Mn, is coupled to decreasing $\delta^{56}$Fe, suggesting a positive fractionation factor ($\alpha$) during sulfide precipitation (consistent with pyrite or chalcopyrite formation) and hence negative pathways for the $\delta^{56}$Fe of the remaining fluid (figure 3.9). If one assumes that sample 77-06 ($\delta^{56}$Fe = -0.50‰) reflects only a negligible influence from subsurface precipitation, samples 27-14 and 60-01 appear to be fractionated relative to 77-06, giving a $\Delta^{56}$Fe$_{\text{Fluid-Sulfide}}$ of -0.16‰ and -0.24‰, respectively. This is well within the range observed for $\Delta^{56}$Fe$_{\text{Fluid-Chalcopyrite}}$ of -0.08 to -0.27‰ (section 3.4.3). Interestingly Cu (and Zn) contents increase progressively along this trend as well (table 3.3), possibly indicating subsurface formation of chalcopyrite, which would be consistent with previously observed fractionation trends (Rouxel et al., 2004b). Furthermore, the least affected sample (77-06) features the highest ratio of Fe to H$_2$S (1.3, table 3.2), while samples affected by increasing levels of subsurface precipitation have lower Fe/H$_2$S, as low as 0.01 for sample 60-01. Likewise, the light Fe isotopic composition of the diffuse fluid sample 27-11 suggests subsurface formation of Fe-sulfides (Fe/Mn ~ 1.4, table 3.2). Temperatures of diffuse fluids were estimated to be less than 25°C indicating slow and continuous cooling in the subsurface. The significantly reduced temperature gradient may favor the formation of pyrite and chalcopyrite under equilibrium conditions and thus result in positive Fe isotope fractionation.
3.5.4 Iron isotope effects during sulfide precipitation in chimney environments

In order to evaluate the Fe isotope effects during precipitation of the collected chimney sulfides, Fe isotope fractionation factors between Fe(II)-aquo-chloro complexes and iron disulfide minerals were estimated based on isotopic partition function ratios determined by Schauble et al. (2001). At 380°C, the maximum temperature measured at Nifonea, Fe isotope fractionation factors α were estimated to be 1.0009 between solid FeS$_2$ and aqueous [FeCl$_4$]$^{2-}$ and 1.0013 between FeS$_2$ and aqueous [Fe(H$_2$O)$_6$]$^{2+}$. However, previous studies documented negative fractionation factors between hydrothermal fluids and precipitates, consistent with experimental work by Butler et al. (2005) that demonstrated systematically negative δ$_{56}$Fe values for FeS precipitates relative to the fluid. Accordingly, zero-age FeS precipitates have δ$_{56}$Fe values that are approximately 0.8‰ lighter than the signature of the corresponding fluid, but during aging precipitates and fluids tend to converge towards the same Fe isotopic composition, reaching a minimum difference of -0.3‰ after roughly 170 h (figure 3.10). The negative δ$_{56}$Fe values of FeS relative to the fluid are interpreted as the result of kinetic isotope effects (Butler et al., 2005) that may have implications for the formation of pyrite under hydrothermal conditions as well. Rouxel et al. (2008) reported δ$_{56}$Fe values for pyrite minerals, collected from chimneys at the 9-10°N EPR field, that were in agreement with predicted kinetic effects during rapid FeS precipitation. It was thus concluded, that rapid formation of pyrite from FeS may preserve the negative (kinetic) fractionation factors
during FeS precipitation. In contrast, slow formation of pyrite, as is suggested to occur below the seafloor (due to conductive cooling), isolated from seawater, is expected to occur under equilibrium conditions, with limited Fe isotope fractionation (Rouzel et al., 2008).

Pyrite minerals collected from NF1 and NF4 display $\delta^{56}\text{Fe}$ more negative than the corresponding fluids (table 3.1), with $\Delta^{56}\text{Fe}_{\text{Fluid-Pyrite}}$ ranging from 0.09 to 0.47‰ (section 3.4.3). These results are consistent with variable kinetic Fe isotope fractionation effects during pyrite formation. When pyrite formation is rapid, such as during the mixing of fluid with seawater, as is characteristic for chimney environments, the maximum kinetic isotope fractionation may be recorded in pyrite (Rouzel et al., 2008).

The negative $\delta^{56}\text{Fe}$ from rapid FeS precipitation would also be preserved by quantitative conversion of FeS to pyrite, even if pyrite formation was rather slow. Both mechanisms are possible explanations for the very negative $\delta^{56}\text{Fe}$ of pyrite from NF4 (-0.97‰, table 3.1) that plots in the range determined for rapidly precipitating FeS. The large $\Delta^{56}\text{Fe}_{\text{Fluid-Pyrite}}$ of 0.47‰ suggests a strong kinetic effect either during precipitation of the FeS precursor or also upon formation of pyrite. At NF1, this is significantly lower ($\Delta^{56}\text{Fe}_{\text{Fluid-Pyrite}} = 0.09‰$), and may indicate later stage remineralization of pyrite with initially lighter Fe isotopic composition. Similar to slow subsurface precipitation of massive sulfides, remineralization is expected to produce $\delta^{56}\text{Fe}$ in pyrite that resembles the signature of the hydrothermal fluid because of increased Fe isotope exchange between the fluid and FeS$_2$ and attainment of near-equilibrium conditions, provided the fluid is isolated from seawater (Hannington et al., 1995; Rouzel et al., 2008).
Likewise, Fe isotope effects during precipitation of chalcopyrite from FeS precursors are expected to reflect equilibrium conditions, with generally positive Fe isotope fractionation factors. This is because chalcopyrite precipitates at high temperatures (usually above 350°C), and thus rapid attainment of isotope equilibrium between FeS precursors, the Fe(II)\textsubscript{aq} reservoir and CuFeS\textsubscript{2} has been suggested to explain the widely observed and theoretically determined positive $\Delta^{56}$Fe between CuFeS\textsubscript{2} and Fe(II)\textsubscript{aq} (Polyakov et al., 2007; Rouxel et al., 2004b; Rouxel et al., 2008).

Chalcopyrite samples from NF1, NF4 and NF6 all display $\delta^{56}$Fe more positive than corresponding end-member fluids (tables 3.1 and 3.3) with $\Delta^{56}$Fe\textsubscript{Fluid-Chalcopyrite} ranging from -0.08 to -0.27‰. These results are interpreted to reflect attainment of isotope equilibrium for higher temperatures, but kinetic effects may be present where $\Delta^{56}$Fe\textsubscript{Fluid-Chalcopyrite} is rather small (sample 66-03). Alternatively, a small value for $\Delta^{56}$Fe\textsubscript{Fluid-Chalcopyrite} may reflect changes in fluid temperature and Fe isotopic composition. A distinct chalcopyrite lining, revealed in the interior of the conduit of NF4 (see section 3.4.1), indicated high fluid temperatures at which the fluid and chalcopyrite may have been in isotopic equilibrium. Increased seawater entrainment (and hence increased temperature gradients) at a later stage, may have shifted the Fe isotopic composition of fluids from NF4 towards higher $\delta^{56}$Fe (e.g. through kinetic effects during FeS precipitation, as
suggested from the very negative $\delta^{56}$Fe in pyrite samples), but at temperatures too low to allow for Fe isotopic exchange between the fluid and chalcopyrite. The comparably large $\Delta^{56}$Fe$_{\text{Fluid-Chalcopyrite}}$ in chalcopyrite from NF1 (and NF6; tables 3.1 and 3.3) on the other hand, may indicate an absence of kinetic isotope effects so that the maximum equilibrium $\Delta^{56}$Fe$_{\text{Fluid-Chalcopyrite}}$ is recorded. Continuous formation of chalcopyrite under equilibrium conditions (e.g. in the subsurface) would result in slightly decreasing $\delta^{56}$Fe over time. The difference in $\delta^{56}$Fe between the chalcopyrite and fluid could increase if isotope exchange were disabled.

The combined information retrieved from Fe isotope fractionation mechanisms during sulfide formation within the chimneys NF1, NF4 and NF6 allow constraints to be placed on the chimney environments, with implications for the processes expected to occur in the dispersing particle plume above the vent orifice. For NF4, a chimney environment characterized by the rapid formation of pyrite can be inferred from the large and negative $\Delta^{56}$Fe$_{\text{Fluid-Pyrite}}$ ($= 0.47\%\delta$). Furthermore attainment of isotope equilibrium for higher temperatures of precipitation is likely to have produced the slightly positive $\Delta^{56}$Fe$_{\text{Fluid-Chalcopyrite}}$ ($= -0.08\%\delta$). Strong kinetic Fe isotope fractionation prevails and is preserved as very negative $\delta^{56}$Fe of pyrite, while the $\delta^{56}$Fe of the corresponding fluid becomes progressively more positive. The suggested chimney environment is dominated by mixing with seawater deep within the vent, resulting in large temperature gradients, which is consistent with the low proportion of original fluid in samples from the vent orifice. This describes a typical chimney environment with $\Delta^{56}$Fe$_{\text{Fluid-Pyrite}}$ and $\Delta^{56}$Fe$_{\text{Fluid-Chalcopyrite}}$ similar to previously reported values (Rouxel et al., 2008). At NF1 (and presumably NF6), on the other hand, slow precipitation or remineralization of pyrite, and equilibrium fractionation during chalcopyrite precipitation, suggest a well sealed chimney interior with only limited seawater mixing (if at all). The well sealed sulfide structure maintains high internal temperatures and thus rapid sulfide formation is only expected to occur in the proximity of the vent orifice(s). Under equilibrium conditions between the fluid and chalcopyrite, the $\delta^{56}$Fe of the fluid decreases slightly with progressive precipitation. Limited Fe isotope fractionation during pyrite precipitation or reworking suggests negligible influence on the fluid $\delta^{56}$Fe. The high proportions of original fluid in samples from the vent orifice and the robust branchy sulfide structure of NF1 support this scenario (table 3.2).
3.5.5 Effects of seawater dilution on the $\delta^{56}$Fe of emanating vent fluids

The mixing of hydrothermal fluids with seawater and the associated sudden temperature drop at the vent orifice leads to the formation of turbulent particle plumes often described as black smoke. These buoyant plumes contain metal sulfides such as FeS, ZnS and CuS as well as PbS, but also FeS$_2$ and CuFeS$_2$ that rapidly forms when cooling vent fluids can no longer maintain their high dissolved metal load. The rapid precipitation of sulfides suggests strong Fe isotope effects within the buoyant plume. However, the magnitude and direction of Fe isotope fractionation may vary significantly depending on the style of venting and the type of precipitating minerals.

Samples of buoyant plumes, dispersing directly above the vent, were collected on three occasions using ROV mounted Niskin bottles. Selected vent sites were chosen accordingly to represent as many different venting styles as possible. Sample 60-02, collected above NF2, represents venting of clear fluids with a distinct two-phase character, while samples 27-15 and 27-16 represent venting of black smoke from NF1. Sample 66-05, collected above NF4, represents black smoker venting as well. Venting style, sulfide precipitation and the resulting Fe isotope effects have been investigated in detail for NF1 and NF4 in section 3.5.4. At NF4, intense mixing between hydrothermal fluid and seawater has been suggested to have occurred within the chimney, causing rapid precipitation of FeS and the subsequent formation of pyrite, thereby preserving negative kinetic Fe isotope fractionation factors. It is likely that precipitation will continue in a similar fashion to the chimney interior and in fact the pathway of $\delta^{56}$Fe during progressive seawater dilution is well described by a $\Delta^{56}$Fe$_{\text{Fluid-FeS}}$ value of 0.47‰ ($\alpha$≈0.9995, for the relationship between $\alpha$ and $\Delta^{56}$Fe see chapter 1, section 1.4) as derived in section 3.5.4. Prolonged rapid precipitation of FeS and pyrite from the dissolved Fe pool may result in corresponding particulates with $\delta^{56}$Fe of -0.86 ± 0.06‰ (corresponding to fluid sample 66-03) and -0.84 ± 0.06‰ (corresponding to buoyant plume sample 66-05), respectively. The pathway of $\delta^{56}$Fe in the remaining dissolved Fe phase may eventually reach values of up to 1.66‰, significantly higher than commonly assumed hydrothermal signatures, and a $\Delta^{56}$Fe$_{\text{Dissolved-Particulate}}$ of ~ 2.2 ‰ (figure 3.11).
At NF1, where sulfide precipitation and the resulting Fe isotope effects are different from the other sites because of a well sealed chimney structure and no significant seawater entrainment, sulfide formation patterns are expected to change dramatically with a sudden temperature drop. Within immediate proximity to the vent orifice, precipitation behavior is expected to be similar to that in the chimney interior, as evident from the $\delta^{56}$Fe of the buoyant plume samples 27-15 and 27-16 (table 3.2) (and thus corresponding particles may continue to have more positive $\delta^{56}$Fe), but will likely change to rapid FeS precipitation soon after. This change over should primarily affect the solid phase, because instantaneously precipitating FeS is expected to have very negative $\delta^{56}$Fe (from kinetic fractionation) now mixing with the rather positive $\delta^{56}$Fe of the particle cloud. At the same time, changes in dissolved $\delta^{56}$Fe will be small in the beginning. The subsequent evolution of $\delta^{56}$Fe is hard to predict; total solid $\delta^{56}$Fe may eventually be almost identical, or even slightly more negative, than the corresponding signature of the residual dissolved phase.

A clear venting fluid with a very light Fe

Figure 3.11
Expected isotope fractionation pathways for the system NF4 are highlighted for dissolved Fe (solid line), instantaneous precipitate (dotted line) and the total solid (dashed line), corresponding to progressive sulfide precipitation from hydrothermal fluid. Isotope fractionation was modeled using Rayleigh fractionation equations and a fractionation factor $\alpha = 0.9995$.

Red data points represent collected fluid and plume samples from site NF4. The blue square indicates the Fe isotopic composition of pyrite from the chimney interior at the respective site. Error bars display analytical uncertainty. Precipitates corresponding to fluid and plume samples are expected to plot on the dotted or the dashed line, according to the magnitude of particle settling from the particle cloud. The total solid (dashed line) represents the pathway of $\delta^{56}$Fe when precipitates are accumulating in the particle plume, while a high degree of particle settling would result in a corresponding particle fraction with its $\delta^{56}$Fe resembling that of instantaneously forming precipitates (dotted line).
isotopic end-member composition has been sampled at NF2. Its isotopic evolution pathway is best fitted by a fractionation factor $\alpha \approx 0.9998$ (see figure 3.4) that suggests the formation of precipitates with a $\delta^{56}\text{Fe}$ that is approximately $0.25\%$ lighter than the source fluid. While the positive isotopic pathway of the dissolved $\delta^{56}\text{Fe}$ and very low Fe/H$_2$S (table 3.2) suggest rapid formation of FeS (and subsequently pyrite), the clear venting precludes large Fe sulfide precipitation, and the suggested $\Delta^{56}\text{Fe}_{\text{Dissolved-Particulate}}$ implies only weak kinetic isotope effects. The large excess of H$_2$S is likely to facilitate pyrite formation from FeS precursors by reaction with H$_2$S or polysulfide compounds. Continued Fe isotope fractionation along this proposed fractionation pathway may produce dissolved $\delta^{56}\text{Fe}$ of up to $0.41\%$ and particulate $\delta^{56}\text{Fe}$ that are up to $\sim1.16\%$ lighter. Iron contents in NF2 fluids are severely depleted (tables 3.2 and 3.3), likely the result of large scale subsurface chalcopyrite precipitation (which also explains the absence of any Cu) as discussed in section 3.5.3. Venting at site NF2 had a very distinct two-phase character and it remains unclear how this may affect precipitation and the evolution of $\delta^{56}\text{Fe}$ in the respective phases.

### 3.6 Conclusions

In this study the Fe isotope systematics of hydrothermal fluids and sulfides from the Nifonea vent field in Vanuatu were investigated. This study provides additional constraints on the geochemical processes influencing the Fe isotope signatures of vent fluids in a young back-arc setting. In back-arc spreading centers, more evolved rock types are common and profound differences in vent fluid compositions arise (Fouquet et al., 1991; Gamo et al., 1997; German and Von Damm, 2006). Results indicate large spatial variability in the fluid Fe isotopic compositions and predominantly very negative $\delta^{56}\text{Fe}$, thereby expanding the known range of Fe isotope variation in hydrothermal fluids towards lighter signatures than observed previously, yielding a minimum $\delta^{56}\text{Fe}$ value of the fluid end-member of $-0.74\%$ (section 3.4.3). These data suggest the presence of a common source fluid that is modified during ascent by a combination of subsurface sulfide precipitation, phase separation and segregation and subsequently by variable degrees of intermixing between vapor and brine prior to venting. Whether the very light Fe isotopic compositions are a direct result
of high water-rock ratios and low-degree leaching, or large scale subsurface sulfide (chalcopyrite) formation, remains unclear; a combination of both effects is likely. A positive correlation between (most) individual end-member $\delta^{56}\text{Fe}$ values and Fe/Mn ratios suggests variable degrees of modification of the common primary end-member (source) fluid (solid lines in figure 3.12) arising from sulfide formation (section 3.5.3); scenario C in figure 3.12. Thereby, multiple “second order end-member” fluids (dashed lines in figure 3.12) are produced, each following individual migration pathways to the surface. Focused discharge of these unevenly modified high-temperature fluids would explain the spatial variability of fluid $\delta^{56}\text{Fe}$ observed at the various venting sites, while diffuse venting is likely to be sourced from fractions following non-focused migration pathways thereby undergoing slow subsurface cooling and mixing with seawater (scenario D, figure 3.12).

Phase separation and non-complete segregation produced fluids with distinctively low Cl contents compared with seawater, and possibly account for some of the variability in Fe isotopic compositions (as evident from the negative correlation of individual end-member $\delta^{56}\text{Fe}$ and Cl, figure 3.7), although its impact is assumed to be rather small compared with subsurface precipitation. Venting of two-phase fluids and visible “flames” of water vapor suggest that phase separation occurs close to the seafloor or even within the chimney structures and thus probably follows subsurface precipitation. Accordingly, phase separation represents another step of modification imposed on the second order end-member fluids (section 3.5.2). The complex interplay of variable degrees of sulfide precipitation and phase separation produces the large spatial variability of individual (“third order”) end-members (dotted lines, figure 3.12) discharged at the seafloor. The Fe isotope effects of both dominating processes are likely to be obscured by each other to a certain degree. In some cases, phase separation (and non-complete segregation) may occur right at the end of an individual fluid migration pathway when reaching the seafloor, thereby creating one individual mixture of vapor and brine. Alternatively, two or three constant mixtures of vapor and brine may emerge from phase separation and non-complete segregation at the end of such a migration pathway, feeding different venting sites. However, the reduced Cl content compared with seawater that is common to all identified end-members requires storage of fractions of brine in the subsurface. Whether it is actually stored or eventually emanates from fractures and interstitials as diffuse fluid
Figure 3.12
Schematic illustration of hydrothermal fluid evolution in the Nifonea vent field, showing multiple grades of modification of a single common source fluid (solid arrows), with a color coded indication of the associated relative shifts in fluid δ56Fe. The Fe isotopic composition of the source fluid is thereby only controlled by water-rock interaction and the preferential leaching of the light Fe isotopes as suggested by Rouxel et al. (2003). Modification of the source fluid by subsurface precipitation of Fe-sulfides and/or phase separation produces “second order end-member” fluids (dashed arrows) that continue to ascent through the crust. Where the subsurface is already sufficiently sealed by previous sulfide precipitation, the source fluid may remain relatively hot preventing further precipitation from occurring (scenarios A, B, E). Such fluids feature high metal contents and may generate black smoker type hydrothermal venting. Different degrees of phase separation and subsequent segregation will influence metal contents and fluid δ56Fe between the different sites. Scenario A describes poor segregation of the separated phases (orange dot-dash arrows) and venting of mixture of vapor and brine with increased Cl contents. Admixing of ‘evolved’ seawater (Mg-free not phase separated, black dot-dash arrow), or cross-mixing with brine from nearby vents (orange dot-dash arrows) that remained within the crust may also occur. However a high degree of phase separation (orange ellipses) and segregation will produce venting fluids with reduced metal contents and relatively heavy fluid δ56Fe (scenario B). Here the brine is largely stored within the crust or migrates laterally (due to the high density of the liquid), where it may enter the unsealed host rock and undergo mixing with diffuse fluids or penetrating seawater.

In areas of a less (scenario C) or completely unsealed host rock (scenario D) increased seawater penetration will induce cooling of the fluid in the subsurface and trigger precipitation of (most likely) chalcopyrite (black crossed lines). This process will greatly influence metal contents and fluid δ56Fe, producing metal depleted fluids with lighter δ56Fe, which may further be altered by phase separation (scenario C). Scenario E describes how intense precipitation of FeS/FeS2 within the chimney environment may further modify the secondary end-member fluid (which resembled scenario A so far but with a lower fluid Fe/H2S) and produce more heavy δ56Fe in the “third order end-member” fluid (dotted arrows) discharged at the seafloor. These precipitation processes continue in the particle plume formed above the vent orifice.
(following mixing of the brine with ascending diffuse fluids or with penetrating seawater) remains unclear. The observed shimmering water in areas of diffuse venting may indicate discharge of high-salinity fluids, but is likely to be an effect of temperature as well. Measured Cl contents of diffuse fluid were elevated but not significantly above seawater levels. Cross-mixing between ascending fluids and residual brine cannot be ruled out and could explain the deviating elemental composition of sample 77-06 (significantly higher Cl content and elevated transition metal concentrations, table 3.3). Upon discharge at the seafloor, fluids follow different evolutionary pathways, largely influenced by the kinetics of sulfide precipitation and hence temperature gradients. These different isotopic pathways may produce significantly altered dissolved $\delta^{56}$Fe in hydrothermal plumes originating from the vent field.

This study generally validates interpretations from previous studies of the Fe isotope systematics in hydrothermal fluids (Beard et al., 2003b; Rouxel et al., 2008; Sharma et al., 2001) for back-arc settings. However, the range of Fe isotopic compositions defined by hydrothermal fluids compared with igneous rocks should be extended. It is suggested that short-lived hydrothermal activity in back-arc settings resulting from eruptive heat pulses (following volcanic eruptions) may produce hydrothermal fluids with very low $\delta^{56}$Fe. High water-rock ratios without significant leaching are assumed to result in preferential mobilization of the light Fe isotopes and relative enrichments of transition metals (Fouquet et al., 1991; German and Von Damm, 2006). In particular, the Cu-rich nature of the system is believed to facilitate large-scale formation of metal sulfides in the subsurface. Although minimal Fe isotope fractionation during subsurface sulfide precipitation was suggested in earlier studies (Rouxel et al., 2008), we relate significant Fe isotope effects to chalcopyrite precipitation in the Nifonea subsurface leaving the remaining fluids depleted in the heavy Fe isotopes (figure 3.9). Sustained high temperature conditions inside chimney structures are suggested to favor slow precipitation of chalcopyrite, while early mixing with seawater will result in the rapid formation of pyrite in the chimney interior with consequences for plume processes and the Fe isotopic fingerprint of hydrothermally derived Fe. This highlights the major importance of sulfide precipitation and Fe/H$_2$S ratios in the fractionation of Fe isotopes, in the subsurface, in chimney structures and in the overlying hydrothermal plumes. For hydrothermal systems in back-arc systems, generally located at lower water depths, we
further suggest a more pronounced influence of phase separation on the $\delta^{56}$Fe of vent fluids resulting from the formation of low-Cl vapor phase fluids where Fe$^{2+}$-aquo-chloro complexes prevail.

Nifonea vent field is likely to represent a special case amongst the bulk of submarine hydrothermal activity, but gives a prime example of the highly dynamic and diverse nature of back-arc hydrothermal systems. It may further provide a potentially good natural laboratory to study plume processes.

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Chapter IV
Isotopic fractionation of iron in a hydrothermal plume above the Nifonea vent field, Vanuatu
Chapter IV

Manuscript: Isotopic fractionation of iron in a hydrothermal plume above the Nifonea vent field, Vanuatu

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The candidate was solely responsible for collection and filtration of seawater samples. Handling of seawater preconcentration was assisted by former postdoctoral fellow Dr. Melanie Gault-Ringold and PhD student John Rolison, while the preparation of particle filters was performed solely by the candidate who also acquired all Fe isotope data independently at the Centre for Trace Element Analysis. Concentration data of filter extracts was acquired at the Centre for Trace Element Analysis by technician Mr David Barr; preliminary Fe concentrations of seawater samples were obtained from flow-injection analysis by former BSc (Hons) student Ella Paterson. Fluid Rare Earth Element concentrations and advice for data reduction were provided by Katja Schmidt.
Isotopic fractionation of iron in a hydrothermal plume above the Nifonea vent field, Vanuatu

Abstract

Multiple Fe sources contribute to the marine dissolved Fe budget, but their relative importance remains largely unconstrained. Isotopic characterization of Fe sources and mass balance calculations are considered as a potential tool to unravel this complex interplay of various Fe fluxes. Hydrothermal discharge has received growing attention as a major source of dissolved Fe to the deep ocean, particularly in areas with little dust deposition. However, studies of Fe isotope fractionation in hydrothermal plumes have resulted in controversial findings with implications for a potential isotopic signature for hydrothermally derived Fe. It has been suggested by Bennet et al. (2009) that the original hydrothermal Fe isotopic composition is massively altered through mineral precipitation and redox processes within hydrothermal plumes. In the following study, direct Fe isotope analysis of the dissolved Fe fraction was utilized for the first time to study the Fe isotope systematics in a hydrothermal plume above the newly discovered Nifonea vent field. Coupled Fe isotope analysis of dissolved and particulate Fe reveals insights into different stages of plume formation and suggests that the isotopic composition of dissolved Fe is strongly fractionated towards heavier isotopic compositions away from end-member hydrothermal fluids, resulting in $\delta^{56}$Fe as low as -0.74‰ and up to -0.19‰ in more distal parts of the plume.
4.1 Introduction

Iron (Fe) is an essential micronutrient and a limiting factor in regulating primary production in parts of the world’s oceans, thereby influencing the global carbon cycle and hence climate (Archer and Johnson, 2000; Boyd et al., 2000; Lefevre and Watson, 1999; Martin, 1990; Martin et al., 1994). Glacial-interglacial climate cycling, occurring over timescales of 10,000 to 100,000 years, may in parts be the result of changes in Fe supply to the oceans from dust aerosols, a major source of Fe to surface waters (Jickells et al., 2005; Kohfeld and Ridgwell, 2009). Hydrothermal venting, on the contrary, is considered relatively constant over short timescales, potentially serving as a buffer of the dissolved oceanic iron inventory against fluctuations in dust deposition (Chu et al., 2006; Tagliabue et al., 2010) provided that hydrothermal Fe is actually transported into the open ocean and not quantitatively precipitated and sedimented to the seafloor, as evident from new research (Bennett et al., 2008; Boyle et al., 2005; Sander and Koschinsky, 2011; Statham et al., 2005; Toner et al., 2009). In particular, in the Southern Ocean, where dust deposition is generally low, the impact of hydrothermal Fe on the oceanic Fe inventory could be more pronounced (Tagliabue et al., 2010). However, the relative importance of these, and other, potential Fe sources remain largely unconstrained, despite the significance of Fe to biogeochemical processes. Investigating the marine biogeochemical cycle of Fe has therefore received much attention in recent years and enormous effort has been put into the development of new techniques for trace-metal clean seawater sampling and the improvement of analytical methods for measuring Fe. In particular, Fe stable isotope analysis of seawater-dissolved Fe (δ⁵⁶Fe) holds great potential as a tool to constrain Fe fluxes to the ocean by characterizing the distinct δ⁵⁶Fe from different sources (Conway and John, 2014; John and Adkins, 2010; Radic et al., 2011). In the deep-ocean, concentrations of dissolved Fe (dFe) vary between ~0.4 and 1 nM depending on water masses (Bergquist and Boyle, 2006; Boyle, 1997; Johnson et al., 1997) and thus novel analytical methods are required to allow for the isotopic analysis of seawater-dissolved Fe (dFe) (Conway et al., 2013; Lacan et al., 2010).

In marine environments δ⁵⁶Fe spans a range of ~4‰ (Conway and John, 2014), with bulk aerosols having ‘unfractionated’ near crustal values of ~0‰ (Beard et al., 2003b;
Mead et al., 2013; Waeles et al., 2007) and input of isotopically light Fe (-3.3‰ to -1.7‰) from reductive dissolution of Fe in continental margin sediments (Homoky et al., 2013; Homoky et al., 2009; Severmann et al., 2006; Severmann et al., 2010). Reduction of Fe(III) in the presence of dissimilatory Fe-reducing bacteria enriches isotopically light soluble Fe(II)\text{aq} in sediment pore waters, as demonstrated by incubation experiments (Beard et al., 1999; Crosby et al., 2007; Homoky et al., 2013; Homoky et al., 2009; Icopini et al., 2004).

Hydrothermal vent fluids are characterized by a dominance of isotopically light Fe as well, ranging from -0.74‰ to -0.12‰ ((Bennett et al., 2009; Rouxel et al., 2008; Severmann et al., 2004; Sharma et al., 2001) and chapter 3). Conway and John (2014), however, observed δ^{56}\text{Fe} values as light as -1.35‰ in a hydrothermal plume near the TAG hydrothermal vent site at the Mid-Atlantic ridge (MAR) during the US GEOTRACES North Atlantic GA03 Zonal Transect. This observed value is significantly more negative than the reported range for vent fluids in general and those previously collected at TAG, where minimum δ^{56}\text{Fe} for vent fluids were no lighter than -0.4‰ (Severmann et al., 2004). Similar discrepancies were observed in the aerosol dominated surface mixed layer where measured dissolved δ^{56}\text{Fe} ranged from +0.3‰ to +0.7‰ (Conway and John, 2014) despite a suggested unfractionated δ^{56}\text{Fe} signature of the aerosol source of ~0‰ (Mead et al., 2013; Waeles et al., 2007). The authors suggest ligand-mediated fractionation during dust dissolution, concentrating heavier Fe isotopes with strong Fe-binding ligands (Ilina et al., 2013). In any case such discrepancies highlight the need to further investigate additional Fe isotope fractionation processes that may occur upon mixing of the source material with seawater.

In nature, isotopic fractionation of Fe is controlled by both biotic and abiotic redox processes, together with additional fractionation (operating under kinetic and/or equilibrium conditions) resulting from non-redox processes (Johnson et al., 2004; Welch et al., 2003). The complex redox chemistry in hydrothermal plumes may very well facilitate alteration of the Fe isotopic signature of emanating vent fluids when entering the ocean. Furthermore, potential effects of organic ligands on the δ^{56}\text{Fe} of dissolved Fe are not sufficiently understood yet. Two existing studies have investigated the isotope fractionation of Fe in hydrothermal plumes, however with conflicting findings. For example, one study suggests preservation of the end-member fluid's Fe isotope
Isotopic fractionation of iron in a hydrothermal plume signature in the plume (Severmann et al., 2004), while the other suggests a significant shift towards a heavier isotopic composition of dFe as the result of Rayleigh fractionation during the rapid precipitation of Fe-sulfides (Bennett et al., 2009). These opposing results were mainly attributed to different Fe/S ratios in the end-member fluids of the respective hydrothermal plumes. Specifically, depending on the proportion of Fe to S, the dissolved Fe released by venting is either transferred into one single phase by near-quantitative Fe-oxyhydroxide formation, or precipitation (and preferential settling) of Fe-sulfides during plume ascent results in up to 50% of the Fe (Rudnicki and Elderfield, 1993) being lost from the plume. However, both studies made use of particulate Fe (pFe) for their isotopic analyses and resulting changes in $\delta^{56}$Fe of dissolved Fe were predicted based on mass balance calculations only. Advancements in preconcentration methods now enable direct analysis of dFe in hydrothermal plume samples (Conway et al., 2013; John and Adkins, 2010; Lacan et al., 2010).

In this study, hydrothermal plumes above the newly discovered Nifonea vent field in the New Hebrides arc in Vanuatu, were sampled and analyzed for their Fe isotope compositions. Previous work (chapter 3) has highlighted the high diversity of venting styles within Nifonea vent field making this site a promising location to study a variety of plume processes and possible mixing between different chemical systems. Abundant diffuse venting may further provide opportunities to see the potential effects of organic ligands on the dissolved $\delta^{56}$Fe. Utilizing new protocols for trace metal preconcentration and separation from seawater, in combination with double spiking procedures and multiple-collector ICP-MS (MC-ICP-MS), we have determined the isotopic composition of dissolved Fe in a range of plume samples. These analyses will provide new insights into the effects that plume processes have on the Fe isotopic composition of dFe and pFe and how a hydrothermal signature of dissolved Fe in the distal parts of a plume may differ from the $\delta^{56}$Fe of the original vent fluid. In order to better evaluate and interpret plume processes, V/Fe ratios are utilized to determine the relative amounts of Fe-oxyhydroxide and Fe-sulfide species amongst the particulates (Feely et al., 1998) along with major and trace element data, and Eu-anomalies are compared as a proxy for the degree of seawater dilution of the plume (Elderfield et al., 1988; Rudnicki and Elderfield, 1993).
4.2 Geological Setting

The geological background of Nifonea has been described in detail previously (chapter 3) and is only summarized briefly here. Nifonea vent field is about 1 km² in size and located in about 1875 to 1885 m water depth inside Nifonea volcano in the southern Vate Trough. The Vate Trough is one of three extensional basins (Coriolis Troughs) forming the back-arc of the Vanuatu Island arc. Abundant hydrothermal activity was found within the caldera, characterized by diffuse low-temperature venting and focused discharge of high-temperature (up to 378°C) fluids. The large areas of diffuse fluid flow indicate that much of the subseafloor permeability has not yet been sealed properly to allow for more focused fluid discharge. This observation is consistent with the absence of older chimneys or sulfide fragments, suggesting relatively young activity for the vent field. The very high fluid temperatures (i.e., 378°C is the hottest vent temperature measured in an arc setting in the western Pacific (Mottl et al., 2011)), chemical composition of vent fluids, and the Cu-rich nature of the chimneys further support the interpretation of a young, post-eruptive high-temperature hydrothermal system resulting from a short-lived pulse of heat following a recent eruption, possibly within the last decade.

Areas of more intense venting are pooled in the eastern part of the vent field where isolated chimney structures, emanating high-temperature black smoker fluids (up to 378°C), can be found in between zones of diffuse venting (<20°C), while the western area of Nifonea, located some 500 m west of the central black smoker field hosts only the latter. These diffuse fluids resemble clouds of milky white color, hanging between pillow basalt structures with not always identifiable emanation sites. The widespread occurrence of this type of venting suggests that the majority of hydrothermal activity at Nifonea is of diffuse nature and likely the source of the persistent particle plume hanging above much of the caldera.

Large-scale subsurface precipitation of chalcopyrite was suggested as the main process producing the very negative $\delta^{56}$Fe of diffuse (-0.61‰) and focused hydrothermal fluids (end-member $\delta^{56}$Fe between -0.74‰ and -0.5‰) as well as the variations in metal concentrations (see chapter 3). Upon discharge at the seafloor, fluids follow different evolutionary pathways, largely influenced by the kinetics of sulfide precipitation and
Isotopic fractionation of iron in a hydrothermal plume

hence temperature gradients. These different Fe isotopic pathways may produce significantly altered dissolved $\delta^{56}$Fe in hydrothermal plumes originating from the vent field.

Figure 4.1. Schematic map of Nifonea vent field with indication of geological features
The western part is characterized by large areas of diffuse venting hosted in broken sheet flow and fractured lobes unable to focus hydrothermal fluid flow. Sites of focused fluid discharge (red chimneys and stars) are limited to the eastern part and occur at the base and on the slopes of fresh pillow mounds and lobes. Red stars indicate high-temperature vents with known fluid properties (see chapter 3 for details), while CTD casts are indicated by blue circles. The first CTD depth profile (station 30) was taken in close proximity of vents NF1, NF4, NF5 and NF6 as well as close to a sampled site of diffuse venting (NF8), while cast 79 was taken ~310 m southeast of the central vent field (and station 30).

4.3 Hydrothermal venting at Nifonea

Several small chimneys (NF2, NF5) were observed to be venting hot (up to 345°C) but clear fluids characterized by low metal contents and very negative fluid $\delta^{56}$Fe, thereby resembling the chemistry of diffuse fluids. Iron isotope fractionation in these vent systems was suggested to be primarily controlled by FeS and FeS$_2$ precipitation (although this is at odds with the lack of black smoke in these systems) and resulting
kinetic isotope effects that are predicted to occur during mineral formation ($\Delta^{56}\text{Fe}_{\text{Fluid-Particle}} \sim 0.25\%$; $\Delta^{56}\text{Fe}$ is explained in section 1.4, chapter 1). This may produce dissolved $\delta^{56}\text{Fe}$ of up to $0.4\%$ and particulate $\delta^{56}\text{Fe}$ that are $\sim 1.2\%$ lighter if $99\%$ of Fe is removed from the aqueous phase during this process.

For black smoker vents, two different evolutionary pathways have been suggested, as exemplified by the Fe isotope systematics of sites NF1 and NF4. At site NF4, similar systematics as in the cases of NF2 and NF5 (precipitation of FeS and FeS$_2$) control Fe isotope fractionation, however, resulting from significantly higher metal concentrations, kinetic isotope effects are much more pronounced with a suggested $\Delta^{56}\text{Fe}_{\text{Fluid-Particle}}$ of $\sim 0.47\%$ potentially producing dissolved $\delta^{56}\text{Fe}$ of up to $1.7\%$ that is $\sim 2.2\%$ heavier than the particulate $\delta^{56}\text{Fe}$ ($\Delta^{56}\text{Fe}_{\text{Dissolved-Particulate}} \approx 2.2\%$) if $99\%$ of Fe is removed from the aqueous phase (see figure 3.10 in chapter 3). These Fe isotopic compositions deviate significantly from the Fe isotopic signatures commonly assumed for hydrothermally derived Fe. Very different mechanisms have been suggested to control Fe isotope fractionation at site NF1 (see chapter 3). For this site, analysis of vent fluids and chimney sulfides revealed that Fe isotope fractionation in this chimney environment is governed by the slow formation of chalcopyrite, rather than the rapid precipitation of FeS and subsequent pyrite formation. Chalcopyrite formation has widely been documented to involve a positive fractionation factor $\alpha$ (see section 1.4 (chapter 1) for an explanation of $\alpha$), and consequently, sulfides forming in the interior of NF1 are generally expected to have more positive $\delta^{56}\text{Fe}$ compared to the hydrothermal fluid. Measurements of buoyant plume dissolved $\delta^{56}\text{Fe}$ above NF1 show no differences with respect to the undiluted end-member fluid (within analytical uncertainty), which is interpreted to indicate the continuation of chalcopyrite formation and resulting Fe isotope effects within the buoyant plume. Particles forming inside the buoyant particle cloud are thus expected to be enriched in the heavy Fe isotopes with respect to the dissolved phase; at least within very close proximity to the vent orifice. However, given the rapid temperature drop associated with mixing between hydrothermal fluid and seawater, particle formation mechanisms are expected to change quickly towards mechanisms dominated by rapid precipitation of FeS or FeS$_2$. Associated with this change in sulfide formation, $\Delta^{56}\text{Fe}_{\text{Dissolved-Particulate}}$ is supposed to change as well, thereafter rather resembling the Fe isotope effects observed at NF4, with significantly lighter $\delta^{56}\text{Fe}$ in fresh FeS precipitates.
How far the dissolved plume $\delta^{56}\text{Fe}$ can depart from the end-member Fe isotopic composition depends on the dissolved fraction remaining upon change of fractionation factor and also oxidation kinetics.

### 4.4 Sampling Methods

#### 4.4.1 Plume sampling

Plume samples were collected using 10 L metal-free Niskin bottles mounted in a 24-position CTD rosette water sampler with a plastic coated frame. Water samples were taken based on real-time feedback from the CTD and in particular the nephelometric turbidity sensor, which had been interfaced into the CTD. Niskin bottles were closed when turbidity anomalies could be detected while moving the CTD upwards. In addition, Mini-Autonomous Plume Recorder-Oxidation-Reduction Potential devices (MAPR-ORP), were deployed with every CTD cast to log variations in redox potential (Eh), allowing for subsequent identification of redox anomalies after CTD recovery (MAPR do not provide real-time feedback). The combination of turbidity and Eh anomalies is a distinctive indicator for a hydrothermal plume. Niskin bottles were sub-sampled from the rosette using acid cleaned tubing and a plastic funnel to shield bottle openings while open. All plume samples were sub-sampled onboard ship under a class 100 laminar-flow clean hood (Slee, Germany) for various analyses of major, minor and trace element concentrations. Each sample was homogenized by shaking prior to subsampling. Aliquots were pressure filtered (under N$_2$ pressure) through 0.4 $\mu$m membranes (Whatman polycarbonate 47 mm), collected in 1 L acid cleaned LDPE bottles (Nalgene, U.S.A.) and immediately acidified with 1 ml concentrated ultrapure HCl (TraceSELECT®Ultra, Sigma-Aldrich (Fluka)). Filter membranes containing removed particulate Fe species were kept frozen; the amount of seawater filtered through was noted.

#### 4.4.2 Background station

Background seawater samples were collected away from any hydrothermal activity in the same way as for non-buoyant plume sampling using the same CTD rosette. Sampling depths were chosen according to the relevant plume depths. Constant signals for Eh and turbidity confirmed the absence of any hydrothermal activity.
4.5 Analytical Methods

4.5.1 Quantification of particulate Fe, Mn, V, Cu and Zn as well as REE in plume samples

Filter membranes (Whatman polycarbonate, 47mm) containing plume particles were digested at the Centre for Trace Element Analysis at the University of Otago (UO). Each filter had approximately 2 L of plume material filtered through it. Filters were heated in 10 ml concentrated q-HNO₃ in closed 30 ml acid cleaned Teflon vials (Savillex U.S.A.) and refluxed at 120°C for 72 hrs. This procedure only partly digests the filter material leaving behind a residue, but allows for complete digestion of the sulfide and oxide phases. Two more 30 ml Teflon vials containing one reagent blank and one filter blank (an unused, acid cleaned filter membrane) were treated in the same way as the samples.

Each leachate was sub-sampled, diluted 100-fold with Milli-Q and 2% ultrapure HNO₃ (to a final acid strength of 2% HNO₃), and measured by quadrupole inductively coupled plasma mass spectrometer, q-ICPMS (Agilent 7500cs, Agilent Technologies, USA) to quantify the concentration of particulate Fe (pFe), Mn (pMn), V (pV), Cu (pCu), Zn (pZn). Undiluted aliquots of the leach solution were used for REE analysis. Results were subsequently adjusted for sample dilution and related to the respective seawater volume filtered for each sample.

Before each analytical session calibration slopes to convert detected count rates to elemental concentrations were determined through repeated measurements of different NIST traceable multi-element solutions (High Purity Standard Inc., SC, USA) at a range of concentrations spanning the expected concentration range of the samples. In order to suppress potential polyatomic interferences on Fe (and other elements of interest) from oxides of argon and particularly calcium, an instrument tune with elevated collision cell helium flow (about 6 ml/min) was employed for Fe (a lower flow rate causing less sensitivity loss was used for other elements). This approach was validated by repeated measurements of an in-house seawater standard that had been stripped of most trace metals and was subsequently doped with known amounts of a multi-element solution.

Analytical consistency was evaluated by regular measurements of standards, duplicates and blanks. Consequently, all samples, standards and blanks were spiked with a known volume of an internal standard to correct for any changes and drift in instrument response due to differing solution matrices. These internal standards are in-house
standards and generally contain Be, Sc, Ge, Rh, In, and Bi as reference elements, which are not expected to occur in the samples in measurable quantities. Standards were routinely measured along with samples to confirm analytical accuracy and precision, while regular analyses of sample duplicates provided an assessment of the analytical uncertainties within each session, with standard deviations typically between 1 and 2% (1SD) for the required elements. The total procedural blank (reagent blanks and those arising from leaching of the filters) was determined to be less than 1% of the lower sample concentrations of V, Mn and Cu, and around 2% of low pFe/pZn sample concentrations, and was thus considered negligible for data evaluation.

4.5.2 Fe isotope analysis of particulate Fe
The remaining volumes of each leachate were evaporated to dryness on a hot plate. The solid residue was subsequently re-dissolved in 10 ml 1% q-HNO₃ and transferred into centrifuge tubes in order to separate filter fragments. Appropriate amounts of sample were spiked with known amounts of a ⁵⁷Fe-⁵⁸Fe double spike and evaporated to dryness. For Fe purification, the resulting solids were re-dissolved in 6 M q-HCl + 0.001% H₂O₂ and loaded onto 500 µl of BioRad AG1-X4 resin, packed into custom made columns from heat shrinkable Teflon. Iron was eluted in 0.05 M q-HCl, followed by evaporation and conversion to nitric form for subsequent Fe isotope analysis by MC-ICPMS.

4.5.3 Analysis of dissolved δ⁵⁶Fe and quantification of dissolved Fe
Analysis of Fe isotopes in the dissolved fraction was carried out at UO. After a preconcentration step involving chelation of metals with a solid-phase ion-exchange resin (Nobias-chelate PA1) and elution with quartz distilled (q) 1 M HNO₃, Fe was purified by ion-exchange chromatography (BioRad AG1-X4) following newly established protocols (see chapter 2). This method quantitatively extracts a broad range of transition metals while significantly reducing matrix elements and is thoroughly described in chapter 2. Samples from CTD cast 30 were purified twice using AG1-X4 resin, as larger amounts of Zn, Mo and U as well as traces of Ni remained after a single purification cycle with the AG1-X4. The complete removal of Ni is particularly crucial, since its most abundant isotope ⁵⁸Ni interferes with ⁵⁸Fe. Procedural blanks were evaluated by processing representative volumes of Milli-Q H₂O in the same way as the samples, and
were always <5 ng Fe for 2 L sample sizes (corresponding to <2% of the natural Fe content of a typical sample).

Iron isotope analyses were carried out on a Nu Instruments Nu Plasma MC-ICPMS after sample introduction through a Nu Instruments DSN-100 fitted with a PFA 80 µl/min self-aspirating nebulizer. The $^{54}$Fe, $^{56}$Fe, $^{57}$Fe and $^{58}$Fe ion beams were measured simultaneously with Faraday collectors during three blocks of 20 cycles, and signal integration times of five seconds. Peaks were centered before each block. Baseline corrections were performed by measuring on-peak zeros in 2% q-HNO$_3$ for 60 sec before every sample.

Instrumental mass fractionation was corrected for using a $^{57}$Fe-$^{58}$Fe double spike in combination with a standard bracketing approach (against IRMM-14) before and after each sample. The double spike technique is well established and not repeated here; for detailed information on this method, the reader is referred to the literature (e.g. Galer (1999); Siebert et al. (2001); Rudge et al. (2009); John (2012) and Millet et al. (2012)) and chapter 2.

The double spike was weighed and added to each sample prior to extraction and therefore accounts for non-quantitative Fe recoveries and potential Fe isotope fractionation during chemical processing. It further allows for quantifying the dissolved Fe (dFe) concentration of each sample using the isotope dilution technique, independently of Fe yields. External precision for repeated measurements of IRMM-14 routinely yielded values of ±0.04‰ to ±0.12‰ (2SD).

**4.6 Results**

The widespread detection of correlated turbidity and redox anomalies at equal depths (between 1500 and 1800 m) across the area southeast of the vent field was interpreted to reflect a large, presumably continuous, non-buoyant hydrothermal plume. This plume was sampled at two different locations, station 30 in the center of the vent field and station 79 approximately 310 m southeast of station 30 following the direction of the predominating currents.
4.6.1 Plume characteristics
During CTD deployment, on-line sensors recorded strong turbidity anomalies between 1500 and 1800 m at station 30 and 1550 and 1750 m at station 79, respectively (figures 4.2a and 4.2b). Accordingly, these depths were chosen for sampling, as the presence of anomalies in turbidity and redox-potential indicate the location of a hydrothermal plume and no such anomalies were detected in the background cast. At station 30, sampling only covered the depth range from 1500 – 1700 m. During this cast, the ship was located directly above the eastern part of the vent field, where several high-temperature chimneys were actively venting hydrothermal fluids (see figure 4.1). In particular, vents NF1, NF4, NF5 and NF6 are clustered in close proximity to each other and CTD station 30. Consequently all of these chimneys are potential sources feeding into the plume detected at this station, but the large areas of diffuse venting are also likely to contribute hydrothermal material (dissolved and particulate). Station 79 was located south of the vent field, with an even stronger turbidity anomaly while the depth range of the plume is narrower. This may represent a more evolved stage of the plume at station 79 than station 30, with larger fractions of total Fe being precipitated, but also contributions from

Figure 4.2
Depth profiles of CTD casts at stations 30 (a) and 79 (b) indicating variations in turbidity [FTU] with depth [m], recorded during the ascent of the CTD. Increased turbidity is a key indicator for a hydrothermal plume. Accordingly a hydrothermal plume was detected at both stations between 1500 and 1800 meter depth.
additional sources are possible. Considering the prevailing currents, the plume sampled at station 79 could represent the combined plume of fluids from all corners of the vent field, even from the western area which hosted intense diffuse venting.

4.6.2 Fe concentrations in the non-buoyant plume
Concentrations of dFe and pFe were determined for samples from stations 30 (1500 m to 1700 m, 50 m sampling increments) and 79 (1500 m to 1625 m, mostly 25 m sampling increments), and are listed in table 4.1.

The background level of pFe was ~5 nM at 1700 m, while dFe was determined as 3 nM at this depth.

At both plume stations, pFe concentrations were at background levels above 1550 to 1500 m. Dissolved Fe concentrations however, were clearly increased above background in the two uppermost sampling depths (1500 and 1550 m) at station 30, while background levels were approached in the respective depths (1500 and 1550 m) at station 79 (dFe = 3.9 nM and 3.4 nM, respectively). These results correlate with observations from turbidity anomalies that suggest a more compact narrowed plume at station 79, and further support the suggestion of station 79 being a more evolved stage of the plume that had already been sampled at station 30.

Furthermore, the data nicely highlights how particulate concentrations increase in depths where the plume is localized, reaching maximum values of 10.92 nM and 18.04 nM at stations 30 and 79, respectively. This trend was expected, as the increased turbidity, used to localize the plume, is a direct result of the elevated particle density. Even the minor ‘spike’ in turbidity in 30-1550, that is not well resolved spatially (table 4.1, figures 4.2 and 4.3), can be identified as an increase in pFe concentration. Consequently, Fe concentrations show two maxima at station 30, either representing one bulky plume or two different plume layers.

Dissolved concentrations of Fe mimic those of pFe at station 30, indicating equal amounts of dissolved and particulate Fe that were more or less homogeneously distributed. However, while the particulate Fe concentration decreased above plume depths (>1500 m), dFe continued to be elevated above the plume, which may indicate incomplete particle formation at the upper end of the plume, or stabilization of the
dissolved species. Both features indicate an early stage of plume formation and may even suggest a buoyant character for the plume sampled at station 30.

Station 79 featured a very different pattern of dFe and pFe in that both reached maximum values only once in the profile, but at different depths. While particulate Fe peaked at ~1600 m, coinciding with maximum turbidity, the dissolved fraction reached its maximum at ~1575 m, paired with reduced pFe. At the most elevated particulate concentration (1600 m), dFe was decreased but increased again at 1625 m coinciding with a lowering in particulate Fe concentration. This pattern is to be expected, considering that dissolved Fe is believed to be transformed into a particulate phase as a result of progressing precipitation.

The total Fe (dFe+pFe) concentration in the entire sampled depth range is higher at station 79 (98 nM) than at station 30 (88 nM), with almost equal proportions of dFe and pFe at station 30, but a larger pFe portion at station 79. The particulate concentration of Fe is expected to increase with time due to progressive Fe precipitation. However, as total Fe increases as well, it seems likely that additional fluid components were incorporated into the plume between stations 30 and 79.

### Table 4.1 Iron concentrations and Fe isotopes measured in samples from the non-buoyant plume

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>dFe [nM]</th>
<th>δ$^{56}$Fe$^a$ [%]</th>
<th>2SE</th>
<th>pFe [nM]</th>
<th>TFe [nM]</th>
<th>δ$^{56}$Fe$^b$ [%]</th>
<th>2SE</th>
<th>Δ$^{56}$Fe$^c$ [%]</th>
<th>2SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>30-1500</td>
<td>8.58</td>
<td>-0.19</td>
<td>0.05</td>
<td>5.23</td>
<td>13.8</td>
<td>-0.30</td>
<td>0.04</td>
<td>0.11</td>
<td>0.06</td>
</tr>
<tr>
<td>30-1550</td>
<td>9.41</td>
<td>-0.73</td>
<td>0.05</td>
<td>9.38</td>
<td>18.8</td>
<td>-0.31</td>
<td>0.04</td>
<td>-0.42</td>
<td>0.06</td>
</tr>
<tr>
<td>30-1600</td>
<td>6.79</td>
<td>-0.32</td>
<td>0.05</td>
<td>6.88</td>
<td>13.7</td>
<td>-0.34</td>
<td>0.05</td>
<td>0.02</td>
<td>0.07</td>
</tr>
<tr>
<td>30-1650</td>
<td>9.76</td>
<td>-0.16</td>
<td>0.05</td>
<td>10.92</td>
<td>20.7</td>
<td>-0.23</td>
<td>0.05</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>30-1700</td>
<td>10.22</td>
<td>-0.28</td>
<td>0.05</td>
<td>10.55</td>
<td>20.8</td>
<td>-0.26</td>
<td>0.05</td>
<td>-0.02</td>
<td>0.07</td>
</tr>
<tr>
<td>79-1500</td>
<td>3.85</td>
<td>-0.18</td>
<td>0.06</td>
<td>5.31</td>
<td>9.2</td>
<td>-0.23</td>
<td>0.04</td>
<td>0.05</td>
<td>0.07</td>
</tr>
<tr>
<td>79-1550</td>
<td>3.44</td>
<td>-0.31</td>
<td>0.05</td>
<td>5.03</td>
<td>8.5</td>
<td>-0.27</td>
<td>0.04</td>
<td>-0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>79-1575</td>
<td>16.55</td>
<td>-0.52</td>
<td>0.05</td>
<td>11.73</td>
<td>28.3</td>
<td>-0.35</td>
<td>0.04</td>
<td>-0.17</td>
<td>0.06</td>
</tr>
<tr>
<td>79-1600</td>
<td>9.0</td>
<td>-0.32</td>
<td>0.05</td>
<td>18.04</td>
<td>27.0</td>
<td>-0.31</td>
<td>0.04</td>
<td>-0.01</td>
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</tr>
<tr>
<td>79-1625</td>
<td>10.22</td>
<td>-0.42</td>
<td>0.05</td>
<td>14.59</td>
<td>24.8</td>
<td>-0.36</td>
<td>0.04</td>
<td>-0.06</td>
<td>0.06</td>
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<tr>
<td>Background</td>
<td>~3</td>
<td>-</td>
<td>-</td>
<td>4.9</td>
<td>-</td>
<td>-0.25</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Fe isotopic composition of dissolved Fe and respective 2*standard error (2SE); $^b$ Fe isotopic composition of particulate Fe and respective 2SE [%]; $^c$ Δ$^{56}$Fe$_{Dissolved-Particulate}$ [%] and the respective 2SE [%] calculated by error propagation

Dissolved Fe (dFe) concentrations and isotopes were measured in filtered samples. Particulate Fe (pFe), and Fe isotopes were measured in the extracted filters corresponding to the respective filtered sample. Total Fe (TFe) was calculated from dFe+pFe.

Background dissolved concentrations were obtained by flow injection, as a contamination issue did not allow for determination of Fe isotopic composition and thus elemental concentration by isotope dilution.
4.6.3 Fe isotope composition of dFe and pFe

4.6.3.1 Fe isotopes in the buoyant plume

On three occasions (NF1, NF4 and NF6) the buoyant plume, dispersing directly above individual vent sites, was sampled with Niskin bottles and processed according to the method used for CTD samples (see section 3.1). Results from analyses of the dissolved phase have been presented in chapter 3 (section 3.5.5) in order to investigate the effects of seawater dilution on the $\delta^{56}$Fe of emanating vent fluids. Rayleigh fractionation models based on these measurements (such as shown in figure 3.10) have been utilized to predict evolutionary pathways of dissolved $\delta^{56}$Fe and associated particulate $\delta^{56}$Fe. The observed Fe isotope results from particulate analyses are presented in table 4.2, together with a summary of the results obtained for the corresponding dissolved phase.

According to table 4.2, particulate Fe isotopic compositions of 27-15, 27-16 and 66-05 are in agreement with the predicted range of $\approx -0.2$ to $0.47\%_\text{o}$ ($\Delta^{56}$Fe$_{\text{Dissolved-Particulate}}$), with higher particulate $\delta^{56}$Fe compared to dissolved values in samples from site NF1, while at site NF4, the forming particulate phase is $0.47\%_\text{o}$ more negative than the associated liquid. Further, it appears that 27-16 indicates a transition towards more kinetic Fe isotope fractionation as suggested in section 3.5.5, since dissolved $\delta^{56}$Fe becomes more positive, while

Table 4.2 Iron isotopes measured in samples from the buoyant plume

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Vent-Site</th>
<th>dFe$^d$ [nM]</th>
<th>$\delta^{56}$Fe$^d$ [%]</th>
<th>2SE [%]</th>
<th>pFe [nM]</th>
<th>TFe [nM]</th>
<th>$\delta^{56}$Fe$^e$ [%]</th>
<th>2SE [%]</th>
<th>$\Delta^{56}$Fe$^f$ [%]</th>
<th>2SE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>27-15$^a$</td>
<td>NF1</td>
<td>2860</td>
<td>-0.66</td>
<td>0.05</td>
<td>499</td>
<td>3753</td>
<td>-0.46</td>
<td>0.04</td>
<td>-0.20</td>
<td>0.06</td>
</tr>
<tr>
<td>27-16$^a$</td>
<td>NF1</td>
<td>2070</td>
<td>-0.64</td>
<td>0.05</td>
<td>893</td>
<td>2569</td>
<td>-0.54</td>
<td>0.04</td>
<td>-0.10</td>
<td>0.06</td>
</tr>
<tr>
<td>60-02$^b$</td>
<td>NF2</td>
<td>853</td>
<td>-0.29</td>
<td>0.05</td>
<td>976</td>
<td>1829</td>
<td>0.14</td>
<td>0.04</td>
<td>-0.43</td>
<td>0.06</td>
</tr>
<tr>
<td>66-05$^a$</td>
<td>NF4</td>
<td>1610</td>
<td>-0.37</td>
<td>0.06</td>
<td>95686</td>
<td>97296</td>
<td>-0.84</td>
<td>0.04</td>
<td>0.47</td>
<td>0.07</td>
</tr>
<tr>
<td>27-11$^c$</td>
<td>NF8</td>
<td>270</td>
<td>-0.61</td>
<td>0.04</td>
<td>1321</td>
<td>1591</td>
<td>-0.22</td>
<td>0.04</td>
<td>-0.39</td>
<td>0.06</td>
</tr>
</tbody>
</table>

$^a$ Black smoker; $^b$ Clear fluid; $^c$ Diffuse venting;
$^d$ Concentration and Fe isotopic composition of dissolved Fe as presented in chapter 3
$^e$ Fe isotopic composition of particulate Fe and 2*standard error (2SE) in [%]
$^f$ $\Delta^{56}$Fe$_{\text{Dissolved-Particulate}}$ [%] and the respective 2SE [%] calculated by error propagation

Dissolved Fe (dFe) concentrations and isotopes were measured in filtered samples and are presented in chapter 3. Particulate Fe (pFe), and Fe isotopes were measured in the extracted filters corresponding to the respective filtered sample. Total Fe (TFe) was calculated from dFe+pFe
particulate \( \delta^{56}\text{Fe} \) decreases toward significantly more negative values. On the contrary, the measured \( \delta^{56}\text{Fe} \) of particulates from 60-02 deviates significantly from the predicted range of compositions (\( \Delta^{56}\text{Fe}_{\text{Dissolved-Particulate}} \approx 0.25\% \), see section 3.5.5, chapter 3) and gives rise to the only positive \( \delta^{56}\text{Fe} \) value obtained from any of the particulates analyzed in this study. In addition to the opposing direction, the apparent \( \Delta^{56}\text{Fe}_{\text{Dissolved-Particulate}} \) (\( \approx -0.43\% \)) is also significantly larger in magnitude than the predicted value (\( \Delta^{56}\text{Fe}_{\text{Dissolved-Particulate}} \approx 0.25\% \)). Also, despite the clear venting, the pFe concentration is particularly high in 60-02. A comparably large \( \Delta^{56}\text{Fe}_{\text{Dissolved-Particulate}} \) was obtained from sample 27-11 (\( \approx -0.39\% \)), which was collected above the diffuse venting site NF8. Alike 60-02, this clear diffusely venting fluid displays significantly increased pFe concentrations, suggesting that similar mechanisms may control Fe concentrations and Fe isotope fractionation in the water column above sites NF2 and NF8.

4.6.3.2 Fe isotopes in the non-buoyant plume

Iron isotope data of particulate and dissolved Fe from both CTD stations (30 and 79) are plotted in figure 4.3. Iron concentration data are displayed as well to help inform the interpretation of the data.

As discussed in the previous section, the depth profile of station 30 (figure 4.3a) is characterized by two obvious Fe maxima coinciding with turbidity anomalies between 1500 m and 1700 m. At the uppermost plume depth of 1500 m, pFe, which was roughly at background concentrations, expressed a \( \delta^{56}\text{Fe} \) of \(-0.3\% \pm 0.04\% \). The background isotopic composition of pFe yielded a mean \( \delta^{56}\text{Fe} \) value of \(-0.25\% \pm 0.04\% \) and suggests that particulate Fe in 30-1500 was, to a lesser degree, influenced by hydrothermal activity, while the dissolved fraction, significantly enriched in Fe relative to background levels, had a \( \delta^{56}\text{Fe} \) of \(-0.19\% \). Considering the strong hydrothermal activity detected in the vicinity of station 30, and the generally negative \( \delta^{56}\text{Fe} \) of the hydrothermally discharged dissolved Fe, this suggests that hydrothermal influence persists even up to 1500 m depth.

For the whole depth profile, particulate \( \delta^{56}\text{Fe} \) covaried with pFe concentration, while the dissolved \( \delta^{56}\text{Fe} \) deviated from the pattern of the corresponding dFe concentration data, showing a significant excursion of \(-0.73\% \) at 1550 m. Consequently, the two Fe maxima with their correlated concentration trends of dFe and pFe, displayed very different
isotopic compositions of dissolved Fe. While the upper maximum coincided with very light $\delta^{56}\text{Fe} (-0.73\%)$, which was as negative as the most negative fluid end-member ($\delta^{56}\text{Fe} = -0.74\%)$, the deeper situated concentration maximum was the isotopically heaviest sample at the whole station ($\delta^{56}\text{Fe}= -0.16\%)$. Furthermore, differences in the pattern of dissolved and particulate $\delta^{56}\text{Fe}$, expressed as changing $\Delta^{56}\text{Fe}_{\text{Dissolved-Particulate}}$, which varied as well between the two Fe maxima, supporting the suggestion of two individual plume layers. While $\Delta^{56}\text{Fe}_{\text{Dissolved-Particulate}}$ is $0.11\%$ and $0.07\%$ in 30-1500 and 30-1650 respectively, a dramatic change in $\Delta^{56}\text{Fe}_{\text{Dissolved-Particulate}}$ to $-0.42\%$ is observed in 30-1550, resembling those $\Delta^{56}\text{Fe}_{\text{Dissolved-Particulate}}$ observed at sites 60-01 and 27-11 ($-0.43\%$ and $-0.39\%$ respectively; table 4.1). In between these two Fe maxima displaying opposing Fe isotope systematics, at 1600 m, dissolved and particulate $\delta^{56}\text{Fe}$ are identical within analytical uncertainty, which also applies to samples taken at 1700 m ($\Delta^{56}\text{Fe}_{\text{Dissolved-Particulate}}$ of $0.02\%$ and $-0.02\%$ respectively).

Other than station 30, CTD station 79 was characterized by only one large turbidity anomaly (within the sampled range), limited to a smaller depth range (1550 m to 1625 m). Thereby, dissolved and particulate Fe reached their maximum values separately and with much higher magnitudes compared to the Fe maxima observed at station 30. Although concentrations of dFe and pFe in the uppermost depths (1500 m & 1550 m) were found to be at background levels, measured $\delta^{56}\text{Fe}$ suggest a hydrothermal influence at these depths. Dissolved $\delta^{56}\text{Fe}$ at 1500 m depth (-0.18%) was similar to the value at the corresponding depth at station 30 (-0.19%), but not resolvable from particulate $\delta^{56}\text{Fe}$ within analytical uncertainty (as opposed to a $\Delta^{56}\text{Fe}_{\text{Dissolved-Particulate}}$ of $0.11\%$ at station 30). While not different in Fe concentration, dissolved and particulate $\delta^{56}\text{Fe}$ in 79-1550 differ by $-0.12\%$ (dFe) and $-0.04\%$ (pFe) from the corresponding values at 1500 m. The following significant increase in dFe in 79-1575 resulted in dissolved $\delta^{56}\text{Fe}$ further shifting towards lighter isotopic compositions, reaching a minimum of $-0.52\%$ yielding a relatively large $\Delta^{56}\text{Fe}_{\text{Dissolved-Particulate}}$ of $-0.17\%$. On the contrary, no resolvable difference (within analytical uncertainty) between dissolved and particulate $\delta^{56}\text{Fe}$ was detected at depth of maximum particulate Fe concentration (1600 m), almost resembling the Fe isotope pattern observed at 1550 m.
4.6.4 Particulate composition

Particulate material extracted from filters was investigated for its contents of Fe, V, Cu and Zn, as well as REE and Y (REY). Particulate P was analyzed as well, however the used filter membranes displayed significant P blanks, and since they were digested to various degrees, it was not possible to reasonably correct for blank P contributions.

4.6.4.1 Major element composition of buoyant plume particulates

Particulate concentrations of Mn (pMn), V (pV), Cu (pCu) and Zn (pZn) varied significantly between particles collected above the selected vent sites. The particulate
ratio of V and Fe \((pV/Fe)\) gives indications for the presence of Fe-oxyhydroxides \((\text{FeOOH})\), because the vanadate ion \((\text{VO}_4^2-)\) preferentially adsorbs onto \text{FeOOH} surfaces ((Feely et al., 1998) this is discussed in more detail in section 4.7.2). The chalcophile elements Cu and Zn on the other side are preferentially incorporated into Fe-sulfides upon their formation, although adsorption onto \text{FeOOH} surfaces is possible as well.

Vanadium ranged from 0.2 to 4.1 nM with \(pV/Fe\) ratios of 0.00004 (66-05) to 0.002 (27-11, 60-02), and the higher values within this range are comparable to those reported for the Pacific hydrothermal vent fields (Feely et al., 1998). The markedly low \(pV/Fe\) ratio of particulates from 66-05 is consistent with field observations at the vent site (NF4). Formation of a dense black smoker particle plume indicated intense precipitation of Fe-sulfides. The highest \(pV/Fe\) ratio on the contrary indicates only limited formation of Fe-sulfides upon venting, and is consistent with the observation of a clear venting fluid at site NF2. Fluids from this venting site (see chapter 3 for details) exhibited very low Fe and Zn concentrations and did not contain any Cu. However, Cu was detected in particulates from 60-02, and may indicate scavenging of Cu from nearby sources. Scavenging generally suggests a high proportion of \text{FeOOH}, which is in agreement with the high \(pV/Fe\) and \(pFe\) despite no visible turbidity. A similar concentration of Cu was detected in the particulate phase corresponding to diffuse sample 27-11, whose \(pV/Fe\) ratio is equally high (0.0023) and thus suggests a high proportion of \text{FeOOH} amongst its particles (Feely et al., 1998). Interestingly, this sample displays the second highest \(pFe\) concentration recorded in this study, although only visible as clear shimmering water. This could indicate very small particle sizes that just partition into the particulate fraction, and a \(pFe\) speciation which does not cause any turbidity \text{Fe-oxyhydroxides}, nanoparticulate pyrite.

The chalcophile elements, Cu and Zn, display a significant spread, with \(pCu\) concentrations ranging between 5.3 and 1340.6 nM and \(pZn\) concentrations ranging from 49.5 to 11568.3 nM. Particulate Zn/Fe ratios ranged from 0.04 to 0.39, while most of the respective source fluids ranged from 0.01 to 0.06 (although a significantly higher ratio of 0.25 was documented for fluids at site 60-01), suggesting preferential precipitation of Zn as polymetallic sulfides relative to Fe. This is consistent with the observation of complete Zn removal in filtered fluid samples (see chapter 3). Similarly,
comparison of $p_{Cu}/Fe$ ratios suggests preferential incorporation of Cu into sulfides relative to Fe, with $p_{Cu}/Fe$ ranging from 0.004 to 0.09 in the buoyant plume, while $Cu/Fe$ ratios between 0.001 and 0.006 were measured in the end-member fluids.

4.6.4.2 Major element composition of non-buoyant plume particulates

Similarly to buoyant plume samples (previous section), particulates extracted from non-buoyant plume samples were analyzed for particulate Fe, V, Cu, Zn and REY (tables 4.3 and 4.4). Concentrations of $p_V$, $p_{Cu}$ and $p_{Zn}$ relative to $p_{Fe}$ are plotted in figures 4.4 (30CTD) and 4.5 (79CTD).

As is obvious from figure 4.4, samples from CTD station 30 display a positive linear correlation between $p_{Fe}$ and the vanadium oxyanion, with an $r^2$ of 0.973 and a positive $y$ intercept. Data from 1550 m displays a significant deviation of the $p_V$ content from the overall trend and was therefore excluded from data regression. Particulate vanadium concentrations ranged from 0.014 nM to 0.039 nM, with the maximum value being observed at 1550 m. Ratios of $p_V/Fe$ are between 0.002 and 0.004, with the highest ratio again restricted to the 1550 m sample. The chalcophile elements Zn and Cu also correlate positively with $p_{Fe}$, with $r^2$ values equal to 0.969 and 0.948 respectively. Similarly to $p_V$, $p_{Cu}$ was significantly enriched relative to $p_{Fe}$ at 1550 m when compared to the overall trend. Although typically ranging from 0.2 nM to 1.07 nM, a sudden increase to 2.5 nM is observed at 1550 m, coupled with an increase in $p_{Cu}/Fe$ ratio to 0.27 (which was otherwise between 0.04 and 0.1). The relatively high Cu contents in the lowest two samples (1650 and 1700 m) may indicate that portions of a buoyant plume have been sampled at station 30, although this is not reflected by the Zn concentrations. Zinc ranged from 0.3 to 0.48 nM with ratios of $Zn/Fe$ between 0.037 and 0.063. An unrealistically high $p_{Zn}$ concentration was determined in sample 30-1550. This datum was excluded as it suggests contamination of the sample. The sudden increase of $p_{Cu}$ in the same sample (30-1550) however, is not attributed to contamination. All Niskin bottles had the formerly inner springs removed and replaced by rubber, and were afterwards soaked in diluted acid prior to CTD deployment. Furthermore, they were thoroughly rinsed in between each deployment. Since $p_{Fe}$ is not anomalously elevated in 30-1550, but only $p_V$, $p_{Cu}$ and $p_{Zn}$, contamination during sampling seems unlikely. During sample processing on the contrary, contamination with Zn is much more likely.
than with Cu or V. Thus the increased concentrations of pV and pCu and the resulting pV/Fe and pCu/Fe are considered to be real in sample 30-1550, while the particulate Zn concentration is considered to be altered due to contamination during sample processing. However, it appears likely that pZn and pZn/Fe also increased in 30-1550 in a natural way (compared to the other depths) just as pV and pCu.

When compared to the sampled vent fluids, both ratios, pZn/Fe and pCu/Fe are distinctly higher, suggesting preferential precipitation of Zn and Cu relative to Fe.

The significantly higher pV and pCu contents and ratios of pV/Fe and pCu/Fe at 1550 m are additional indicators for at least two individual plume layers with distinctly different characteristics in the station 30 profile. The high pV content suggests a high proportion of FeOOH particles (VO₄H₂⁻ is efficiently scavenged onto FeOOH; see also section 4.7.2

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<td>0.014</td>
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</table>

ᵃ Black smoker; ᵇ Clear fluid; ᶜ Diffuse venting

* Estimated ratio of hydrothermal and lithogenic input, calculated as Fe/(Fe+Mn+Al)

Particulate Mn (pMn), Fe (pFe), V (pV), Cu (pCu), and Zn (pZn) were measured in the extracted filters corresponding to the respective filtered sample.
of the discussion), which may also scavenge Cu from solution. In general however, station 30 seems to be rather dominated by Fe-sulfide species, which rather incorporate chalcophile elements such as Cu and Zn. The slopes of pZn vs. pFe and pCu vs. pFe are significantly steeper than pV vs. pFe suggesting a stronger enrichment of pZn and pCu are with increasing pFe and thus a higher proportion of Fe-sulfides (with incorporated Zn and Cu).

Figure 4.4
Relationships between particulate V, Zn and Cu relative to particulate Fe (pFe) in plume samples from CTD station 30 ranging from 1500 to 1700 m depth. Anomalous values for V and Cu at 1550 m suggest interception of a separate plume layer with the otherwise coherent plume. Linear regression therefore excludes sample 30-1550. Data for pZn in the respective sample was excluded because anomalously high values suggested contamination.
At CTD station 79, the oxyanion V is again positively correlated to pFe, with an $r^2$ of 0.993 and a positive $y$ intercept. Particulate V concentrations were between 0.021 nM and 0.063 nM, while pV/Fe ratios ranged from 0.0034 to 0.0046, significantly higher than at the previous CTD station (30). Similarly, the chalcophile elements Zn and Cu correlate positively with pFe, with pZn concentrations ranging from 0.18 nM to 0.60 nM and pCu contents of between 0.07 nM and 0.24 nM. The pZn content within the sampled depth range is thereby higher when compared to station 30, whereas pCu is lower. Ratios of pZn and pFe range between 0.031 and 0.037 (lower than at station 30) with one particularly low exception (0.021). This belongs to sample 79-1575 (1575 m), which is characterized by pZn and pCu values deviating from the main trend. While pZn/Fe is lower in this particular sample, pCu/Fe is increased above the main trend with a value of 0.018 compared to 0.011-0.013 otherwise.

Besides sample 79-1575, elevated pCu concentration and pCu/Fe are observed in sample 79-1550 as well, reaching pCu/Fe of 0.026. With these two anomalies, the pCu versus pFe trend resembles a negatively curved relationship, as has been previously observed for chalcophile elements in neutrally buoyant plumes (Edmonds and German, 2004) and is interpreted to reflect preferential removal of particulate chalcophile elements from the plume by settling and/or oxidative dissolution. Thereby pZn is lost sooner than pCu from a plume (Edmonds and German, 2004) explaining the opposing deviation of pZn and pCu from their respective main trends at 1575 m, with elevated pCu and decreased pZn. While pCu is elevated in sample 79-1550 as well, no pronounced anomaly in pZn is visible. However, these different behaviors may indicate the presence of two individual plume layers in the station 79 depth profile as well, potentially corresponding to the maxima of dissolved Fe (1575 m) and pFe (1600 m), respectively. The presence of two individual and chemically distinct plume layers would also explain the high variability in dissolved and particulate $\delta^{56}$Fe observed at station 79 (figure 4.3b).
4.6.4.3 Rare earth elements and yttrium (REY) composition of buoyant and non-buoyant plume particulates

Rare earth elements (REE) and yttrium concentration profiles, collectively referred to as REY, are good examples of so called “particle-reactive” tracers that exhibit generally positive correlations with particulate iron concentrations in hydrothermal plumes. Thereby pREE/Fe ratios are higher at increasing distances from the vent site due to continuous scavenging as the particles disperse (German et al., 1991; German et al., 1990; Sherrell et al., 1999).

The uptake fluxes of these elements associated with hydrothermal Fe-oxyhydroxide particles thereby exceed the dissolved REY freight of hydrothermal fluids by far. Consequently, hydrothermal plumes must act as ‘sinks’ rather than ‘sources’ for these
elements, sometimes even causing local depletion relative to ambient water column concentrations (e.g. Klinkhammer et al. (1983)). Results for rare earth elements and yttrium (REY) from extracted particle filters are presented in table 4.4.

Table 4.4 Particulate rare earth element concentrations and Eu anomalies in Nifonea plume samples

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</tr>
<tr>
<td>79-1500</td>
<td>1.79</td>
<td>0.58</td>
<td>0.56</td>
<td>0.10</td>
<td>0.35</td>
<td>0.10</td>
<td>0.03</td>
<td>0.13</td>
<td>0.13</td>
<td>0.03</td>
<td>0.07</td>
<td>0.05</td>
<td>0.89</td>
</tr>
<tr>
<td>79-1550</td>
<td>1.61</td>
<td>0.61</td>
<td>0.53</td>
<td>0.09</td>
<td>0.31</td>
<td>0.12</td>
<td>0.04</td>
<td>0.14</td>
<td>0.11</td>
<td>0.03</td>
<td>0.06</td>
<td>0.06</td>
<td>0.97</td>
</tr>
<tr>
<td>79-1575</td>
<td>2.32</td>
<td>0.71</td>
<td>0.50</td>
<td>0.13</td>
<td>0.54</td>
<td>0.09</td>
<td>0.05</td>
<td>0.12</td>
<td>0.13</td>
<td>0.03</td>
<td>0.08</td>
<td>0.09</td>
<td>1.57</td>
</tr>
<tr>
<td>79-1600</td>
<td>3.37</td>
<td>0.95</td>
<td>0.62</td>
<td>0.16</td>
<td>0.63</td>
<td>0.12</td>
<td>0.07</td>
<td>0.17</td>
<td>0.17</td>
<td>0.04</td>
<td>0.09</td>
<td>0.10</td>
<td>1.47</td>
</tr>
<tr>
<td>79-1625</td>
<td>2.62</td>
<td>0.79</td>
<td>0.48</td>
<td>0.13</td>
<td>0.58</td>
<td>0.08</td>
<td>0.04</td>
<td>0.17</td>
<td>0.15</td>
<td>0.05</td>
<td>0.17</td>
<td>0.09</td>
<td>1.01</td>
</tr>
<tr>
<td>Background</td>
<td>2.16</td>
<td>0.68</td>
<td>0.65</td>
<td>0.13</td>
<td>0.43</td>
<td>0.12</td>
<td>0.05</td>
<td>0.19</td>
<td>0.16</td>
<td>0.04</td>
<td>0.10</td>
<td>0.07</td>
<td>0.89</td>
</tr>
</tbody>
</table>

a Eu/Eu* was calculated as 2*(Eu/Eu_C1 Chondrite)/(Sm/Sm_C1 Chondrite) + (Gd/Gd_C1 Chondrite)

Reference values for normalization against C1 chondrite are from Anders and Grevesse (1989)

Distribution patterns of the pREY result from contributions of both seawater and hydrothermally sourced dREYs to the plume particles, with their respective characteristics. Particles formed in the early stages of the plume usually reflect the REY composition of the vent fluid, typically displaying a strong enrichment of light REEs (LREE; La to Eu) over heavy REEs (HREE; Dy to Lu) and a relatively large positive Eu-anomaly (Eu/Eu*) (Douville et al., 2002; Dubinin, 2004; Edmonds and German, 2004;
German et al., 1990; Mitra et al., 1994; Rudnicki and Elderfield, 1993). With progressive plume dilution, the REY particle composition is expected to change and more closely reflect seawater REY patterns. As seawater has no Eu-anomaly, Eu/Eu* decreases towards unity and thus may be considered as a general measure of seawater dilution and hence Fe oxidation with progressive plume dilution (Elderfield et al., 1988; Rudnicki and Elderfield, 1993).

The collected data suggests generally increasing pSm/Fe ratios, a proxy for overall REE/Fe (Sherrell et al., 1999), with decreasing particulate Fe. The lowest and highest ratios were determined for samples 30-1700 and 79-1500/79-1550, respectively, which is consistent with observations of the highest REE/Fe at the most distant location from the vent site (see above) and supports the model of a continuous plume stretching from station 30 to station 79. However, relatively high pSm/Fe were obtained for separately sampled buoyant plume samples 27-11, 27-15, 27-16 and 60-02 despite high pFe. In previous studies from hydrothermal plumes in the Atlantic and Pacific, yttrium and the REEs were shown to exhibit slightly curved relationships with particulate iron (Edmonds and German, 2004; German et al., 1991; German et al., 1990; Mitra et al., 1994; Sherrell et al., 1999). German et al. (1990) were the first to report this behavior, which they attributed to continuous uptake of REEs from seawater. After an initial co-precipitation of both vent- and seawater-derived REEs with newly formed particles, these Fe-oxyhydroxides are undersaturated with respect to surface adsorption leading to scavenging of dissolved, particle-reactive species as the plume disperses through the water column (Edmonds and German, 2004; German and Von Damm, 2006). As particles continue to scavenge REEs while the plume becomes progressively more diluted, pREE/Fe ratios become higher in non-buoyant (far-field) plume particles (and consequently at low pFe) than in near-field (buoyant plume) samples; dissolved REE concentrations within the plume are thereby drawn below those of ambient seawater (Edmonds and German, 2004; Mitra et al., 1994).

Plume particles from Nifonea display similar behavior (figure 4.6), but seem to follow steeper slopes (pY vs. pFe and pEr vs. pFe), such as those observed in the plume at 9°45’N EPR (yellow crosses in pEr vs. pFe, figure 6; Sherrel et al. (1999)). In particular, Y and Er data suggest higher REY/Fe ratios at low pFe consistent with data from the EPR (although no Y data are available for 9°45’N EPR). Younger particles, potentially
representing more buoyant behavior, were shown to fall below these curves because hydrothermal precipitates are assumed to continue to adsorb REEs from seawater as they disperse in the plume and age (Edmonds and German, 2004; German et al., 1990). Plume particles from station 30 plot below the curve, as is evident from the datasets of pY, pNd and pEr as well as pEr and pFe for 79-1575 and 79-1600. The close proximity of station 30 to the central vent field already suggests that the sampled plume is rather young. However, considering the relationships of pREYs and pFe, these samples further appear to still represent a buoyant stage of plume formation, which is also reflected in the rather high Eu-anomalies. The buoyant plume samples 27-15, 27-16 and 66-05, although not shown in figure 4.6, also plot beneath the curve in accordance with expected behavior, while 27-11 and 60-02 plot above the curve for unknown reasons. Because 79-1575 and 79-1600 deviate from the trend indicated by the EPR data, while 79-1500, 79-1550 and 79-1625 follow this trend, these two samples must be younger relative to plume particles sampled above and below. Again, this is accompanied by higher Eu-anomalies in these depths.

Figure 4.6
Particulate Y, Nd and Er [pM] concentrations in plume particles from stations 30 (red squares) and 79 (green triangles) against particulate Fe [nM]. Nd and Er were chosen as representative light and heavy REE, respectively. For comparison literature data from the TAG plume (blue diamonds, (German et al., 1990)) and 9°45’N EPR (yellow crosses, (Sherrell et al., 1999)) is shown as well where available.
4.7 Discussion

4.7.1 Source of plume particles

Vent environments are generally very dynamic and turbulent settings. Therefore, it is crucial to carefully determine whether particulate samples have been affected by entrained re-suspended sediments. This is particularly important for samples that were collected close to the seabed. German et al. (1991) have used a classification tool developed previously by Bostrom et al. (1969) to distinguish between hydrothermal and lithogenic components. While Al, Mn and Fe are all enriched in sediments, Al only occurs as a trace element in hydrothermal fluids, whereas Mn, although enriched, is present as a reduced dissolved species and only slowly precipitated, in sharp contrast to Fe (Trocine and Trefry, 1988). Accordingly, with low particulate Mn and Al values, hydrothermal particulate material should yield high values of the ratio Fe/(Fe+Mn+Al). The buoyant plume samples collected immediately above the vent sites, have Fe/(Fe+Mn+Al) values that range from 0.4 (60-02) to 1.0 (66-05, table 4.3). The black smoker derived plume samples from vent 27-14 have Fe/(Fe+Mn+Al) values of 0.8 indicating a high proportion of hydrothermal material (80%), while the diffuse sample is at 0.5. Consequently significant detrital input cannot be ruled out for samples 60-02 and 27-11, with unforeseen consequences for particulate δ⁵⁶Fe. However, sediment cover was observed to be virtually absent as the seafloor at Nifonea vent field comprised mainly of fresh, young basalts. Moreover, unusually high Al contents were observed in fluids venting from site 60 (Schmidt et al., in prep), but it remains unconstrained how this could affect the composition of plume particles. Diffuse sample 27-11 was demonstrated to have common properties with 60-02 such as particulate V and chalcophile contents, Fe/H₂S ratio and Δ⁵⁶FeDissolved-Particulate and may feature elevated dissolved Al contents as well.

Amongst CTD samples, Fe/(Fe+Mn+Al) ratios range from 0.6 to 0.8 (table 4.3), whereby the deepest samples generally express higher values (0.7 and 0.8 at stations 30 and 79 respectively) than the shallower ones (0.6 at 1500 m), only intercepted by sample 30-1550 with a value of 0.8 (the highest value amongst 30CTD samples). The uppermost samples are consistent with the background ratio (0.6). All samples with values of at least 0.7 are assumed to be predominantly hydrothermal precipitates. Despite their
lower values, 60-02 and 27-11 particulates are regarded as hydrothermal precipitates as well considering the negligible sediment cover. However, caution is advised for interpretation of their particulate $\delta^{56}$Fe.

4.7.2 Particle formation

As presented in section 4.6.4.2, particulate Fe is positively correlated with oxyanions such as vanadium and chalcophile elements like Cu and Zn (figures 4.4 and 4.5). These relationships result from precipitation of Fe-sulfides and Fe-oxyhydroxides as the buoyant plume evolves and has been observed in several other vent systems, such as TAG, Rainbow and 5°S (Bennett et al., 2009; Edmonds and German, 2004; German et al., 1991). Formation of Fe-oxyhydroxides is accompanied by scavenging of oxyanions (such as VO$_4$$^2-$), with constant molar ratios of pV/Fe dependent only on the local dissolved phosphate concentration (Feely et al., 1998; Trefry and Metz, 1989). Chalcophile elements such as Cu and Zn, on the contrary, are incorporated into Fe-sulfides in hydrothermal plumes although they may also adsorb onto Fe- and/or Mn-oxyhydroxides when H$_2$S concentrations are insufficient (Bennett et al., 2009). The linear relationship between pCu and/or pZn and pFe at station 30, which shows characteristics of a buoyant plume, suggests no preferential loss of Fe-sulfides from the plume.

Quantitative determination of the relative amounts of Fe-oxyhydroxides and Fe-sulfides is possible by utilization of the particulate V/Fe ratios. Feely et al. (1998) have demonstrated that V/Fe ratios in hydrothermal particles across the ocean basins are inversely correlated with dissolved phosphate. Although the dissolved V concentration in the deep ocean is uniformly constant at about 35-37 nmol/kg (Collier, 1984; Jeandel et al., 1987), vanadate competes with the phosphate oxyanion for available sites during scavenging onto Fe-oxyhydroxides, whereby phosphate prevails. Consequently, concentrations of V in hydrothermal particles are higher in areas where seawater dissolved phosphate is reduced than in areas with high dissolved phosphate (Feely et al., 1994; Feely et al., 1998; Trefry and Metz, 1989). Although the V/Fe ratio of plume particles was initially considered invariant once Fe-oxyhydroxides had formed in the buoyant or non-buoyant plume and scavenged the vanadate oxyanion, Edmonds and German (2004) raised concerns about the validity of this assumption as they observed
increasing $p_{V/Fe}$ ratios with progressing plume evolution. At a more evolved stage, the proportion of Fe-sulfide to Fe-oxyanion particles will shift towards the latter, creating more available sites for adsorption of $VO_4^{2-}$.

Dissolved phosphate at the background station was determined as 1.48 µmol/L, which compares well to vent fields in the south Atlantic (1.6 µmol/L at 5°S; Bennett et al. (2009)), but is lower than measurements from the South Pacific (the southern EPR 13°S-19°S gives a value of 2.5 µmol/L; Feely et al. (1996)). Utilizing the inverse relationship established by Feely et al. (1998), an average $p_{V/Fe}$ ratio of 0.0042 is estimated for Fe-oxyhydroxide particles according to the measured phosphate concentration. Equation (4.1) allows for calculating the fraction of FeOOH (hereafter $X'_{FeOOH}$) present in the collected plume particles based on the $p_{V/Fe}$ ratio.

$$X'_{FeOOH} = \frac{(V/Fe)_{measured}}{(V/Fe)_{expected}}$$  \hspace{1cm} (Equation 4.1)

The fraction of coexisting Fe-sulfide ($X'_{FeS}$) is hereafter calculated as:

$$X'_{FeS} = 1 - X'_{FeOOH}$$  \hspace{1cm} (Equation 4.2)

Results (as shown in table 4.5) indicate generally decreasing $X'_{FeS}$ with increasing pFe, which is consistent with a larger proportion of Fe-sulfides forming during the early stages of plume rise. Particles formed immediately above the black smoker chimneys (27-15/16, 66-05) are characterized by high fractions of Fe-sulfides ($X'_{FeS}$), which is consistent with high pCu and pZn and the respective relation to pFe (high pCu/Fe and pZn/Fe, see section 4.6.4.1). Consistent with their high $p_{V/Fe}$ ratios, high pFe and yet clear venting (see 4.6.4.1), particles from site 60-02 and the diffusely venting site 27-11 display high proportions of Fe-oxyhydroxides (table 4.5). Fine-grained FeOOH cause less turbidity compared to Fe-sulfides and explain the clear fluids and yet high pFe. Iron present as Fe-sulfides ($X'_{FeS} = 0.46$ and 0.5 in 27-11 and 60-02 respectively) is suggested to represent nanoparticulate FeS or FeS$_2$ (that just partitions into the particulate fraction) since it does not appear to cause any turbidity.

Plume casts also indicate generally decreasing $X'_{FeS}$ with increasing pFe. Moreover, $X'_{FeS}$ is generally lower in the depth profile from station 79, even at lower pFe, indicating progressive oxidation of the plume.
Table 4.5 Calculated fractions of Fe-oxyhydroxides (FeOOH) and Fe-sulfides (FeS) in plume samples

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Depth [m]</th>
<th>In particulate fraction</th>
<th></th>
<th></th>
<th>Relative to total Fe</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>27-11</td>
<td>1863</td>
<td>0.54</td>
<td>0.46</td>
<td>0.45</td>
<td>0.38</td>
<td>0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27-15</td>
<td>1861</td>
<td>0.22</td>
<td>0.78</td>
<td>0.05</td>
<td>0.19</td>
<td>0.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27-16</td>
<td>1860</td>
<td>0.22</td>
<td>0.78</td>
<td>0.04</td>
<td>0.15</td>
<td>0.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60-02</td>
<td>1873</td>
<td>0.50</td>
<td>0.50</td>
<td>0.27</td>
<td>0.26</td>
<td>0.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>66-05</td>
<td>1862</td>
<td>0.01</td>
<td>0.99</td>
<td>0.01</td>
<td>0.97</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30-1500</td>
<td>1500</td>
<td>0.64</td>
<td>0.36</td>
<td>0.24</td>
<td>0.14</td>
<td>0.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30-1550</td>
<td>1550</td>
<td>1.00</td>
<td>0.00</td>
<td>0.50</td>
<td>0.00</td>
<td>0.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30-1600</td>
<td>1600</td>
<td>0.59</td>
<td>0.41</td>
<td>0.30</td>
<td>0.20</td>
<td>0.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30-1650</td>
<td>1650</td>
<td>0.46</td>
<td>0.54</td>
<td>0.24</td>
<td>0.28</td>
<td>0.47</td>
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<td></td>
</tr>
<tr>
<td>30-1700</td>
<td>1700</td>
<td>0.44</td>
<td>0.56</td>
<td>0.22</td>
<td>0.29</td>
<td>0.49</td>
<td></td>
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</tr>
<tr>
<td>79-1500</td>
<td>1500</td>
<td>0.95</td>
<td>0.05</td>
<td>0.55</td>
<td>0.03</td>
<td>0.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>79-1550</td>
<td>1550</td>
<td>1.00</td>
<td>0.00</td>
<td>0.59</td>
<td>0.00</td>
<td>0.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>79-1575</td>
<td>1575</td>
<td>0.89</td>
<td>0.11</td>
<td>0.37</td>
<td>0.05</td>
<td>0.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td>79-1600</td>
<td>1600</td>
<td>0.83</td>
<td>0.17</td>
<td>0.55</td>
<td>0.11</td>
<td>0.33</td>
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<tr>
<td>79-1625</td>
<td>1625</td>
<td>0.81</td>
<td>0.19</td>
<td>0.48</td>
<td>0.11</td>
<td>0.41</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Considering the relationship of pZn and/or pCu to pFe, shown in figures 4.4 and 4.5, with y intercepts ≥ 0 for Zn and ≤ for Cu, the sulfide fraction appears to have equal proportions of Zn and Fe, but relatively less Cu at low pFe at station 30, while Cu- and Zn-bearing sulfides make up a higher proportion at station 79. The immediately forming focused particle plumes above vent sites are dominated by Fe-sulfides with $X^V_{FeS}$ of at least 80% for designated black smokers and ~50% at clear venting sites. Higher pCu/Fe ratios, and accordingly a larger proportion of Cu-bearing sulfides are consistent with the proposed relatively slow formation of mostly chalcopyrite particles at site 27-14 and the resulting Fe isotope effects. On the contrary, the pCu/Fe ratio of 66-05 is significantly smaller. Particle formation at this site is suggested to have been dominated by rapid FeS and/or pyrite formation, which is reflected in the observed Fe isotope effects, and thus Cu is more likely to be present as CuS.

Although $X^V_{FeS}$ generally decreases with increasing pFe, the coherent trend at station 30 is disrupted at 1550m, where dissolved and particulate Fe increase in a sudden spike, while $X^V_{FeS}$ drops to zero indicating a largely oxidized layer. The oxidation rate of Fe is primarily controlled by ambient deepwater pH and [O$_2$] and is influenced to a lesser
extent by the chemical composition of vent fluids (Field and Sherrell, 2000). Because pH as well as [O$_2$] decreases systematically from the Atlantic to the Pacific oceans, oxidation rates in the Pacific are expected to be rather slow, with an estimated half-life time for Fe(II)$_{aq}$ in the range of roughly two hours, as observed at the southern (17°S) East Pacific Rise (Field and Sherrell, 2000). Consequently, the sudden drop towards a completely oxidized particulate fraction (increase of $X^V_{FeOOH}$ by 40%) within 50 m is unlikely to result from progressive oxidation of the plume, also because $X^V_{FeOOH}$ decreases again at 30-1500 so that it resembles the value at 30-1600.

A depth profile of Eu-anomalies (Eu/Eu*, see section 4.6.4.3) calculated for plume particles collected at stations 30 and 79 is shown in figure 4.7a and b, respectively. The significant decrease of Eu/Eu* down to background levels in 30-1550 is in sharp contrast to the bordering depths. The extent of a positive Eu-anomaly is a measure of plume dilution and hence Fe oxidation and thus suggests that a more evolved stage of plume formation, compared to the rest of station 30, is recorded in 30-1550.

The multitude of indications provides striking evidence for a separate plume layer at 30-

![Figure 4.7](image-url)

**Figure 4.7**

Eu-anomalies (Eu/Eu*) of plume particles vs. depth from CTD stations 30 (a) and 79 (b). Eu-anomalies were calculated from C1 chondrite normalized REE data following the method described by Edmonds and German (2004); see also section 4.6.4.3. Red line indicates Eu/Eu* of background seawater particulates, which don’t display a positive Eu-anomaly.
Given the high degree of oxidation, this plume layer is interpreted to be older and more evolved than adjacent plume layers, likely representing the persistent particle plume hanging above much of the caldera and considered to be sourced by the widespread diffuse hydrothermal activity. Diffuse fluids, such as 27-11 show signs of earlier oxidation, with high $X_{\text{FeOOH}}$ (table 4.5) and significantly smaller Eu/Eu$^*$ (0.96, table 4.4) close to the site of emanation, and are consistent with the large $\Delta^{56}\text{Fe}_{\text{Dissolved-Particle}}$ of -0.42‰ observed in sample 30-1550. Above and beneath 30-1550, samples 30-1500 and 30-1600 are similar with respect to their $X_{\text{FeOOH}}$ values, while Eu/Eu$^*$ increase with depth. In 30-1650 and 30-1700, Eu/Eu$^*$ increase to 2.36 and 2.25 while $X_{\text{FeOOH}}$ is <0.5, suggesting a much more reducing environment and a stronger influence of the hydrothermal REE contribution in this part of the sampled plume.

For comparison, chondrite normalized dissolved REE concentrations in vent fluids from 27-14 and 77-06, both potential source fluids for the buoyant plume at station 30, yielded Eu/Eu$^*$ of 3.05 and 2.75, respectively (calculated as explained in section 4.6.4.3 based on raw data from (Schmidt et al., in prep). Particulates from the buoyant plume samples taken above 27-14 and 66-03 (another potential source) show Eu/Eu$^*$ of 2.99 and 2.94 (27-15 and 27-16 respectively), as well as 2.8 (66-05, taken above vent 66-03). Consequently, the depth profile at station 30 is proposed to have captured the interception of a buoyant black smoker plume by a more evolved layer of oxidized plume, suggested to originate from the large areas of diffuse venting in the North and West of the central vent field. Whether the black smoker plume is fed by a single vent source or represents a combination of multiple sources remains unconstrained; as outlined in section 4.6.1, vents 27-14, 66-03, 66-06 and 77-06 are located within the ultimate proximity to station 30, but also 66-01, although further afield (roughly 130 m west north west), is a potential plume source vent. Because the degree of plume dilution is generally expected to increase vertically as well within a buoyant plume, the higher remaining positive Eu-anomaly in 30-1650 (Eu/Eu$^*$ = 2.36) when compared to 30-1700 (Eu/Eu$^*$ = 2.25) may be seen as a hint for more than one major contributing vent source. Plume station 79 is generally more oxidized than station 30, as is evident from $X_{\text{FeOOH}}$ >0.8 and reduced Eu-anomalies (tables 4.4 and 4.5). Complete oxidation and no marked influence of hydrothermal REE sources is indicated for 79-1500 and 79-1550, where dissolved and particulate Fe concentrations also do not exceed background levels. The
depth range of the highest Fe concentrations (dFe and pFe) coincides with higher Eu/Eu* and slightly reduced $X^{V}_{FeOOH}$ suggesting an evolved plume stage. The dissolved Fe maximum thereby correlates with the highest positive Eu-anomaly at station 79, indicating that 79-1575 is the least diluted yet largely oxidized portion of plume in this depth profile. The high degree of oxidation coupled with a still distinct contribution of hydrothermal REE sources to the plume particles are typical features of a non-buoyant hydrothermal plume (Edmonds and German, 2004). The very small Eu-anomaly in 79-1625 despite the relatively low $X^{V}_{FeOOH}$ (0.81) may indicate a differently sourced plume body with only minor hydrothermal REE input.

4.7.3 Plume sources
Although the plume sampled at station 30 has been identified as a buoyant portion of a potentially larger plume, with at least two distinguishable origins, and a range of further potential contributors, attribution to specific vents has proven difficult. Generally it is very likely that a multitude of black smokers feed one common plume, however, Fe isotopic compositions of dissolved and particulate Fe indicated very distinguished properties of the individual depth layers. Since Nifonea was shown to host a range of very different black smokers (see chapter 3), it is only natural to assume those differing Fe isotopic properties could originate from specific fluids with their very characteristic chemical properties. However, although $\delta^{56}$Fe of both dissolved and particulate Fe and the resulting $\Delta^{56}$Fe$^{Dissolved-Particulate}$ are known for the particle clouds forming above selected vent sites, it was not possible to match plume layers at station 30 to individual vent sites based on Fe isotope data (although this worked well for 30-1550 and diffuse sample 27-11). Furthermore, despite a range of indications, it is not sufficiently resolved whether both plumes, sampled at stations 30 and 79, belong to a single continuous plume.

In an attempt to relate CTD samples to hydrothermal sources and investigate the affiliation of the plumes sampled at both CTD stations, chondrite normalized REE patterns of plume particles were compared in an attempt to match key characteristics of their respective REE distribution patterns where available (figure 4.8). REEs were shown to behave conservatively during very early mixing of hydrothermal fluids and seawater because there is no substantial precipitation of REEs associated with sulfide formation (Mitra et al., 1994). This is particularly important for buoyant plume sample 66-05, where
Chapter IV

Upon adsorption of REEs onto Fe-oxyhydroxides, early formed particles will reflect the dissolved REE composition of the vent fluids, typically expressing a strong enrichment of LREEs and a large positive Eu-anomaly (Douville et al., 2002; Dubinin, 2004; Edmonds and German, 2004; German et al., 1990; Mitra et al., 1994; Rudnicki and Elderfield, 1993). In contrast, typical patterns of seawater (and thus of the ambient deep water hosting plume placement) include a significant HREE enrichment and LREE depletion as well as a pronounced negative cerium anomaly (Dubinin, 2004; Elderfield et al., 1988; German et al., 1990; Rudnicki and Elderfield, 1993; Sherrell et al., 1999). Consequently, with hydrothermally sourced dissolved REEs being used up and seawater sourced REEs gaining stronger influence, REE distribution patterns in plume particles are expected to shift from LREE enriched patterns towards a more even distribution. The positive Eu-anomaly will vanish gradually with an increasing influence of seawater sourced REEs, while at the same time, a negative cerium anomaly will grow in size. While inter-element fractionation during uptake of REEs from seawater produces very similar patterns, anomalies for Ce and Gd are unique to each data set thereby creating the main differences in the overall pattern shape.

Figure 4.8
Chondrite normalized REE distribution patterns of plume particles collected at stations 27 (-11, -15, -16), 30, 66-05 and 79. For 27-14, the dissolved REE pattern was provided to allow for comparison (from Schmidt et al. (in prep)). Individual patterns were aligned in order to demonstrate common distribution features and do not represent similar concentrations.

Reference values for normalization against C1 chondrite are from Anders and Grevesse (1989).
(Sherrell et al., 1999). In fact, the Gd concentration (in combination with Eu content) and Ce-anomaly determine the characteristic features common amongst some of the samples. As previously suggested from the Fe isotope data and Eu-anomaly, 30-1550 (which was interpreted to originate from large scale diffuse hydrothermal activity) and 27-11 (the diffuse fluid sample) resemble each other strongly in terms of their REE distributions. Very similar Sm, Eu and Gd contents as well as the slightly curved HREE pattern are found in this combination only in 27-11, 30-1550 and 79-1625. The size of the Ce-anomaly thereby increases from 27-11 to 79-1625, which is consistent with increasing distance from the vent source. Sample 30-1500, taken just 50 m above 30-1550 on the other hand, differs distinctly from 30-1550, but shares common features (low Gd, upwards curved HREEs) with 30-1650 but not 30-1700, which is consistent with their respective Fe isotopic compositions. Consequently, at least two different vents appear to fuel the buoyant black smoker plume and their respective portions do not seem to mix well as their individual REE patterns and Fe isotopic characteristics are preserved. When attempting to match 30-1650 and 30-1700 to potential sources, 30-1650 compares well with 27-15 and 27-16, while 30-1700 instead resembles 66-05, although these groupings are not reflected in the Fe isotope data. These similarities do not necessarily prove that 30-1650 and 30-1700 originate solely from 27-15/16 and 66-05 respectively, but they suggest a major impact of the specific vent source on the respective plume layer, while other contributions of other vent sources may be minor. The mid layer of station 30 (30-1600) is likely a mixed layer, combining characteristics of 30-1550 and 30-1650.

When considering station 79, the normalized REE distributions of the upper two samples, 79-1500 and 79-1550 are indistinguishable from the REE distribution in particles collected at the background station. Solely a more pronounced negative Ce-anomaly, indicating a mostly seawater derived particle REE distribution, differentiates the REE patterns in background particles from those in particles of samples 79-1500 and 79-1550. This similarity between samples 79-1500 and 79-1550 and the background station is also reflected in the concentration data and δ^{56}Fe of particulate Fe. However, since dissolved δ^{56}Fe diverge towards more negative values in 79-1550, a hydrothermal contribution seems likely. Samples 79-1575 and 79-1600 (where dFe and pFe reach their maxima) display only slightly different REE patterns than 79-1500 and
79-1550, but they are virtually identical to 30-1600. Sample 30-1600 was suggested to represent a mixed layer, combining influences from samples 30-1550 and 30-1650, two very distinct plume layers at station 30. When samples 79-1575 and 79-1600 share a common REE pattern with sample 30-1600, this supports the hypothesized continuity of one major plume from station 30 to 79, whereby the individual plume layers identified at station 30 are merged into 79-1575 and 79-1600. The REE distribution in particles of sample 79-1625 on the contrary shares characteristics of those found in samples 27-11 and 30-1550, suggesting addition of hydrothermal material from diffuse sources. Altogether, samples from station 79 (except 79-1625) display all characteristics of a non-buoyant plume, such as reduced Eu-anomalies, a high degree of oxidation, and seawater-like REE distributions suggesting an evolved plume with no fresh addition of new hydrothermal material. Accordingly, the station 79 plume is considered to represent the prolonged, stretched and thinned continuation of the buoyant plume sampled at station 30. Consequently, since the 79-1500 and 79-1550 pFe shows no differences from background levels, and dFe in 79-1500 and 79-1550 is at most marginally affected by hydrothermal activity, all of the plume at station 30 must be compressed and narrowed to a thin band beneath 1550 m and above 1625 m, where fresh input with likely a diffuse origin was demonstrated.

4.7.4 Iron isotope fractionation in the buoyant and non-buoyant plume
While most of the variation of δ⁵⁶Fe between individual plume layers is easily attributed to variations in plume composition and evolutionary stage, the Fe isotope systematics within each respective layer are yet to be understood. Kinetic Fe isotopic fractionation during precipitation of Fe-sulfides is the most fundamental isotopic fractionation process in a buoyant hydrothermal plume, preferentially incorporating the light Fe isotope into the particulate (sulfide) fraction (Butler et al., 2005; Polyakov et al., 2007; Rouxel et al., 2008). Buoyant plume samples collected from just above the vent orifices were demonstrated to be largely affected by sulfide precipitation (see chapter 3 and section 4.3 this chapter), even though kinetic isotope effects were not obvious in all samples (these are however expected to shift towards rapid sulfide precipitation and hence kinetic Fe isotope fractionation, see section 4.3). Whether rapid precipitation of Fe-sulfides continues to control Fe isotope
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fractionation even in the still buoyant plume at station 30 is questionable. Admittedly the time of plume rise is typically \( \leq 1 \) h after the fluids emanate from the vent orifice, a time range that is largely controlled by oceanic stratification rather than fluid temperatures (German and Von Damm, 2006; McDuff, 1995). However, the vent-fluid/seawater mixture is thought to become undersaturated with respect to FeS within \(~5\) min of exiting the vent and then particle formation is dominated by Fe-oxidation (McDuff, 1995). On the contrary, Eu/Eu* in 30-1650 and 30-1700 argue against very strong plume dilution and fluids displayed very low Fe/H\(_2\)S ratios (down to 0.01, see chapter 3); also, \( X_v^{FeS} \) are still at 0.54 and 0.56 respectively. However, the presence of Fe-sulfide particles in these samples does not preclude that particle formation itself is already dominated by Fe-oxidation and precipitation of Fe-oxyhydroxides.

Besides the kinetic isotope effects associated with rapid Fe-sulfide precipitation, oxidation of Fe is the second fundamental isotopic fractionation process in a buoyant hydrothermal plume. Other than sulfide precipitation, Fe-oxidation will control Fe isotope fractionation during the buoyant plume ascent and lateral non-buoyant plume dispersal. These processes can be divided into (1) partial oxidation of Fe(II)\(_{aq}\) to Fe(III)\(_{aq}\) whereby the heavy isotope is preferentially incorporated in the ferric Fe fraction (Anbar, 2004; Balci et al., 2006; Welch et al., 2003), and (2) precipitation of Fe(III)\(_{aq}\) into ferrihydrite, whereby the light isotope is potentially fractionated due to kinetic isotope effects, the magnitude of which depend on the rate of precipitation (Skulan et al., 2002). Due to the instability of Fe(III)\(_{aq}\) in seawater, both processes usually go hand in hand with partial oxidation of Fe(II)\(_{aq}\) to Fe(III)\(_{aq}\) followed by immediate precipitation of Fe(III)\(_{aq}\) into ferrihydrite, producing overall enrichment of the heavy isotope within the particulate phase. This was suggested by Bullen et al. (2001), who measured an \( \alpha_{ferrihydrite-Fe(II)aq} \) of 1.0009 during oxidation of Fe (II)\(_{aq}\) at room temperature.

A similar fractionation factor of \( \alpha = 1.0004 \) is needed to explain the observed Fe isotope fractionation in sample 30-1550. Using an initial \( \delta^{56}\text{Fe} \) of \(-0.61\%o \pm 0.04\%o\), as determined for diffuse fluids, and a Rayleigh fractionation model (Rayleigh fractionation is explained in chapter 3), a fractionation factor of 1.0004 requires roughly 99% of the Fe(II)\(_{aq}\) in sample 27-11 and \(~75\)% of the Fe(II)\(_{aq}\) in sample 30-1550 to remain in the reduced form in order to explain the particulate \( \delta^{56}\text{Fe} \) of \(-0.22\%o \) and \(-0.31\%o \pm 0.04 \%o\), respectively. Considering the low temperature gradients in areas of diffuse venting,
precipitation rates may be slow and consequently fractionation during Fe(III)$_\text{aq}$ precipitation should be close to zero (Skulan et al., 2002). Furthermore, the observed diffuse venting did not appear to cause any rapid Fe-sulfide precipitation and hence, the particulate $\delta^{56}\text{Fe}$ in the respective samples and those potentially originating from diffuse venting is not obscured by remaining FeS that likely inherit very negative $\delta^{56}\text{Fe}$. Due to their small particle size and reduced density (compared to Fe-sulfides), Fe-oxyhydroxides are less likely to settle out of the plume and will hence escape in large proportions to the distal parts of the plume (Edmonds and German, 2004; Lilley et al., 1995; Mottl and McConachy, 1990). Accordingly, at the stage of plume evolution recorded in 30-1550, Fe loss from this plume body is unlikely; instead the particulate Fe fraction will grow by addition of Fe from the dissolved phase. The majority of Fe in the dissolved phase is assumed to be present as colloidal Fe-oxyhydroxides that will grow in size as more Fe(II)$_\text{aq}$ is oxidized and subsequently will separate into the particulate phase (Bennett et al., 2009). This resembles closed system behavior with respect to Fe isotopes and consequently particulate and dissolved $\delta^{56}\text{Fe}$ will converge once the majority of Fe(II)$_\text{aq}$ is oxidized.

More difficult do understand are the fractionation mechanisms in those samples from station 30 that contain significant portions of Fe-sulfides. Their particulate $\delta^{56}\text{Fe}$ is controlled by the balance between the remaining Fe-sulfides and Fe-oxyhydroxides but also by the balance between Fe-oxyhydroxides present in the dissolved and particulate phase (Bennett et al., 2009). Since particle formation is most likely dominated by the precipitation of Fe-oxyhydroxides at this stage, the remaining Fe-sulfide portion will shrink. Any sulfides that do not settle to the seafloor will be dissolved or re-mineralized to Fe-oxyhydroxides (Metz and Trefry, 1993; Severmann et al., 2004). However, since Fe-sulfides still make up a large proportion of pFe and inherit potentially very negative $\delta^{56}\text{Fe}$, their Fe isotopic signatures are capable of ‘diluting’ those of freshly forming Fe-oxyhydroxides. The portion of the latter steadily grows instead as more dissolved Fe-oxyhydroxide complexes grow big enough (due to colloidal coagulation) to partition into the particulate phase (Bennett et al., 2009). The Fe-sulfide proportions relative to total pFe against measured particulate $\delta^{56}\text{Fe}$ of 30-1650 and 30-1700 as well as the suggested sources (27-15/16 and 66-05, see 4.7.3) are shown in figure 4.9, demonstrating excellent correlation ($r^2 = 0.97$) and suggesting similar FeS and FeOOH
end-member $\delta^{56}\text{Fe}$ in particulates of these samples. These tightly linked Fe isotope systematics strongly support the hypothesis of vents 27-14 and 66-03 being major contributors to those plume portions of station 30 thought to be fueled by black smokers (30-1650 and 30-1700). Samples 30-1500 to 30-1600 and 27-11 are plotted as well for comparison. These relationships clearly highlight the very different properties of 30-1550 compared to the rest of station 30 and that both 30-1500 and 30-1600 (which otherwise resemble REE patterns of 30-1650) are affected by partial mixing with 30-1550.

The relationship between %FeS and particulate $\delta^{56}\text{Fe}$, displayed in figure 4.9, shows increasingly lighter Fe isotopic composition of particulates with increasing percentages of Fe-sulfide. From this relationship, the Fe isotopic composition of the pure Fe-sulfide end-member is estimated at $\delta^{56}\text{Fe} \sim -0.82\%o$, which is identical within error to the signature for particulates from buoyant plume sample 66-05 (see section 4.6.3.1) that was almost purely composed of Fe-sulfides (see table 4.5). This corresponds to kinetic isotope fractionation upon rapid precipitation of FeS (see chapter 3 and Butler et al. (2005)). Amongst the black smoker vent sites primarily sourcing the station 30 plume (27-14 and 66-03), clearly 66-03 with its very high Fe-concentrations and pronounced black smoker plume formation must deliver the greater portion of dFe and pFe to the plume and thus the FeS end-member $\delta^{56}\text{Fe}$ of the 66-03 particulate fraction also appears as the FeS end-member $\delta^{56}\text{Fe}$ of 30-1650 and 30-1700. Particles from other sources may have been oxidized already prior to joining the plume. The Fe isotopic composition of every depths particulate phase is determined by the relative proportions of the Fe-sulfide end-member and a Fe-oxyhydroxide end-member in the respective sample.

![Figure 4.9](image)

The relationship between the proportion of Fe-sulfides in total pFe (% FeS) -as presented in table 5- and particulate $\delta^{56}\text{Fe} [\%o]$. Red squared include 30-1650 and 30-1700 that represent the buoyant black smoker plume as well as 27-15/16 and 66-05 that are supposed to source the lower part of 30CTD. Diffuse sample 27-11 is shown as green diamond, while the remaining samples of 30CTD are shown as blue diamonds. Samples 30-1500 and 30-1600 appear as mixtures between the main plume and 30-1550.
The Fe-oxyhydroxide end-member, as determined from figure 4.9, is significantly more enriched in the heavy Fe isotopes with an estimated $\delta^{56}\text{Fe} \approx +0.49\permil$. As more dissolved Fe(II)$_{\text{aq}}$ becomes oxidized and eventually partitions into the particulate phase, heavy Fe-oxyhydroxides progressively ‘dilute’ the light Fe isotopic composition inherited by remaining Fe-sulfides. Consequently, particulate $\delta^{56}\text{Fe}$ will become increasingly heavy. At the same time, rudimentary Fe-sulfides will either dissolve, thereby adding isotopically light Fe to the dissolved Fe pool, or re-mineralize to Fe-oxyhydroxide producing another FeOOH end-member with very light $\delta^{56}\text{Fe}$ if transferred quantitatively (Metz and Trefry, 1993; Severmann et al., 2004). Some Fe-sulfides may also persist as nanoparticulate pyrite, which were shown to settle out of the plume more slowly than larger Fe-sulfides and are more resistant to oxidation than dissolved Fe(II) and FeS (Yucel et al., 2011). Since most nanoparticulate pyrite partitions into the dissolved Fe fraction, it may represent a stable species of isotopically light Fe (provided the precipitation of nanoparticulate pyrite follows the same Fe isotope systematics as larger Fe-sulfides and pyrite), resistant to oxidation, and thus ‘buffering’ the dissolved $\delta^{56}\text{Fe}$ against stronger shifts towards a heavier Fe isotopic composition.

Relatively high detected Eu-anomalies and large proportions of Fe-sulfides found amongst particulate Fe in samples 30-1650 and 30-1700 hint for a rather young evolutionary stage. At this stage the immediate influence of specific vent sources is still very pronounced and oxidation processes are just slowly beginning. A much more advanced stage of plume evolution is recorded at station 79. At this station, the particulate fraction is almost entirely composed of Fe-oxyhydroxides, and is mostly enriched in the heavy Fe isotopes compared to dissolved Fe, particularly in sample 79-1575. Whether this results from dissolution of Fe-sulfides or coupled oxidation of Fe(II)$_{\text{aq}}$ and subsequent precipitation of ferrihydrite, or a combination of both, remains unconstrained.

Finally, adsorption of Fe(II) onto Fe-oxyhydroxides or Fe-sulfides can fractionate Fe isotopes in a buoyant hydrothermal plume, whereby the heavy isotopes of Fe(II)$_{\text{aq}}$ are preferentially adsorbed to mineral surfaces (Icopini et al., 2004; Matthews et al., 2008; Mikutta et al., 2009; Teutsch et al., 2005). The adsorbed isotopically heavy Fe fraction can theoretically be desorbed again, resulting in the dissolved fraction being enriched.
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with heavy Fe, or undergo oxidation on the mineral surface, which is the most likely scenario under oxygenated conditions (Bennett et al., 2009). Trace metal and REE data have demonstrated that adsorption onto Fe-oxyhydroxides is widespread; adsorption of Cu and Zn onto Fe-oxyhydroxides has been suggested as well (see section 4.6.4.1). Consequently, it is readily possible that dissolved Fe(II)\textsubscript{aq} is also adsorbed, particularly given the obvious slow oxidation kinetics. Samples 30-1550 and 79-1575, where the particulate phase is significantly enriched in the heavy Fe isotope compared to the dissolved fraction, are potential candidates where adsorption induced Fe isotope fractionation may occur; these samples also have the highest proportions of FeOOH amongst their particulate Fe ($X^V_{\text{FeOOH}}$). Considering the relatively high dFe concentrations in 79-1575 compared to both adjacent samples and those of station 30 (as well as no evidence for the addition of fresh material between stations 30 and 79, see previous section), and it’s very light $\delta^{56}\text{Fe}$, this sample may even present an example where dissolved Fe(II) with low $\delta^{56}\text{Fe}$ was desorbed from FeOOH surfaces, now contributing to the dissolved phase.

Iron isotopic fractionation related to complexation by organic ligands has been debated as well, but remains poorly constrained. Studies by Brantley et al. (2004) and Dideriksen et al. (2008) resulted in controversial findings, either pointing towards the light or the heavy isotope being enriched in the organically bound fraction, although a more recent study by Morgan et al. (2010) supports the latter. However, organic ligands and increased dissolved organic carbon contents have been associated with areas of diffuse venting (Lang et al., 2006; Sander and Koschinsky, 2011; Sander et al., 2007) such as those widely distributed all across Nifonea. Diffuse fluids showed the highest fractionation between dissolved and particulate Fe ($\Delta^{56}\text{Fe}_{\text{Dissolved-Particulate}}$ of -0.39‰) that prevailed in those plume portions attributed to a diffuse origin (30-1550, $\Delta^{56}\text{Fe}_{\text{Dissolved-Particulate}}$ of -0.42‰). Since stabilization of dissolved Fe by organic ligands would prevent precipitation and facilitate transport of dFe to the distant parts of the plume and further (Bennett et al., 2008; Lang et al., 2006; Sander and Koschinsky, 2011; Toner et al., 2009), 79-1575 with its high dFe concentration at increased distance to the central vent field might represent an example for a large proportion of ligand complexation. Again, this sample displays a comparatively large $\Delta^{56}\text{Fe}_{\text{Dissolved-Particulate}}$ of -0.17‰. Furthermore, even if not actively produced in areas of
high-temperature venting, organic ligands could also be entrained into the buoyant plumes from areas of diffuse venting and complex with dissolved Fe species (Bennett et al., 2008; German et al., 2015; Toner et al., 2009). However, there is no indication specifically for Fe isotope fractionation induced by organic complexation in samples from the Nifonea plume.

4.8 Conclusion

Hydrothermal plume formation above the Nifonea vent field was shown to be controlled by a number of processes and vent sources. The individual properties of highly diverse black smoker fluids and clear diffuse fluids are combined in a common plume that was sampled in a young evolutionary stage at station 30 and again in a more advanced evolutionary stage at station 79 roughly 310 m southeast of station 30. Very heterogeneous Fe isotope patterns of pFe and dFe, provided by direct Fe isotope analysis of the dissolved fraction, revealed at least three major contributing sources that were linked to specific vent sites by trace element analysis of plume particles. Large quantities of dissolved Fe appear to come from entrainment of diffusely venting fluids into the plume, such as predicted by German et al. (2015).

The combined information suggests that plume processes in the Nifonea plume are far more complex than the simple mixing of multiple components. Intense precipitation of Fe-sulfides has produced a significant depletion of the light Fe isotopes in black smoker derived plume portions. Particulate and dissolved Fe have isotopic signatures heavier than their respective source fluids, which average at particularly low $\delta^{56}$Fe (down to -0.66‰ end-member composition). These findings support suggestions made by Bennett et al. (2009) that Fe loss during buoyant plume rise will fractionate the original Fe isotope composition in typical hydrothermal systems where considerable Fe-sulfide precipitation occurs. The large quantities of hydrothermal material originating from diffusely venting fluids are likely to be more or less excluded from this process. Because of the low temperatures of diffuse fluids (>25°C) and the resulting low temperature gradients upon mixing with seawater, intense precipitation of Fe-sulfides is unlikely (and not observed). Furthermore, since the fluids are not expelled in a strongly focused way
they are prone to early oxidation. In the more focused stream of hydrothermal discharge, reduced conditions prevail longer and thus oxidation may be delayed. Upon the onset of oxidation of dissolved Fe however, incomplete Fe(II) oxidation and ferricydrite precipitation shift particulate $\delta^{56}\text{Fe}$ to heavier isotopic compositions than dissolved Fe as the plume evolves; this will affect diffusely expelled fluids and focused venting fluids equally.

Very light dissolved Fe isotopic compositions in largely oxidized plume layers may indicate dissolution of Fe-sulfides formed during the buoyant stages or desorption of unoxidized Fe(II) from mineral surfaces only favored by comparable slow oxidation kinetics. Both formerly adsorbed Fe species and Fe(II) from Fe-sulfide dissolution may contribute to the dissolved Fe pool, prevented from precipitation by stabilizing organic ligands (entrained into the plume from diffuse venting areas) that facilitate transport of dFe to the distal parts of the plume and beyond (Sander and Koschinsky, 2011).

Fe isotopes have been discussed widely as a potential tool to unravel the relative importance of the various Fe sources contributing to the marine dissolved Fe budget and previous publications included mass balance calculations using suggested hydrothermal end-member $\delta^{56}\text{Fe}$ (e.g. Conway and John (2014)). However, neither the Fe isotopic composition of high-temperature vent fluids nor the extremely negative dissolved $\delta^{56}\text{Fe}$ values found in incompletely oxidized plume layers provide a robust isotopic signature for hydrothermally derived Fe. As shown, the original Fe isotope composition of the source fluids will be severely fractionated in most hydrothermal systems due to loss of Fe from the plume; the dissolved Fe fraction will become increasingly heavy with respect to Fe isotopes. Accordingly, previously used hydrothermal end-members in mass balance calculations were too light resulting in an underestimation of the quantity of hydrothermal Fe needed to explain deep ocean dissolved $\delta^{56}\text{Fe}$.

The relationship between progressing plume dilution (expressed as particle Eu/Eu*) and particulate $\delta^{56}\text{Fe}$ shown in figure 4.10a suggests a very narrow range of plume particle $\delta^{56}\text{Fe}$ far before plume dilution approaches background levels. Calculated Eu-anomalies of end-member vent fluids (dissolved fraction Eu-anomalies) are plotted as well and show excellent correlation on a linear regression line with the most evolved plume particle and background particle composition ($r^2 = 0.97$). Only particles with demonstrably buoyant, and thus immature character, scatter to both sides of this line.
This observation is consistent with those obtained from the Rainbow hydrothermal plume by Severmann et al. (2004). Dissolved $\delta^{56}$Fe, however (4.10b), are much more scattered particularly at increased plume dilution, although this may be a consequence of the multitude of individual plume layers and diverse venting in Nifonea.

Consequently, a hydrothermal Fe isotopic fingerprint depends on a number of parameters, such as end-member composition and plume processes and will likely be different between most hydrothermal systems. Particulate and dissolved $\delta^{56}$Fe are not necessarily linked and thus it is recommended to collect both fractions when attempting to relate a high-Fe water mass to hydrothermal activity as at least one of them may provide indications of a potential hydrothermal origin. Collection of the particulate matter further allows utilization of additional tracers, including trace elements that will enhance opportunities to track hydrothermal Fe. As is evident from figure 4.10b, a relatively light dissolved Fe isotopic composition is likely to indicate hydrothermally sourced Fe, but the same source may also produce a significantly heavier isotopic fingerprint. Since the chosen hydrothermal end-member will have an effect on the estimated relative
importance of the hydrothermal contribution, caution is advised when choosing the hydrothermal signature to be used in mass balance calculations. Although station 79 already represents a more evolved plume portion it is expected that the plume will stretch further out and that plume processes will continue to modify dissolved and particulate $\delta^{56}\text{Fe}$ in the different plume layers along the trail of plume dispersion. It is suggested that once the plume is fully oxidized and well mixed, particulate and dissolved $\delta^{56}\text{Fe}$ within the plume will converge towards uniform Fe isotopic signatures of $\text{dFe}$ and $\text{pFe}$. This conversion of $\text{pFe}$ towards a uniform Fe isotopic composition is already approached in the stage of plume evolution that was captured at station 79 as demonstrated by the narrow range of $\delta^{56}\text{Fe}$ at low $\text{Eu/Eu^*}$ (figure 4.10a). A similar conversion of $\text{dFe}$ towards a uniform Fe isotopic composition, reducing the spread of $\delta^{56}\text{Fe}$ observed for $\text{dFe}$ at similarly low $\text{Eu/Eu^*}$ (figure 4.10b) is hypothesized to occur in the more distal parts of the plume. More plume studies are necessary to investigate Fe isotopes even in the distal parts of hydrothermal plumes where plume processes have already had their maximum effect on $\delta^{56}\text{Fe}$.

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Chapter V

Conclusions and Future Perspectives
5.1 Summary and Conclusions

Iron is known to be an essential micronutrient controlling primary productivity in large areas of the global ocean, where plankton growth is limited by the availability of Fe. Since primary production and the drawdown of CO₂ are directly linked to climate processes, the marine biogeochemistry of Fe receives much attention and is one of the key aspects of the international GEOTRACES program, which aims to understand trace-element distribution and cycling in the oceans. Stable isotopes of Fe act as an important tool to aid in understanding the biogeochemical processes affecting the global Fe inventory. Furthermore iron isotopes have been utilized to ‘fingerprint’ and quantify dissolved Fe from different sources allowing modeling of their relative contributions based on δ⁵⁶Fe sections across ocean basins, as published by Conway and John (2014). Hydrothermal discharge is amongst the most important sources fueling the deep ocean with dissolved Fe, and may have increased significance in the Southern Ocean as suggested by recent studies (Fitzsimmons et al., 2014; Resing et al., 2015). However, neither the processes controlling the Fe isotopic composition of hydrothermal fluids nor those modifying the original vent δ⁵⁶Fe during plume rise and dispersal are sufficiently constrained. Hydrothermal fluids were shown to cover a range of Fe isotopic compositions from δ⁵⁶Fe = -0.2 - -0.7‰ (Rouxel et al., 2008). Plume processes may either significantly alter this isotopic signature or not affect it at all, as suggested by two previous studies investigating the subject (Bennett et al., 2009; Severmann et al., 2004), imposing large uncertainty onto any generalized Fe isotopic fingerprint of hydrothermally derived Fe and raising concerns about the utilization of such hydrothermal end-members in mass-balance calculations.

In order to decrease the uncertainty associated with hydrothermal Fe isotopic signatures one primary focus of this thesis was to investigate Fe isotope fractionation in a hydrothermal system and the modifications of its hydrothermal signature arising from plume processes after venting. The latter was largely aided by direct Fe isotope analyses of the dissolved Fe fraction in the hydrothermal plume dispersing away from the investigated vent field. The development of the underlying analytical methods facilitating seawater Fe extraction, preconcentration and purification as well as the
improvement of analysis routines for MC-ICPMS was another primary focus of this study.

Chapter I detailed the existing knowledge about the marine biogeochemical cycle of Fe and why it attracts so much attention in current research projects. The sources and sinks controlling the marine Fe budget were discussed and the significance of the hydrothermal contribution was highlighted. Stable Fe isotopes were introduced as a valuable tracer because they aid in understanding the relative proportions of various sources of dissolved Fe that determine the Fe inventories of ocean basins.

Chapter II concerned the analytical methods adapted and developed to study the Fe isotopic composition of a range of marine samples including seawater. The chapter highlights the difficulties associated with analyses of Fe in seawater and the measures taken to ensure reliable data. A preconcentration set-up utilizing pre-packed columns and custom made sample reservoirs was favored over batch extraction due to better (and thus cleaner) handling and because it enabled higher sample throughput. Tests with varying sample pH revealed no obvious dependency between Fe recoveries and sample pH at time of extraction within a pH range of 4.5 to 5.5. However, Fe yields in general varied significantly leaving room for improvements. More rigorous sample acidification prior to pH re-adjustment or UV radiation is suggested to overcome low Fe recoveries. For purification of Fe from trace metal concentrates the BioRad AG-MP1 (BioRad, USA) was shown to provide better separation of Fe and Zn compared to the BioRad AG1-X4. A two-stage Fe purification protocol is highly recommended to efficiently remove remaining traces of Zn, U, and especially Ni, which forms an isobaric interference with Fe (58Ni on 58Fe) and demonstrably caused severe shifts in measured δ56Fe, even at trace levels. A two-stage purification protocol may use the AG-MP1 resin or a combination of AG-MP1 and AG1-X4. Furthermore, during isotope analysis on the Nu Plasma, an elevated RF power of 1400 (normally operated at 1300) was found to reduce the formation of polyatomic interferences (mostly Ar based) on analyte peaks without compromising sensitivity.
Chapter III examined what controls the Fe isotopic composition of hydrothermal vent fluids in a back-arc spreading centre, exemplified by a newly discovered Nifonea vent field in Vanuatu. In agreement with previous studies host rock composition could not be linked to significantly influence vent fluid $\delta^{56}\text{Fe}$. Instead, it is rather the water-rock ratio or subsurface precipitation that controls the isotopic composition of Fe in hydrothermal fluids; processes that resemble each other in hydrothermal systems in every tectonic setting. Consequently, fluids emanating into the deep ocean from submarine hydrothermal systems in all oceans may define a similar range of $\delta^{56}\text{Fe}$, shifted to low values by -0.2 to -0.74‰ compared to igneous rocks. Solely phase separation may more pronouncedly fractionate Fe isotopes in hydrothermal systems hosted in back-arc settings, which is attributed to the very low Cl vapor fluids as they typically occur in back-arc hydrothermal systems with their shallower depths. Accordingly, it appears more likely that the range of $\delta^{56}\text{Fe}$ from -0.2 to -0.74‰ for hydrothermal vent fluids may be valid for the global ocean.

Chapter IV provides direct measurements of dissolved $\delta^{56}\text{Fe}$ in the hydrothermal plume that originates from Nifonea vent field. With those analyses comes direct evidence that vent fluid Fe isotopic compositions cannot be used straight away in models addressing the relative proportions of Fe input from different sources into a respective ocean basin. It is shown that dissolved Fe is strongly fractionated towards heavier isotopic compositions compared to end-member fluid $\delta^{56}\text{Fe}$ during plume dispersal due to redox transformations of Fe, precipitation of Fe-sulfides and Fe-oxyhydroxides, and Fe loss from the plume as particles settle out. Accordingly, previously used hydrothermal end-members in mass balance calculations were too light resulting in the underestimation of the proportion of hydrothermal Fe needed to explain deep ocean dissolved $\delta^{56}\text{Fe}$. Therefore, although fluid end-member $\delta^{56}\text{Fe}$ may display the same range in all submarine hydrothermal systems (which is already relatively large, ranging from -0.2 to -0.74‰), the degree of modification of these original fluid Fe isotopic compositions arising from plume processes depends on a number of parameters (such as vent fluid Fe/H$_2$S ratios or oxidation kinetics of the plume) that will vary significantly from vent field to vent field.
This thesis provides new insights into Fe isotope fractionation in seafloor hydrothermal vent systems and hydrothermal plumes, with implications for the utilization of Fe stable isotopes to estimate the relative contributions from multiple Fe sources to the dissolved Fe budget. In search of a distinctive fingerprint to identify hydrothermally derived Fe, knowledge about the fundamental processes controlling the Fe isotopic composition of vent fluids was significantly expanded with the first field study to observe phase separation induced Fe isotope fractionation. New insights were gained about plume processes and their role in the modification of original vent fluid $\delta^{56}$Fe, thereby mediating between the two pioneering studies of Severmann et al. (2004) and Bennet et al. (2009). Both proposed mechanisms (conservative behavior of Fe opposed to alteration of the dissolved Fe isotopic composition) may occur in any hydrothermal plume, depending on Fe/H$_2$S ratios in the respective source fluid. Direct measurements of the dissolved Fe isotopic composition in plume samples further support the predictions from mass balance calculations by Bennet et al. (2009) that a remaining dissolved Fe species may be isotopically heavier than the original vent fluid. However, these results also reveal the very complex interplay of various processes affecting Fe isotopes in hydrothermal plumes. This precludes a generalized isotopic signature for hydrothermally derived Fe and instead rather requires characterization of hydrothermally sourced Fe according to ocean basin (oxidation kinetic systematically slow down from the North Atlantic to the North Pacific along thermohaline circulation) and venting style (the degree of Fe-sulfide formation contributes strongly to the alteration of original fluid $\delta^{56}$Fe, and is a function of Fe/H$_2$S). On the other hand, since most aerosol deposition is assumed to have a Fe isotopic composition similar to Bulk Silicate Earth, and input from sediment dissolution is restricted to continental margins and thus easily excluded, any light isotopic composition ($\delta^{56}$Fe < 0) measured in seawater may hint at hydrothermal Fe. The search for a distinctive fingerprint to identify hydrothermally derived Fe will continue.

5.2 Future Perspectives

The presented study contains detailed information about new ion-exchange protocols and analysis routines enabling direct Fe isotope analysis of dissolved Fe species. This method was demonstrated to yield highly accurate and precise Fe isotope data. As the
issues arising from trace amounts of residual matrix (particularly Ni) reveal, refinements of the method are necessary before it becomes routine. But the advanced preconcentration set-up has laid the ground for high throughput processing of seawater samples and extraction of Fe, Zn, and Cd for isotope analyses from the same sample. In order to use Fe isotopes to their full potential, a much more comprehensive data set is necessary. That includes seawater data from ocean basin transects of depth profiles but also small scale studies with high spatial resolution. Particularly plume processes and their effect on the Fe isotopic composition of both dissolved and particulate hydrothermal Fe need to be studied in more detail. While the effects of Fe-sulfide precipitation on dFe and pFe are relatively well documented, they are only relevant in the very first stage of plume rise. For the remaining spatial extent of the plume however, partial oxidation of dissolved Fe followed by precipitation of Fe-oxyhydroxides, and dissolution of Fe-sulfides and stabilization of dissolved Fe through organic and inorganic ligands are the dominant processes and their respective effects on the Fe isotopic composition of dFe and pFe are not well documented yet. Full length and height transects of non-buoyant plumes are required, covering even the more distal parts. Sampling and analyses should not only target Fe isotopes but also the predominant speciation of dissolved as well as particulate Fe. Rare Earth Elements and the Eu-anomaly also provide a useful indication for the extent of Fe oxidation. Furthermore, differentiation between soluble and colloidal Fe within the dissolved fraction should be attempted, since stabilized dissolved hydrothermal Fe can be either in form of nanoparticles or complexed by ligands.

Although vent fields located in the back-arc spreading centers of the SW Pacific were shown to host highly diverse hydrothermal venting (which probably complicates plume processes), the back-arc basins are often strongly segmented by volcanic ridges and thus isolated from each other and the larger ocean basins. Thus they may provide excellent natural laboratories to study the fate of hydrothermally derived Fe. The Coriolis Troughs in Vanuatu for example, subject of chapters 3 and 4, are separated from the main Pacific with its multitude of Fe inputs. The biogeochemistry of Fe in these enclosed basins is consequently expected to be mainly controlled by Fe fluxes from the discovered intense hydrothermal activity, with only few Fe inputs from outside that would potentially obscure the hydrothermal influence on seawater dissolved $^{56}\delta$Fe. No major
rivers drain into the Coriolis Troughs and hence sediment dissolution can be excluded as a significant Fe contribution, but due to the relative proximity of the Australian continent they may receive air-borne Fe input through dust deposition. Consequently the isotopic composition of dissolved Fe in the waters of the Coriolis Troughs may either be solely hydrothermally sourced or represent a mixture of hydrothermal and atmospheric Fe isotopic compositions.
References & Appendix
References


Reference & Appendix


Appendix

Cleaning protocols for sampling and processing equipment

Nalgene 1L HDPE and LDPE sampling bottles

1. Soaked in 5% v/v Citranox (low phosphate detergent) bath for at least one week
2. Rinsed five times with distilled water
3. Filled with 6N reagent grade (AR) HCL and soaked in a 10% v/v AR-HCl bath for at least four weeks
4. Rinsed five times with Milli-Q
5. Filled to the neck with Milli-Q and to the top with 8N q-HCL for at least four weeks
6. Double bagged and stored with dilute q-acid until needed for sampling

Nalgene Teflon reagent bottles

1. Reflux in 5% v/v Citranox overnight at 110°C
2. Rinsed five times with Milli-Q
3. Reflux in 6N AR-HCl for at least 2 weeks at 110°C
4. Rinsed five times with Milli-Q
5. Reflux in 7N AR-HNO₃ for at least 2 weeks at 110°C
6. Rinsed five times with Milli-Q
7. Reflux in 6N q-HCl overnight at 110°C
8. Rinsed five times with Milli-Q
9. Reflux in 7N q-HNO₃ overnight at 110°C
10. Rinsed five times with Milli-Q
11. Dried in the laminar flow bench

7ml, 15ml and 30ml Savillex Teflon beakers used for sample processing

1. Reflux in 6N AR-HCl overnight
2. Rinsed five times with Milli-Q
3. Cleaned with ethanol soaked Kimwipes
4. Rinsed five times with Milli-Q
5. Reflux in 5% v/v Citranox overnight at 110°C
6. Rinsed five times with Milli-Q
7. Reflux in 6N AR-HCl for at least 2 weeks at 110°C
8. Rinsed five times with Milli-Q
9. Reflux in 7N AR-HNO₃ for at least 2 weeks at 110°C
10. Rinsed five times with Milli-Q
11. Reflux in 6N q-HCl overnight at 110°C
12. Rinsed five times with Milli-Q
13. Reflux in 7N q-HNO₃ overnight at 110°C
14. Rinsed five times with Milli-Q
15. Dried in the laminar flow bench

BioRad AG1-X4 and AG-MP1 resins, Nobias-chelate PA1 resin (cleaned in a 1L Teflon bottle)

1. Rinsed with Milli-Q five times
2. Soaked in 8M q-HCl for at least three days (rinsed twice with Milli-Q in between)
3. Rinsed with Milli-Q five times
4. Soaked in 2M q-HNO₃ for at least three days (rinsed twice with Milli-Q in between)
5. Rinsed with Milli-Q five times
6. Stored in 0.1% v/v q- HNO₃ until needed

BioRad polypropylene columns (2.5ml resin bed)

1. Soaked in 5% v/v Citranox for at least one week
2. Rinsed five times with Milli-Q
3. Soaked in 6N AR-HCl bath for at least four weeks
4. Rinsed five times with Milli-Q
5. Soaked in 4N q-HCl bath at least overnight

HDPE first stage sample loading reservoirs with modified caps and Teflon connectors

1. Rinsed with Milli-Q just after use
2. Soaked in 6N AR-HCl for at least overnight
3. Rinsed five times with Milli-Q
4. Soaked in 6N q-HCl bath for at least overnight

Small Teflon columns (500 µl resin bed)

1. Rinsed with Milli-Q after use
2. Soaked in 6N AR-HCl on 110°C hotplate for at least one week
3. Rinsed with Milli-Q five times
4. Soaked in 6N q-HCl on 110°C hotplate for at least overnight