



Input and particle-reactivity of transition metals from subgroups IV, V and VI in the water column of the Atlantic Ocean

By

Sandra Pöhle

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Approved Dissertation Committee

Prof. Dr. Andrea Koschinsky

Jacobs University Bremen

Prof. Dr. Michael Bau

Jacobs University Bremen

Prof. Dr. Martin Frank

GEOMAR Helmholtz Centre for Ocean Research Kiel

Prof. Dr. Per S. Andersson

Swedish Museum of Natural History Stockholm

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Department of Physics and Earth Sciences

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Summary

This PhD-study is embedded in the international GEOTRACES program and focuses on the distribution of the 9 different metals titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (V), niobium (Nb), tantalum (Ta), vanadium (V), molybdenum (Mo), and tungsten (W) from subgroups IV, V, and VI of the periodic table of elements in seawater. In the marine system, these metals are of special interest for different reasons: (a) biologically important as micronutrient (V, Mo), (b) biologically important as microtoxin (oxidized Cr redox species, Cr(VI)), (c) contribution to the formation of valuable ore deposits on the seafloor (Ti, Zr, Hf, Nb, Ta, W), (d) application of isotopic composition as proxy for paleo-oceanographic conditions (Hf, Mo, Cr).

As some of these metals are present in the range of pmol/kg in seawater (Ti, Zr, Hf, Nb, Ta, W) preconcentration prior to their analysis is required. Within the context of this study, an online-preconcentration method using the SeaFAST system and subsequent analysis via ICP - MS has been developed for the determination of Ti, Zr, Nb and W in one analytical run and for V and Mo in a separate run, according to their natural concentrations. First results for Hf and Ta obtained in this study are promising, while the SeaFAST system cannot be applied for the determination of Cr and its redox species. The SeaFAST system consists of an autosampler, a sample loop, and a preconcentration column. Preconcentration and matrix separation processes are performed simultaneously. An external 4-point calibration was applied with calibration standards matching the salinity of the seawater samples. Spike experiments with filtered North Sea water showed nearly quantitative recovery. High recovery rates up to 99 % were achieved for dissolved V and Mo in the certified seawater reference standard NASS-6. This multi-elemental method needs only a small sample volume (50 ml for two runs) and requires approx. one hour for the preconcentration and analysis of six (trace) metals in seawater.

The described method has been applied to 194 seawater samples collected at 16 stations located in the (sub)tropical Atlantic (GEOTRACES research cruise M81/1) in areas influenced by different parameters such as weathering processes close to the Canary Islands, Saharan dust input off West Africa, and mixing with freshwater close to the Amazon estuary in the Brazil Basin.

Results on dissolved Zr and Nb concentrations reveal deviations from the typical depth patterns of a particle-reactive metal. The concentration of Zr increased with depth, whereas the distribution of Nb was predominantly conservative except off West Africa. While atmospheric input from the Canary Islands served as a source for Nb, deposited

particles originating from the Saharan desert served as sorption sites for Nb and Zr. Freshwater discharge from the Amazon probably provides Zr and Nb to surface waters close of the Amazon plume. A linear relationship for Zr and Si has been observed for most stations, revealing a coupling of Zr to the Si cycle. A sequential filtration approach applied to Pacific seawater samples (research cruise SO229) showed that the fraction $< 0.015 \mu\text{m}$ combines almost all dissolved Zr ($< 0.2 \mu\text{m}$). Hence, organic ligands, e.g. siderophores, may complex and stabilize Zr in the dissolved phase leading to the observed increase with depth.

Depth profiles of Mo and W reveal deviations from the commonly assumed conservative depth distribution, which seem to correspond to specific parameters such as atmospheric input and freshwater discharge. Off West Africa at approx. 20°W , an area influenced by Saharan dust deposition, Mo and W were slightly depleted in surface waters indicating sorption onto deposited mineral particles. Contrary, Saharan dust seems to be a source for dissolved V in surface waters. Release of V and Mo from riverine particulate matter transported with the Amazon might cause the slightly higher concentrations of both metals compared to sampling sites not affected by the Amazon discharge. Since W is assumed to be higher concentrated in the Amazon compared to the average Atlantic seawater, mixing with freshwater might explain the increase in concentration in this area. Although Mo is essential for enzymatic processes biologically influenced distribution patterns with depth have not been observed in the investigated area in the Atlantic Ocean.

The interest in Cr isotopes increased significantly in the past five years due to their application as a paleoproxy for ancient seawater. As a base for these studies Cr speciation under varying oxygen conditions has been investigated at three stations in the Pacific (filtered samples, research cruise GP13) and three in the Atlantic (unfiltered samples, research cruise M81/1) applying a cathodic adsorptive stripping voltammetric method. The hexavalent Cr species, Cr(VI), was the dominant species throughout the water column in the South Pacific reflecting the depth profile of Cr(total), while Cr(III) was abundant at a rather constant background concentration of around $1.73 \pm 0.54 \text{ nmol/L}$. Dissolved oxygen did not significantly affect the distribution of Cr redox species in the South Pacific samples. A consistent trend in the distribution of Cr(total), Cr(VI), and Cr(III) in the Atlantic Ocean has not been observed. Trivalent Cr and Cr(total) concentrations off West Africa were lower compared to the area investigated in the West Atlantic, which might be due to sorption onto deposited mineral particles. In the South Pacific and the (sub)tropical Atlantic, Cr(III) consisted almost quantitatively of Cr(III_unreactive), which is the Cr(III) fraction of stable organic or inorganic complexes. Photoreduction processes and organic complexation seem to control Cr(III) concentrations in both investigated areas.

This spatially high resolved study on metals from subgroups IV, V, and VI highlights the influence of regional parameters on the distribution of dissolved Zr, Nb, V, Mo, W, and Cr in the Atlantic Ocean and details the understanding of their (bio)geochemical processes

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1 Objectives of this thesis and structure

1.1 Objectives of this thesis

This PhD-thesis focuses on the depth distribution of elements of the subgroups IV, V, and VI of the periodic table of elements in seawater. Titanium (Ti), zirconium (Zr), and hafnium (Hf) belong to subgroup IV. Subgroup V consists of vanadium (V), niobium (Nb), and tantalum (Ta). Subgroup VI consists of chromium (Cr), molybdenum (Mo), and tungsten (W). Several of these elements are characterized as micronutrients (V, Mo) and microtoxins (Cr), whereas all of these elements are considered as high-tech elements and are required for various industrial applications.

Most of the elements of interest in this study are present in seawater in the range of pmol/kg (Ti, Zr, Hf, Nb, Ta, W). The determination of ultratrace metals in seawater is challenging and faces two major problems: (1) due to the very low concentration range preconcentration is required and (2) the seawater matrix needs to be separated since seawater components may interfere during the analytical detection or produce artefacts which may cover inner parts of the analytical device. Moreover, the laboratory environment needs to be optimized to reduce potential contamination risks during sample pretreatment. Also metals which are present in the range of nmol/kg (V, Mo) benefit from matrix separation due to the reduction of matrix interferences during the analysis. This study aims at the determination of metals from subgroup IV, V, and VI (except Cr) trace metal-clean collected seawater samples applying the commercially available online-preconcentration system, SeaFAST.

Titanium, Zr, Hf, Nb, and Ta belong to the group of high-field strength elements (HFSE) and are enriched in valuable ore deposits on the seafloor such as ferromanganese nodules and crusts, which are discussed as potential new resources. These metals are characterized by their particle-reactive behavior in the marine water column, and a decrease in concentration with depth is expected. Nonetheless, the concentration of dissolved Zr had been found to increase with depth in the Pacific Ocean (Firdaus et al., 2011, 2008). A source for Zr in deep waters was suggested to explain the observations in this specific region in the Pacific but whether this is a global feature is not yet fully understood. Deviations from the expected depth profiles have also been reported for Hf and Ta (Firdaus et al., 2008) showing an increase in concentration with depth. This research question

also applies to the water depth distributions of Ti and Nb which are also particle-reactive. Studies on this physico-chemical group of metals and their behavior in the marine environment have been published for the Pacific Ocean (Firdaus et al., 2011, 2008; McKelvey & Oriens, 1993; Sohrin et al., 1998a). Only a few studies about Ti, Zr, and Hf are available for the Atlantic Ocean (Godfrey et al., 1996; Skrabal, 2006), while data about dissolved Nb and Ta have not yet been published for the Atlantic. Both, the Pacific and Atlantic Ocean, are influenced by different sources, e.g. dust, riverine, and hydrothermal input, which might affect the concentration range and the depth distribution patterns of the elements of interest. Hence, this study aims to narrow this gap of knowledge providing data on dissolved Ti, Zr, Hf, Nb and Ta for the Atlantic Ocean. An interoceanic comparison with published data for the Pacific Ocean is intended which may reveal regional features.

Dissolved V, which is essential for bioproductivity as an enzyme component (Almeida et al., 2001), has been reported to display a nutrient-like depth profile in oceanic waters (Jeandel et al., 1987). A slight depletion in surface waters compared to deep waters has been observed with a more pronounced effect in the Pacific Ocean (Collier, 1984) than in the Atlantic Ocean. This work provides a spatially high resolved study on dissolved V in the Atlantic revealing potential regional sources of V to surface waters or scavenging mechanisms for dissolved V.

Tungsten and Mo are present in the Earth's Upper Continental Crust in a similar concentration range. Their concentrations, however, differ significantly in the marine environment, where the concentration of dissolved W is by a factor of 2000 lower compared to dissolved Mo. Dissolved W and Mo are assumed to be conservatively distributed in the oceanic water column. Nevertheless, significant deviations from the conservative water depth profiles have been observed in estuaries (Rahaman et al., 2014, 2010; Strady et al., 2009) and in the Okinawa Trough in the East China Sea (Sohrin et al., 1999). This indicates that W and Mo differ in their biogeochemical behavior, although they both belong to subgroup VI of the periodic table of elements, and similarities regarding their chemical properties can be expected. By now, a few studies about dissolved W and Mo in the Pacific Ocean have been published (Firdaus et al., 2008; Sohrin et al., 1999, 1987), while the number of publications for the Atlantic is limited (Hartung, 1991; Morris, 1975). This study intends to elucidate the biogeochemical cycling of dissolved W and Mo in the Atlantic Ocean and to compare obtained data with depth profiles published for the Pacific Ocean.

The redox speciation of Cr in the oceanic water column is of interest for this PhD-project. In seawater, Cr is mostly present in two oxidation states, +III and +VI, and both species differ in their physico-chemical properties influencing their bioavailability and toxicity. Thermodynamic calculations predict Cr(VI) to be the dominant species in oxic sea-

water but significant amounts of Cr(III) have been observed in the oceanic water column (Sander et al., 2003a). Recently, Cr isotopes have been applied to reconstruct oxygen conditions of ancient and modern oceans (Bonnand et al., 2013; Frei et al., 2011). Since every Cr redox reaction influences the ratio between the Cr isotopes, it is essential to understand the biogeochemical behavior of Cr as a base for the interpretation of isotopic data.

Global climate change will affect the current conditions of the world oceans, e.g. changes in continental run-off, atmospheric deposition, and the distribution of dissolved oxygen, which has a significant influence on the geochemical conditions for trace metals in marine waters. Biological activity of the elements of interest, their accumulation on ore deposits on the seafloor as well as their previously mentioned applications, either in the scientific or industrial sectors, demonstrate the importance to understand their biogeochemical cycling in the oceanic water column.

1.2 Structure of this thesis

This cumulative PhD-thesis comprises eight chapters of which the first presents the objectives of this thesis and its structure. Chapter 2 provides an overview of the physico-chemical properties of the elements of interest in marine waters as well as a description of the up to now applied analytical methods for their determination in seawater. Chapter 3 includes a published manuscript about the newly developed method. Its application is described in chapters 4 and 5, of which the first one is a published manuscript. Cr redox speciation in the marine water column is presented in chapter 6 followed by the concluding remarks for the whole thesis in chapter 7. Finally, a section about the related scientific work closes this work (chapter 8). References for all chapters including the published manuscripts are summarized in the bibliography section.

The introduction (chapter 2) provides an overview about the properties of the metals of subgroups IV (Ti, Zr, Hf), V (V, Nb, Ta), and VI (Cr, Mo, W) in the marine environment. The concentration range of these elements in seawater and their distribution with depth is described with a special focus on the Atlantic and Pacific Ocean. The relation of the elements of interest to biological activity, to potential sources, e.g. dust deposition or riverine discharge, and to scavenging processes, e.g. adsorption processes, in the oceanic water column is highlighted. Their distribution patterns in specific environments, e.g. hydrothermal plumes or anoxic basins, are also included in chapter 2. An overview of the up to now applied analytical techniques to determine the nine metals in seawater is provided followed by a subsection on the methods used within this thesis. Additionally, the sampling sites, the sampling techniques, and the pretreatment of all seawater samples collected for the analysis within this work are described.

In the third chapter a method development for the analysis of trace metals (Ti, Zr, V, Nb, Cr, Mo, W) in seawater using the commercially available SeaFAST-device for preconcentration combined with subsequent inductively coupled plasma - mass spectrometry (ICP - MS) analysis is presented. The method enables simultaneously performed preconcentration of the elements of interest and matrix separation. The preconcentrated sample is directly transported to the analytical device (ICP - MS) decreasing the risk of contamination significantly compared to off-line methods. The newly developed method and its application to Atlantic seawater samples is presented in the paper '**Determination of Ti, Zr, Nb, V, Mo and W in seawater by a new online-preconcentration method and subsequent ICP-MS analysis**', which has been published in the journal *Deep Sea Research: Part I* (Poehle et al., 2015).

An application of this method to determine dissolved Zr and Nb in Atlantic seawater is presented in chapter 4. Seawater samples were collected during a GEOTRACES research cruise (M81/1, RV Meteor, Feb. - March 2010) on an Atlantic transect from the Canary Basin along the West African coast crossing the Mid-Atlantic Ridge towards the Caribbean. The slight increase in concentration with depth observed for dissolved Zr in the Atlantic agrees with studies about dissolved Zr in the Pacific Ocean. A correlation between dissolved Zr and Si has been observed for most stations indicating that Zr may couple to the Si cycle in the oceanic water column through e.g. sorption onto Si particles and release in deep waters. In order to investigate the role of colloids for potential stabilization of dissolved Zr in deep waters a sequential filtration approach ($< 0.015\ \mu\text{m}$ and $< 0.2\ \mu\text{m}$) was performed on Pacific seawater samples collected close to a hydrothermal plume (cruise SO229, RV Sonne, July 2013). The results reveal that the colloidal fraction ($0.015\ \mu\text{m} - 0.2\ \mu\text{m}$) plays only a minor role for the dissolved Zr phase. Organic complexation with e.g. siderophores contributing to the fraction $< 0.015\ \mu\text{m}$ might be a viable explanation for the observed increase in concentration. Along the Atlantic transect dissolved Nb showed a conservative distribution with depth, except for a slight surface minimum off the West African coast, and the concentration range agrees with studies published for the Pacific Ocean. Data on dissolved Nb have only been published for the Pacific Ocean, and we present for the first time data for the Atlantic Ocean. This manuscript entitled '**Depth distribution of Zr and Nb in seawater: The potential role of colloids or organic complexation to explain non-scavenging-type behavior**' has been published in the journal *Marine Chemistry* (Poehle & Koschinsky, 2017).

In chapter 5 water depth profiles of dissolved V, Mo, and W in the Atlantic Ocean are presented, which were obtained after application of the previously described online-preconcentration method. Seawater samples have been collected during GEOTRACES cruise M81/1. The results reveal deviations from the nutrient-like behavior of V in the marine water column and from conservative distributions of dissolved Mo and W. Data on dissolved aluminum (Al) were obtained from the same research cruise and imply that Saharan dust may have been deposited prior to the sampling campaign. Correlation of

these data with data on dissolved V, Mo, and W reveal that deposited mineral particles affect the distribution of V, Mo, and W significantly off West Africa. Riverine input from the Amazon may be significant in the West Atlantic as deduced from results on dissolved Fe from previous studies. The observed deviations from nutrient-like behavior for V and conservative distribution for W and Mo correlate with regional influences which are discussed in the manuscript '**Sources, biogeochemical cycling and depth distribution of dissolved V, Mo and W in the Atlantic Ocean**'. This manuscript is presently in preparation for submission.

The distribution of dissolved Cr(total) and its dominant redox species in seawater, Cr(VI) and Cr(III), in filtered Pacific samples (GEOTRACES research cruise GP13, June 2011) is presented in chapter 6. Although the hexavalent Cr species dominated throughout the water column, significant amounts of Cr(III) were observed. Photoreduction in surface waters and subsequent stabilization of Cr(III) by organic ligands may explain the observed Cr(III) abundance. The main part of Cr(III) consists of Cr(III_unreactive), which confirms our assumption of organic complexation. Unfiltered Atlantic seawater samples collected during GEOTRACES research cruise M81/1 have also been investigated. The area investigated in the East Atlantic is influenced by Saharan dust deposition and lower Cr(total) and Cr(III) concentrations in surface waters have been observed there compared to the samples collected in the West Atlantic. Sorption processes onto deposited mineral particles off West Africa may explain the observed lower concentrations in the East Atlantic. The significant abundance of Cr(III) at the three Atlantic sites may be explained by similar mechanisms as discussed for the Pacific samples. Data obtained in this study reveal that the oxygen conditions do not affect the Cr speciation to a significant extent and imply that redox-initiated fractionation of Cr isotopes may not occur under these conditions. The associated manuscript entitled '**Significant abundance of Cr(III) in oxic seawater: implications of stabilization mechanisms**' is prepared for submission to the journal *Marine Chemistry*.

Chapter 7 comprises concluding remarks and prospective research goals followed by chapter 8 which presents related scientific work such as stays abroad and conference proceedings.

At the end of the thesis the bibliography section contains all references cited in this thesis including also the references of the published manuscripts.

2 Introduction

This PhD-project is embedded into the international GEOTRACES program, which focuses on the determination of trace elements and their isotopes (TEI's) in the marine environment to identify processes and quantify fluxes controlling their distribution (<http://www.geotraces.org/>). Scientists worldwide from approx. 35 nations are involved in this program. They participate in research cruises, and provide their data on TEI's to build up a comprehensive database. In 2014 an important goal was achieved by releasing the first GEOTRACES intermediate data product (IDP) which includes hydrographic and geochemical parameters collected during 15 cruises within the past 3 years (Figure 2.1) and provides a better understanding about the biogeochemical cycles of TEI's and the ocean circulation.

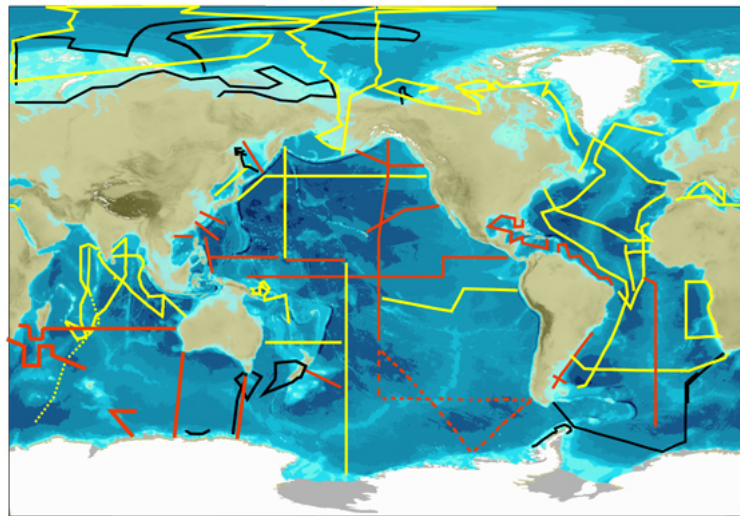


Figure 2.1: Overview of planned sections (red), completed sections (yellow), and completed sections contributing to the IPY (International Polar Year - black) within the GEOTRACES program.

The international program is a continuous effort providing quality-controlled datasets, sections plots and 3D scenes on the distribution of TEIs in many oceanic basins, and in 2016 the IDP version 3 has already been released.

Major sources of trace metals to the marine environment are dust particles, riverine discharge, release from the shelf sediment, and hydrothermal input. Depending on the geochemical properties trace metals undergo various processes in the marine water column, e.g. incorporation into biological matter, sorption processes, and redox reactions.

An overview of the general sources and sinks of trace metals in seawater is displayed in Figure 2.2.

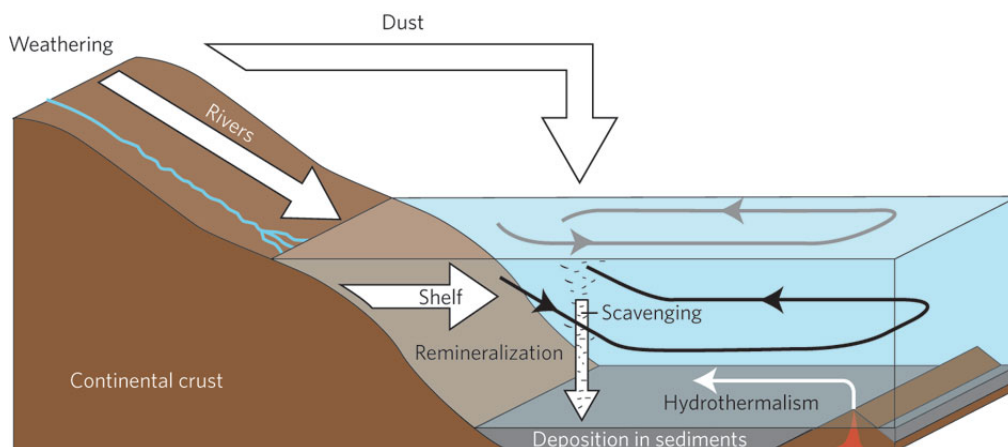


Figure 2.2: Sources and sinks of trace metals in seawater (Frank, 2011).

This PhD-work focuses on the determination of trace metals from subgroups IV, V, and VI of the periodic table of elements and results obtained will be provided to the international GEOTRACES community. Seawater samples have been collected on two GEOTRACES cruises: (1) research cruise M81/1 in February 2010 covered an area in the (sub)tropical Atlantic and (2) research cruise GP13 in June 2011 investigated an area in the South Pacific.

The following subsections provide an overview of the physico-chemical properties of the elements of interest in seawater. The metals are arranged according to their belonging to the groups of the periodic table of elements.

2.1 Subgroup IV: Ti, Zr, and Hf

The dissolved concentrations of the particle-reactive trace metals Ti, Zr, and Hf belong to the group of the high field strength elements (HFSE) and are characterized by their small ionic radii and high charges. They are present in seawater as neutrally charged (Ti(OH)_4 , Zr(OH)_4 , Hf(OH)_4) or negatively charged hydroxide species (Ti(OH)_5^- , Zr(OH)_5^- , Hf(OH)_5^-) which cause their high particle-reactivity.

2.1.1 Titanium

Titanium (Ti) is abundant in the Earth's Upper Continental Crust with a concentration of 0.086 mol/kg (McLennan, 2001). Its concentration, however, in Atlantic surface waters has been reported to range between 50 - 100 pmol/L (Dammshäuser et al., 2013), whereas Pacific surface and deep waters showed concentrations of 4 - 8 pmol/L and 200 - 300 pmol/L, respectively (Orians & Boyle, 1990). This demonstrates that the input

of Ti to the World Ocean through fluvial sources is reduced by up to 90 % at low salinities in estuarine mixing zones caused by coagulation of colloidal metals or adsorption onto particles (Skrabal, 1995). The laboratory study by Schneider et al. (2015a) on the distribution of dissolved Ti in estuarine mixing zones reported a strong depletion of dissolved Ti at low salinities. A distinct increase in concentration was observed at mid-salinities released from either marine or riverine particles probably due to changes in surface charges of particulate or colloidal matter. The neutrally charged Ti species ($\text{Ti}(\text{OH})_2^0$) is the dominant form (Byrne, 2002) in seawater and shows a pronounced tendency towards particles resulting in a short residence time of 100 - 200 years (Orians & Boyle, 1990). The water depth profile of Ti deviates from a typical particle-reactive pattern and shows a slight depletion in surface waters followed by an enrichment in deep waters in the North Pacific possibly caused by biological uptake in surface waters and deep remineralization at the sediment-water - interface (Orians & Boyle, 1990). Skrabal & Terry (2002) observed near-bottom maxima of Ti in the Mid-Atlantic Bight and reported potential release from marine sediments and corresponding benthic fluxes of Ti.

Since Ti is a promising tool to trace atmospheric dust input over longer time scales (Dammshäuser et al., 2011), this study aims to provide data of dissolved Ti for the (sub)tropical Atlantic with the potential use for future dust flux models.

2.1.2 Zirconium and Hafnium

Zirconium (Zr) and hafnium (Hf) show abundances in the Earth's Upper Continental Crust of 2.08 mmol/kg and 0.03 mmol/kg, respectively (McLennan, 2001), while they are less abundant in seawater ranging in ultratrace concentrations of around 155 pmol/kg and 0.33 pmol/kg, respectively (Firdaus et al., 2011). Since both metals enter the marine environment mainly through riverine input, dissolved Zr seems to get preferentially scavenged in estuaries compared to dissolved Hf.

The negatively charged hydroxide species, $\text{Zr}(\text{OH})_5^{-1}$ and $\text{Hf}(\text{OH})_5^{-1}$, dominate over the neutrally charged species, $\text{Zr}(\text{OH})_4^0$ and $\text{Hf}(\text{OH})_4^0$, in seawater and are responsible for the high particle-reactivity of both trace metals (Byrne, 2002). Hence, a decrease in dissolved concentration with increasing water depth is expected due to sorption processes onto sinking particulate matter (Figure 2.3). However, deep Pacific waters were reported to be enriched in Zr compared to surface waters (Firdaus et al., 2011, 2008; McKelvey & Orians, 1993). Inputs from coastal and bottom sources were suggested for Zr, and a nutrient-like scavenging-regeneration behavior may cause the distinct depth pattern of dissolved Zr observed in the northeastern Atlantic Ocean (Godfrey et al., 1996). Moreover, complexation with organic ligands might play an important role stabilizing Zr as colloiddally bound metal species in the dissolved phase (Poehle & Koschinsky, 2017).

The determination of Hf in seawater gained more attention in recent years, since its isotopic composition is a promising proxy to assess changes in continental weathering in

the past (van de Flierdt et al., 2002).

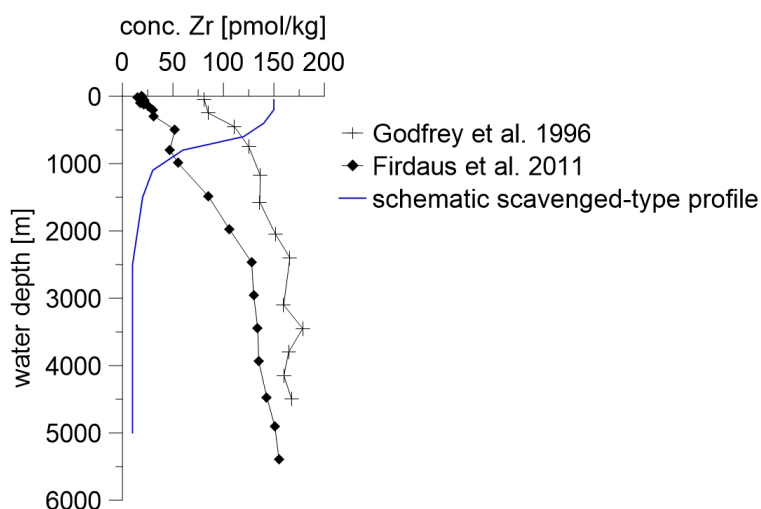


Figure 2.3: The blue pattern displays the typical water depth profile of particle-reactive elements in seawater. Water depth profiles of dissolved Zr in the North Atlantic (data taken from Godfrey et al., 1996), and the South Pacific (data taken from Firdaus et al., 2011-supplementary material) show an opposing behavior to the typical pattern.

The effects of the lanthanide contraction cause similar atomic and ionic radii of Zr and Hf. Both trace metals also resemble in their geochemical behavior, and, thus, they are classified as chemical twins. The ratio between both elements is expected not to be significantly affected by biogeochemical processes. Distinct changes in the Zr/Hf-ratio have been reported indicating a more pronounced removal of Hf from deep waters compared to Zr (Firdaus et al., 2011). Since the distribution of this chemical twin pair was suggested to trace paleocirculations in combination with other parameters (Frank, 2011), it is essential to assess their fractionation. Therefore, more research on both metals is needed since their distributions in seawater seem not to be as simple as previously assumed.

2.2 Subgroup V: V, Nb, and Ta

2.2.1 Vanadium

The average concentration of vanadium (V) in river waters has been calculated to be 14 nmol/kg (Gaillardet et al., 2014), while V was observed at concentrations of 35 ± 3 nmol/kg in the Atlantic and at 45 - 52 nmol/kg in Pacific waters (Jeandel et al., 1987). The higher concentrations in seawater compared to river waters indicate that atmospheric deposition could be a source for V in the marine environment.

A conservative depth distribution was observed in Atlantic waters (Jeandel et al., 1987), while a slight surface depletion has been observed in the Pacific Ocean (Collier, 1984).

An increase in concentration of V in deep marine waters has been reported from Atlantic waters via the South Atlantic and Indian Ocean to the Pacific Ocean. This correlates with the biological recycling of V (Middelburg et al., 1988), since V is required for the formation of enzymes in various algae and fungi species (Almeida et al., 2001). Hence, the depth distribution pattern of V may be described as that of a bioactive element and resembles the cycling of the nutrient phosphate.

The most stable oxidation state of V in seawater at neutral pH is +V, and fully hydrolyzed vanadate species (HVO_4^{2-} , H_2VO_4^- , NaHVO_4^- , Wehrli & Stumm, 1989) are dominant. These V species are characterized by low particle-reactivity, and complexation with organic matter does not significantly affect the distribution of V in seawater (Shiller & Boyle, 1987; Turner et al., 1981). In contrast, the reduced V form (VO^{2+}) is scavenged from the dissolved phase and transported to anoxic organic-rich sediments (Emerson & Husted, 1991). At hydrothermally active sites V has been reported to be removed from the dissolved phase only in the buoyant part of the hydrothermal plume, since V appeared probably in its reduced cationic form (German et al., 1991).

Since V is applied in various industrial processes, e.g. the steel industry, it may be used as a parameter for anthropogenic input to the oceans (Moskalyk & Alfantazi, 2003).

2.2.2 Niobium and Tantalum

Niobium (Nb) and tantalum (Ta) belong to the group of HFSE like Zr and Hf. Their abundances in the Earth's Upper Continental Crust has been reported to be 125 $\mu\text{mol/kg}$ for Nb and 5.1 $\mu\text{mol/kg}$ for Ta (Hu & Gao, 2008), while they occur in seawater in ultratrace concentrations, 3.1 pmol/kg and 0.087 pmol/kg, respectively (Firdaus et al., 2011). Both trace metals are mainly introduced through riverine input, and significant removal in estuaries causes the observed pronounced decrease in concentration from fluvial to the marine environment. In seawater, neutrally and negatively charged hydroxide species ($\text{Nb}(\text{OH})_5^0$, $\text{Ta}(\text{OH})_5^0$, $\text{Nb}(\text{OH})_6^{-1}$, $\text{Ta}(\text{OH})_6^{-1}$) are assumed to be the dominant forms (Byrne, 2002), although Nb and Ta may also be present as oxyacids like V which belongs to the same subgroup V of the periodic table of elements (Sohrin et al., 1998a).

A slight depletion of dissolved Nb had been observed in North Pacific surface waters (Firdaus et al., 2011), while Sohrin et al. (1998a) reported a rather homogeneous distribution from surface to deep waters for Nb and Ta, 3.0 - 3.8 pmol/kg and 0.08 - 0.20 pmol/kg, respectively. Both metals can be considered as a pair of chemical twins, like Zr and Hf. The uniform depth patterns of Nb and Ta reveal a lower reactivity in seawater compared to Zr and Hf. Nevertheless, variations of the Nb/Ta ratio have been observed in Pacific waters indicating a preferential scavenging of Ta compared to Nb, despite their chemical similarities. The fractionation processes may already start in estuaries (Firdaus et al., 2011). Until now dissolved Nb and Ta have only been investigated in the Pacific Ocean, and thus it cannot be excluded that the reported water depth profiles might reflect regional

features.

2.3 Subgroup VI: Cr, Mo, and W

2.3.1 Chromium

Chromium (Cr) enters the marine environment through atmospheric and riverine input (Geisler & Schmidt, 1992), but its application in various industries, e.g. metallurgy and the production of pigments, adds also an anthropogenic fraction to the oceans through the discharge of industrial effluents. In the marine environment dissolved Cr(total) is present in two stable oxidation states: Cr(III) which is predominantly present as $(\text{Cr}(\text{H}_2\text{O})(\text{OH})_2^+)$ and Cr(VI) present as chromate (CrO_4^{2-}) . Both redox species differ significantly in their physico-chemical properties (Gardner & Ravenscroft, 1996). While Cr(III) has a strong tendency to sorb onto particulate matter and is an essential micronutrient, Cr(VI) is characterized by low particle-reactivity and high solubility in seawater and acts as a microtoxin crossing cell membranes (Kotaś & Stasicka, 2000).

Marine Cr(total) can also be divided into (1) reactive Cr which includes free and labile bound species and (2) unreactive Cr. The first fraction consists of the chemically inactive Cr(VI) which does not form complexes with organic ligands, and Cr(III_reactive) which has no or only labile bound organic ligands. The second fraction consists of Cr(III_unreactive), meaning that Cr(III) is bound in stable complexes.

Thermodynamic calculations for oxic seawater predict Cr(VI) to be the dominant redox species (Elderfield, 1970) which contrasts observations in seawater and results obtained from samples collected at hydrothermally active sites in the Pacific Ocean (Sander et al., 2003a). Complexation with organic ligands stabilizing Cr(III) in the dissolved phase as well as photoreduction of Cr(VI) to Cr(III) have been suggested as explanations for the significant amounts of Cr(III).

The redox species of Cr have been studied widely in river waters (D'Arcy et al., 2016; McClain & Maher, 2016; Pettine et al., 1992) and waste waters (Gürkan et al., 2012). But studies on Cr redox species are limited to a few in the marine environment (Pettine et al., 1997, 1991; Pettine & Millero, 1990; Sander et al., 2003a; Sander & Koschinsky, 2000). Recently, Cr isotopes have been used as tracers for past atmospheric oxygen conditions (Crowe et al., 2013) and for the oxygenation history of the atmosphere-ocean system (Frei et al., 2011, 2009). Every redox-reaction in seawater directly influences the distribution of Cr isotopes (Paulukat et al., 2016; Scheiderich et al., 2015; Semeniuk et al., 2016), since the lighter isotope is preferentially used in chemical reactions. With the increasing number of applications of Cr isotopes (Bonnand et al., 2013, 2011) it is essential to understand the biogeochemical cycling of Cr and its redox species, Cr(III) and Cr(VI), in the marine water column as a base for isotopic studies.

2.3.2 Tungsten and Molybdenum

Although tungsten (W) and molybdenum (Mo) are almost equally abundant in the Earth's Upper Continental Crust with concentrations of 7.61 $\mu\text{mol/kg}$ and 6.25 $\mu\text{mol/kg}$, respectively (Hu & Gao, 2008), W is less abundant (40 - 51 pmol/kg, Firdaus et al., 2008) in seawater compared to dissolved Mo (97 - 105 nmol/kg, Firdaus et al., 2008). This indicates a preferential removal of W probably due to sorption onto particulate matter in estuaries or in the marine environment. Both metals are present in seawater as oxyacids (WO_4^{2-} and MoO_4^{2-}), and they have been reported to be conservatively distributed with depth (Collier, 1985; Sohrin et al., 1987). Nevertheless, Sohrin et al. (1999) reported anomalously high concentrations of W (254 pmol/L) below 1000 m water depth in the Okinawa Trough, East China Sea, possibly caused by hydrothermal activity. Significantly higher W concentrations (0.21 - 123 nmol/kg) compared to its average concentration in seawater have been reported for hydrothermal fluids (Kishida et al., 2004), and W was suggested as a parameter to assess water-rock interactions during hydrothermal cycling. In fluid-seawater mixing zones W increases linearly with increasing magnesium (Mg) concentration while the Mo concentration decreases due to the formation of sulfides and subsequent precipitation. Hence, hydrothermal active sites may not only represent a source but also an oceanic sink due to the precipitation of emitted metals and metals from ambient seawater with Fe(oxy)hydroxides from the plumes (Elderfield & Schultz, 1996). The pronounced release of W from anoxic sediments of the continental shelf might also cause differences in the distribution between W and Mo in seawater (Sohrin et al., 1999).

Dissolved Mo shows conservative depth patterns, although it is an essential element for biological processes (Mendel, 2005). Deviations from this pattern have been observed in anoxic basins (Alb ric et al., 2000; Colodner et al., 1995) and in estuarine mixing areas (Rahaman et al., 2014, 2010; Schneider et al., 2016; Strady et al., 2009) which were often due to ad- and desorption processes with particulate matter. The formation of larger Mo enriched aggregates caused non-conservative behavior in sandy tidal flat areas (Dellwig et al., 2007). However, deviations related to biological processes have not yet been reported. The natural dissolved concentration of Mo exceeds the biological needs and the sensitivity of the applied methods might not have been sufficient to detect small variations in concentration to trace the involvement of Mo in biological processes. The interest in Mo isotopes increased during the past 10 years, and they have been studied in riverine fluxes (Archer & Vance, 2008), during adsorption processes in the marine environment (Barling & Anbar, 2004; Goldberg et al., 2009), and were applied as proxies to trace global redox changes (Scott & Lyons, 2012; Xu et al., 2012).

Tungsten and Mo are chemical analogues, but their behavior in the marine environment seems to differ. Dissolved W and Mo have been studied widely in the Pacific (Collier, 1985; Firdaus et al., 2008; Sohrin et al., 1999, 1987). For the Atlantic Ocean a few studies are published for Mo (Morris, 1975; Riley & Taylor, 1972), and only one study

focused on W in the North Atlantic (Hartung, 1991).

2.4 State-of-the-art analytical methods

2.4.1 Determination of Ti, Zr, Hf, V, Nb, Ta, Mo, and W in seawater

Published methods for the analysis of trace metals in seawater often consist of two separate steps: (1) a preconcentration and matrix separation process and (2) the analytical determination. Since the dissolved concentrations of Ti, Zr, Hf, Nb, and Ta in seawater are in the range of nmol/kg, preconcentration is necessary to increase the signal to noise ratio prior to the analysis. Single-element methods have been used for the preconcentration and determination of dissolved Ti and Zr in seawater. Voltammetry was applied to determine dissolved Ti (Croot, 2011), and MnO₂-impregnated fibres were used to extract Zr from large volume seawater samples (Norisuye et al., 2000).

Multi-elemental methods have been published for the simultaneous preconcentration of Zr and Hf using co-precipitation with Fe(hydroxide) (Boswell & Elderfield, 1988; Godfrey et al., 2008, 1996) or applying a solid-phase extraction with the resin Chelex 100 (McKelvey, 1994; McKelvey & Orians, 1998, 1993). A simultaneous determination of Zr, Nb, and W has been published using a manually synthesized resin, TSQ-8HQ (Firdaus et al., 2007). This preconcentration process was performed in a closed system decreasing the risk of contamination significantly. Vanadium and Mo are required for biological processes in the marine water column, and small variations in concentration might elucidate biological activity or other processes, e.g. scavenging. The detection of these small changes in concentrations is challenging, since both metals are present in the range of nmol/kg in seawater which is high. Matrix-separation prior to the analysis decreases potential interferences during the analytical detection and minimizes the risk of the formation of residues from the seawater matrix in the analytical device. Solid-phase extraction of V has been performed using Chelex 100 resin prior to the detection of total V with inductively coupled plasma - atomic emission spectrometry (ICP - AES) (Dupont et al., 1991) and of the two redox species, V(V) and V(IV), after sequential elution with graphite furnace atomic absorption spectrometry (Wang & Sañudo-Wilhelmy, 2008). Dissolved Mo was preconcentrated with Cobalt - APDC (ammonium pyrrolidine dithiocarbamate) and was detected via the thermal atomization - atomic absorption spectrometry (AAS) (Collier, 1985).

The procedure blank of these methods is very low compared to the natural concentrations of the elements of interest in seawater. Sample preparation and analysis, however, often take several days, which is time-consuming and cost-intensive especially if single-element methods are applied. The analysis of several trace metals in the same analytical run and the application of a closed system connecting preconcentration and the analytical device directly will reduce the amount of applied chemicals, costs and time.

2.4.2 Determination of Cr redox species

Different techniques have been applied for the determination of Cr(III), Cr(VI), and Cr(total). Due to the low concentration of dissolved Cr in seawater preconcentration has been applied often prior to the analysis. Furthermore, seawater is a challenging matrix for trace metal analysis due to the potential clogging of some parts of the analytical device and the interferences of seawater components during the analysis. Therefore, matrix separation is an essential process in sample preparation.

The first step, sample storage of seawater dedicated to redox speciation, is crucial and requires conservation of the initially present distribution of the redox species avoiding interconversion of the species. Field measurements of Cr redox species is an important approach to secure the immediate species distribution and to reflect the realistic pattern. Mugo and Orians (1993) presented a sensitive sea-going method to determine Cr(III) and Cr(total) in seawater samples. Trivalent Cr, Cr(III), forms volatile chelates with 1,1,1-trifluoroacetylacetylone (HTFA) and was preconcentrated in the organic phase during the subsequent solvent extraction. Electron-capture gas chromatography was applied for the detection of Cr(III). The concentration of Cr(total) was determined after reduction of Cr(VI) to Cr(III) applying the same analytical method as described for Cr(III). On-site preconcentration of Cr(III) and of the combined fraction of Cr(III) and Cr(VI) using electrodeposition on a coiled-filament assembly made from rhenium (Re) was applied to seawater samples (Badiei et al., 2012). The analysis was performed in the laboratory with near torch vaporization (NTV) and subsequent detection via ICP - AES.

An online-preconcentration of Cr(III) and Cr(total) and the subsequent detection with ICP - MS is a suitable method with a reduced risk of contamination during sample handling (Hirata et al., 2000) in case preconcentration alone or combined with the analysis cannot be performed in the field. Manually prepared columns filled with iminodiacetate resin were used to preconcentrate Cr(III). After reduction of Cr(VI) to Cr(III) the concentration of Cr(total) was determined applying the same preconcentration method. Within 5 min the detection of Cr(III) and of Cr(total) in a seawater sample has been performed.

Another approach for the Cr speciation analysis in seawater demonstrated the direct determination of the main redox species, Cr(III) and Cr(VI) (Guerrero et al., 2012), instead of calculating Cr(VI) after determining Cr(total) as performed in the methods described previously. Using a flow-injection system Cr(III) and Cr(VI) have been retained on two different resins. The resin Amberlite IRA 910 anion exchange accumulated Cr(VI) as dichromate, while Cr(III) passed this column and sorbed onto the resin DPFH-gel (1-(di-2 pyridyl)methylene thiocarbonohydrazide). Both species were eluted individually with the same eluent, and the concentration was determined within a single scan by ICP - MS.

A variety of different preconcentration processes (liquid-liquid extraction, solid-phase extraction) and analytical techniques (ICP - AES, ICP - MS) have already been published for the speciation analysis of Cr in seawater. A voltammetric method for the direct analysis

of Cr(total), Cr(VI), and Cr(reactive) (Sander & Koschinsky, 2000) will be described later in subsection 2.5.2.

2.5 Analytical methods applied within this study

2.5.1 Online-preconcentration system method and ICP - MS analysis

Within this study we applied an online-preconcentration system called SeaFAST which consists of three basic components: (1) sample loop, (2) preconcentration column, and (3) two valves controlling processes for the sample loop and the preconcentration column (Figure 2.4).

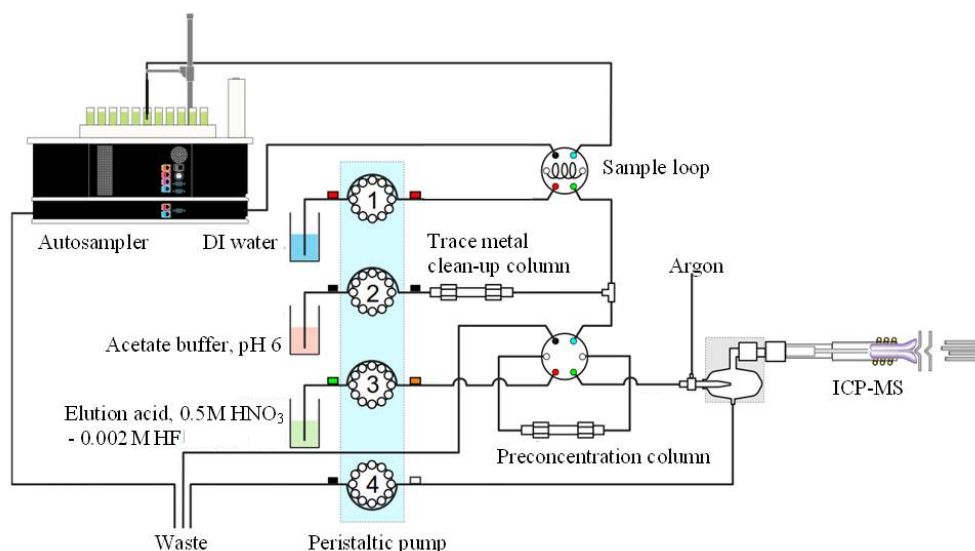


Figure 2.4: Schematic set-up of the SeaFAST preconcentration system (taken from Poehle et al., 2015).

The pre-packed preconcentration column of the SeaFAST system contains a chelating resin. The resin complexes cations and oxoanions by the two functional groups, ethylenediamine triacetic acid (EDTriA) and iminodiacetic acid (IDA), which are immobilized on a polymer backbone (Figure 2.5). Chelating resins are a subgroup of an ion exchange resin and are characterized by a higher selectivity. Metals are retained through coordinative covalent bonds or in combination with electrostatic interactions. The majority of the transition metals, all lanthanides and Al, gallium (Ga), indium (In), tin (Sn), lead (Pb) from main groups III and IV of the periodic table of elements are complexed by EDTriA and IDA. Since alkaline and alkaline earth metals pass the resin, matrix separation is performed simultaneously to the preconcentration process of the elements of interest. Elution of the retained metals with an appropriate eluting acid (0.5 mol/L HNO₃ - 0.002 mol/L HF) is performed in counter-current direction. The preconcentrated sample is directly trans-

ported to the quadrupole ICP - MS via a microflow concentric nebulizer and a cyclonic spray chamber. The transient signal is acquired in the appropriate time frame.

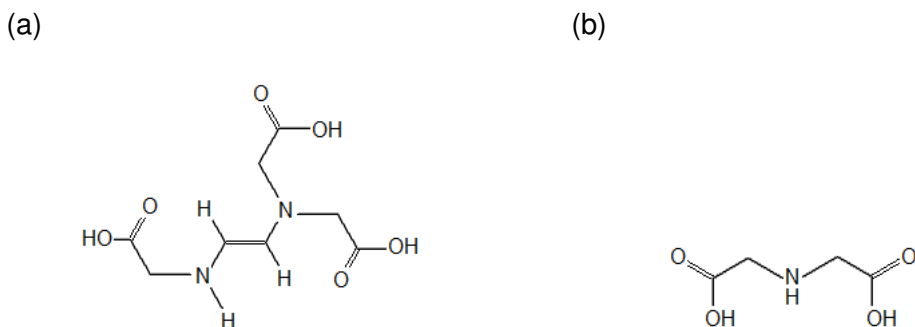


Figure 2.5: Chemical structures of ethylenediamine triacetic acid (a) and iminodiacetic acid (b).

The size of the sample loop can vary between very small volumes of 100 μL and comparably high volumes of 8 mL. Depending on the concentration of the elements of interest in seawater a suitable sample loop can be chosen. Since the majority of the metals investigated in this study are present in ultratrace concentrations (pmol/kg), an 8 mL sample loop was used. Molybdenum and V are present in the range of nmol/kg in seawater, and a smaller sample volume would be sufficient for the preconcentration leading also to a shorter time for the complete analysis. The sample loop, however, was not changed, since a higher priority was given to the potential risk of contamination due to opening the system to change the sample loop. A slightly longer time required for preconcentration and analysis of dissolved Mo and V was accepted.

2.5.2 Voltammetric analysis

Published methods for redox speciation analysis in seawater can be divided in two major groups: (1) separation of the redox species applying e.g. solid-phase extraction prior to the analytical detection and (2) direct analysis of the redox species in the seawater sample.

In this work a voltammetric method has been chosen for the direct determination of Cr(total), Cr(VI), and Cr(reactive) in the seawater sample. The analysis requires only a small sample volume of 30 mL, 10 mL per analytical run. The sample pretreatment is straight-forward and consists only of the pH adjustment of the sample and addition of chemicals. The applied method is cost-effective compared to methods which include separation of the redox species e.g. for Mo (Wang et al., 2009) and V (Wang & Sañudo-Wilhelmy, 2008).

A cathodic stripping voltammetry (CAAdSV) was applied to seawater samples, and the concentrations of Cr(total), Cr(VI), and Cr(reactive) were determined (Sander & Koschinsky, 2000). A hanging mercury drop electrode (HDME) served as a working electrode, whereas a platinum electrode and Ag/AgCl (3 mol/L) electrode were used as auxiliary

and reference electrode, respectively. In principle, this method uses the reduction of Cr(VI) to Cr(III) which forms electrochemically active complexes with diethylenetriamine-pentaacetic acid (DTPA) (Figure 2.6).

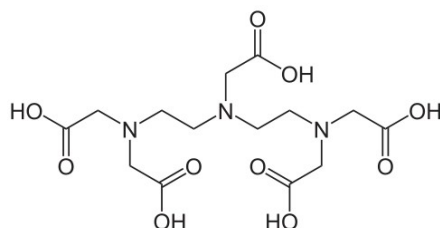


Figure 2.6: Structure of diethylenetriaminepentaacetic acid (DTPA).

For the determination of Cr(total) 10 ml of a seawater sample were filled into a quartz glass tube, and 50 μ l 30 % HCl and 20 μ l 30 % H₂O₂ were added. This mixture was placed into a UV-Digester (Metrohm) for 60 min at 90 °C. Decomposition of organic matter might release Cr to the dissolved phase. This Cr fraction as well as the initially present reduced Cr species, e.g. Cr(III), were oxidized to Cr(VI) during the UV-treatment. After the digestion step the sample was allowed to cool down to room temperature prior to the adjustment of the pH to 5.2 with 5 mol/L NaOH. The pretreated sample was buffered with a 1 mol/L ammonia-acetate buffer which was prepared of a glacial acetic acid and an ammonia solution. The 0.15 mol/L DTPA - 1 mol/L acetate buffer mixture (1 ml) and the 5 mol/L NaNO₃ (2 ml) were added to 10 ml sample volume resulting in total concentrations of 0.015 mol/L DTPA, 0.1 mol/L ammonia acetate buffer and 1 mol/L NaNO₃. The sample was then purged for 3 min, and the voltammetric analysis started under the conditions shown in Table 2.1.

Parameter	Operation conditions
Mode	Differential pulse
Stirrer [rpm]	2000
Purging time [s]	180
Nitrogen gas pressure [bar]	1
Deposition potential [V]	-1
Deposition time [s]	60
Equilibrium time [s]	5
Start potential [V]	-1
End potential [V]	-1.3
Pulse time [s]	0.04
Voltage step [V]	0.005951
Voltage step time [s]	0.4
Sweep rate [V s ⁻¹]	0.0149
Peak position [V]	-1.2 $\pm$ 0.08

Table 2.1: Parameters of the voltammetric determination

After UV-digestion all initially present Cr redox species exist as Cr(VI) in the form of

chromate which does not interfere with the added complexing agent DTPA (Sander et al., 2003b). At approx. - 50 mV Cr(VI) is reduced irreversibly to Cr(III) which forms immediately a Cr(III)/DTPA-complex on the mercury electrode surface. This electrochemically active complex is reduced further to Cr(II) at approx. - 1200 mV. The reoxidation to Cr(III) can be initiated by nitrate which serves as an oxidative catalyst increasing the voltammetric signal. A 2-fold standard addition was performed adding appropriate amounts of a 1.92 $\mu\text{mol/kg}$ Cr(VI)-standard solution which was prepared weekly with de-ionized (DI) water. The concentration of Cr(total) was calculated using the peak height.

A non-digested seawater sample aliquot was used for the determination of Cr(VI). After pH adjustment to 5.2 with a glacial acetic acid, and the addition of the DTPA-buffer mixture, and the nitrate solution the sample was purged for 3 min and a waiting period of 30 min started to allow that the present Cr(III) complexes with DTPA. A homogeneous 2-step reaction was suggested for the complexation of hydrated Cr(III) with the added DTPA (Sander et al., 2003b). In the first reaction step an electroactive 1:1 Cr(III)/DTPA-complex is formed which does not sorb significantly onto the electrode surface. An electrochemically inactive form, probably a 1:2 Cr(III)/DTPA-complex, is produced in the second reaction step and the Cr(III)-ion is sterically shielded by two DTPA molecules. After the waiting time the analysis was started as described in Table 2.1.

For the determination of Cr(reactive) the pH of a non-digested seawater sample was adjusted to 5.2, the chemicals DTPA-buffer mixture and oxidative catalyst were added, and the determination started as shown in Table 2.1.

While Cr(total), Cr(VI), and Cr(reactive) were measured directly further fractions can be calculated. Subtraction of Cr(VI) from Cr(total) results in Cr(III) and Cr(VI) being subtracted from Cr(reactive) results in Cr(III_{reactive}).

Reagent blanks of Cr(total) were measured daily using DI water and were used to correct all results obtained for Cr(total), Cr(VI), and Cr(reactive).

2.6 Sampling sites and sampling equipment

The description of the sampling sites and the respective sampling procedures is divided into two subsections according to the two research topics investigated in this study:

- Analysis of trace metals (Ti, Zr, Hf, V, Nb, Ta, W, Mo) in seawater including the role of the colloidal phase (subsection 2.6.1)
- Chromium redox speciation in the marine water column (subsection 2.6.2).

2.6.1 Samples collected for the trace metals analysis

Within this GEOTRACES project seawater samples were collected during two research cruises. Seawater collected in the (sub)tropical Atlantic during research cruise M81/1 was

filtered applying 0.2 μm pore size filters, and samples collected in the Pacific Ocean during research cruise SO229 were filtered sequentially (0.2 μm and 0.015 μm) to investigate the colloidal fraction of the trace metals of interest.

The cruise track of the GEOTRACES research cruise M81/1 (GA11, Feb. 4th - March 8th, 2010) covered parts of the (sub)tropical Atlantic. The vessel started in the Canary Basin sailing southwards at 20°W along the West African coast and turned westwards at approx. 11°S towards the Brazil Basin to finally end in the Caribbean (Figure 2.7).

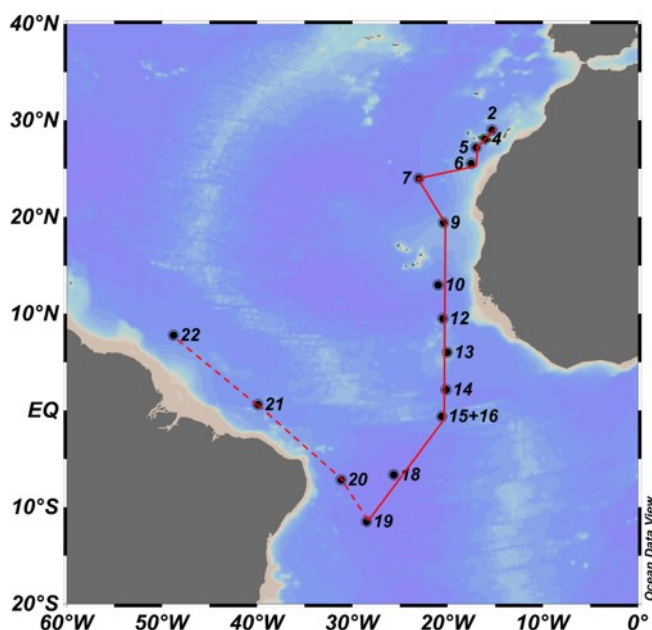


Figure 2.7: Map of research cruise M81/1 taken from Poehle et al. (2015). The numbers indicate station names. The solid red line connects sampled stations during the NE - SW transect, and the dashed red line connects stations sampled during the SE - NW transect.

Hence, areas influenced by different parameters, e.g. mineral input close to the Canary Islands, Saharan dust input off West Africa, and mixing with riverine freshwater close to the mouth of the Amazon in the western Atlantic, were covered.

Prior to the sampling campaign the high density polyethylene (PEHD)-bottles were cleaned in 3 steps: (1) rinsed with DI water, (2) filled with 0.5 mol/L HNO_3 - 0.01 mol/L HF and stored for 2 days at 60°C, (3) rinsed and filled with DI water and stored for 2 days at 60°C. After a final rinse with DI water the bottles were double sealed in plastic bags and packed for shipping.

Seawater samples were collected with a trace metal-clean conductivity, temperature, depth (CTD)-rosette equipped with 24 12 L Teflon coated GO-FLO water samplers, a Kevlar cable, and a specific mobile winch provided by the U.S. GEOTRACES partners. During the downcast of the CTD the water samplers were open and flushed with seawater. Sampling was performed during the upcast in specific depths, whereby the samplers

2.6. SAMPLING SITES AND SAMPLING EQUIPMENT

were closed controlled from on board the vessel allowing the bottles to be flushed with the respective water masses. Immediately after the CTD was back on-deck, the in- and outlet of the samplers were capped with plastic bags to reduce the risk of contamination. The samplers were then brought to a clean laboratory container (provided by U.S. GEOTRACES partners), where subsampling and filtration (0.2 μm cellulose acetate filters, Sartobran P-MidiCaps) were conducted.

The 1 L subsamples were stored in PEHD-bottles and had been acidified with HCl and HF (both ultrapure, Roth) to final concentrations of 0.02 mol/L - 0.002 mol/L, respectively. Finally, the seawater samples were stored dark and cool until the analysis in the home laboratory had been performed.

In total, 194 0.2 μm filtered seawater samples were collected at 16 stations in the (sub)tropical Atlantic, each resolved with approx. 15 different depths.

Research cruise SO229 (July 2013) covered a hydrothermally active area in the South Pacific, and was a good opportunity to receive seawater samples to investigate the colloidal phase of the trace metals of interest in this work. During this cruise the area east of the Vanuatu archipelago was covered with the main focus being on the hydrothermal activity along the island arc.

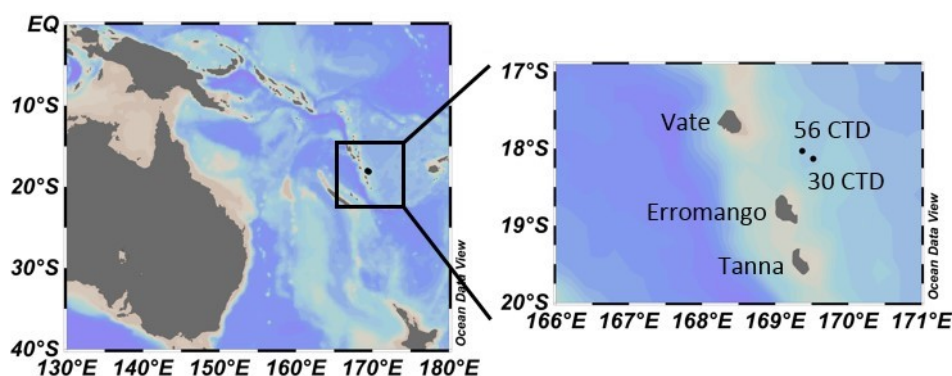


Figure 2.8: Sampling sites during SO229 (July 2013) for the investigation of the colloidal fraction of trace metals; 30 CTD represents the hydrothermally influenced water column, and 56 CTD represents the seawater background sample (taken from Poehle & Koschinsky, 2017).

A CTD-rosette frame equipped a turbidity sensor (SBE 911, Seabird Electronics) and 24 10 L NISKIN bottles was deployed. The sampling was performed during upcast of the CTD, and the water samplers were closed from on board the vessel between 1500 and 1700 m water depth at a location at the Nifonea Ridge (Figure 2.8, 30 CTD), southeast of the island Vate. At this specific site hydrothermalism was previously detected by a remotely operated vehicle (ROV KIEL 6000, Haase et al., 2009). Anomalously high Fe concentrations were detected compared to seawater concentrations from sites not being influenced from hydrothermal activity confirming the presence of a hydrothermal plume (Kleint et al., 2016).

A seawater background sample was collected north of the hydrothermal active area at 1600 m water depth (Figure 2.8, 56CTD) using the same sampling device.

Directly after the CTD was back on-deck subsampling and further treatment of the samples have been performed in a specifically prepared shipboard laboratory. Adhesive mats and air filters were used to approach the requirements to work with seawater samples dedicated to trace metal analysis. Subsamples were filtered sequentially with 0.2 μm cellulose acetate filters (Sartorius) and 0.015 μm polycarbonate filters (Sigma-Aldrich) under a clean bench and filled into PEHD-bottles. Acidification was performed with HCl and HF (both ultrapure, Roth) to final concentrations of 0.02 mol/L and 0.002 mol/L, respectively. The samples were stored under cool and dark conditions until the analysis in the home laboratory was conducted.

The cleaning procedures of the PEHD-bottles were identical with the three-stage process described for the Atlantic samples.

2.6.2 Samples for the analysis of Cr redox species

During GEOTRACES research cruise M81/1 seawater samples for the analysis of Cr redox species have been collected with the trace metal-clean CTD as described in subsection 2.6.1. Subsampling was performed in the clean laboratory container on board, and the unfiltered aliquots were filled in 100 ml low density polyethylene (PELD)-bottles, stored frozen on board, and transported back to the home laboratory under freezing conditions. Prior to the analysis the respective seawater sample was allowed to thaw overnight in a refrigerator at 4°C.

The cleaning process of the (PELD)-bottles consisted of 4 steps. At first the bottles were filled with 0.5 mol/L HNO_3 - 0.1 mol/L HF and stored for 3 days at 60°C. After a thorough rinse with DI water the bottles were filled with 0.5 mol/L HCl and stored again for 3 days at 60°C. The bottles were then soaked in DI water and packed in sealable plastic bags for transport.

Samples have been collected at three stations, and each was resolved with approx. 20 different depths (Figure 2.9). The first station (station 12 = station A1) was located off the West African coast and was probably influenced by Saharan dust input, while the other two stations (stations 18 = station A2 and 20 = Station A3) represent an open ocean area in the western Atlantic basin.

2.6. SAMPLING SITES AND SAMPLING EQUIPMENT

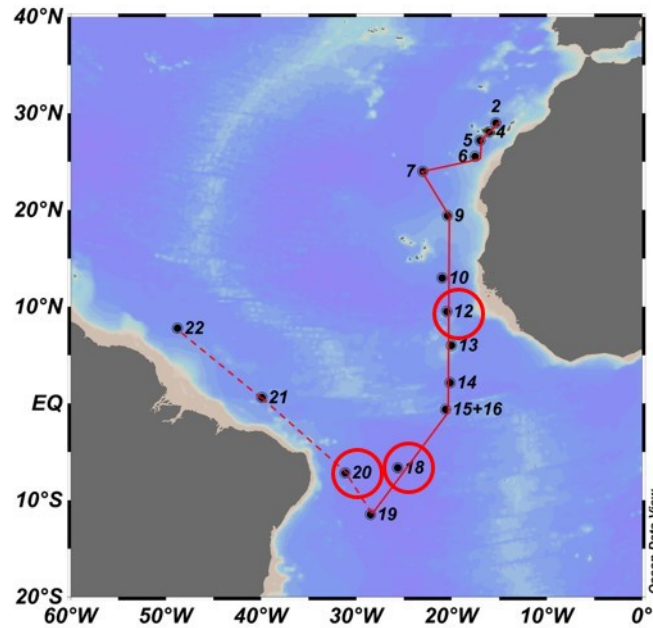


Figure 2.9: Stations sampled during research cruise M81/1. The red circles indicate the three stations selected to collect samples for Cr redox speciation analysis.

During GEOTRACES research cruise GP13 (June 2011) in the South Pacific seawater samples have been collected and filtered on board ($0.2\mu\text{m}$). The investigated area at the Kermadec Arc is known for its hydrothermal activity between the Australian and the Pacific Plate. We used the opportunity to obtain seawater samples from the South Pacific which were not influenced by hydrothermally active sites. Along a transect at 32°S three stations (P1, P2, and P3) have been selected for Cr speciation analysis and each was resolved with approx. 20 different depths (Figure 2.10).

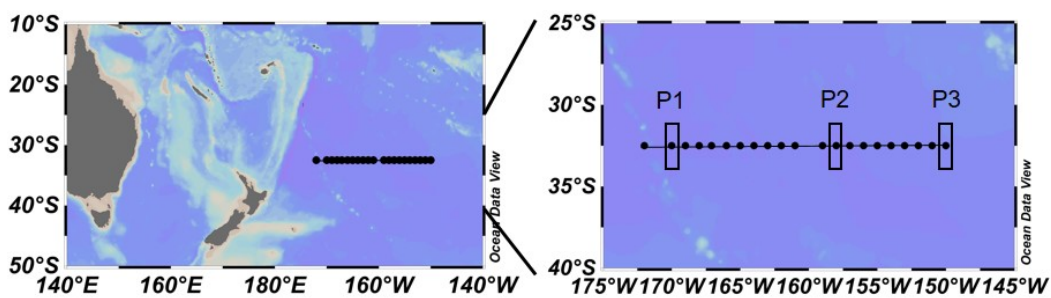


Figure 2.10: All stations sampled during GEOTRACES cruise GP13 (June 2011) are shown on the left side. Stations selected for Cr redox speciation (P1, P2, and P3) are indicated with a black frame in the close-up of all stations of GP13 (right).

Samples were taken with 12 NISKIN bottles which were mounted onto an autonomous trace metal-clean Rosette frame (General Oceanics, USA). The water samplers were controlled from on board the vessel and closed during upcast of the CTD. Directly after

the CTD was back on-deck the water samplers were brought into a clean laboratory container, and filtration was performed using 0.2 μm polycarbonate filter cartridges. The filtered aliquots were stored frozen in 100 ml PELD-bottles and transported under freezing conditions back to the home laboratory. The night before the analysis was started the respective sample was stored in a refrigerator at 4 °C and allowed to thaw overnight. The cleaning process of the PELD-bottles was performed in accordance with the procedure described for the Atlantic sampling bottles.

3 Preconcentration and analysis of trace metals

Title of publication

Determination of Ti, Zr, Nb, V, W and Mo in seawater by a new online-preconcentration method and subsequent ICP - MS analysis

Authors and affiliations

Sandra Poehle^{*1}, Katja Schmidt¹, Andrea Koschinsky¹

* Corresponding author. Tel.: +49 0421 2003261,

E-mail address: s.poehle@jacobs-university.de

¹ Earth and Space Sciences, School of Engineering and Science, Jacobs University Bremen
Campus Ring 1, 28759 Bremen, Germany

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Instruments and Methods

Determination of Ti, Zr, Nb, V, W and Mo in seawater by a new online-preconcentration method and subsequent ICP–MS analysis

Sandra Poehle^{*}, Katja Schmidt, Andrea Koschinsky

Earth and Space Sciences, School of Engineering and Science, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany



Abstract

We present a new method for the determination of Ti, Zr, Nb, V, W and Mo in seawater by adapting the online-preconcentration procedure with the system seaFAST and subsequent analysis by ICP-MS to these metals. The trace elements Ti, Zr, Nb and W are present in seawater in ultratrace concentrations in the range of pmol kg^{-1} , whereas Mo and V, which are biologically essential elements, are present in the concentration range of nmol kg^{-1} . The online - preconcentration system we used consists of an autosampler, a sample loop, a preconcentration column and two valves controlling the sample loop and the preconcentration processes. The pre-packed preconcentration column contains a chelating resin with two functional groups, ethylenediamine triacetic acid (EDTriA) and iminodiacetic acid (IDA), immobilized on a polymer backbone. The preconcentration process was optimized for loading the sample and subsequent rinsing to remove residues of seawater matrix prior to elution with the optimized elution acid (0.5 M HNO_3 -0.002 M HF). We used acidified North Sea seawater (0.02 M HCl - 0.002 M HF) for the method development. Samples and calibration standards were loaded onto the preconcentration column and after elution directly transferred to the quadrupole ICP-MS and measured immediately. Best results were achieved with matrix-matched calibration standards (0.6 M NaCl - 0.02 M HCl - 0.002 M HF) simulating acidified seawater samples. Titanium, Zr, Nb and W are measured simultaneously in one run, whereas V and Mo are determined simultaneously in a separate run. Low procedure blanks were calculated for Ti, Zr, Nb, W (635, 14.5, 1.35, 10.2 pmol kg^{-1}) and for V and Mo, 9.79 and 5.61 nmol kg^{-1} , respectively. Very good spike recoveries achieved with spiked North Sea water demonstrate the applicability for all six elements. Analysis of the seawater standard NASS-6 gave recoveries of 97-99% (0.9 - 2.2% standard deviation, SD) for Mo and V. We also provide Zr, Nb and W data for this reference standard. The applicability of the online - preconcentration method was demonstrated for samples collected during a GEOTRACES cruise in the Atlantic.

Due to the low limit of quantification, LOQ, and SD, this method enables the determination of ultratrace concentration levels for Ti, Zr, Nb and W as well as the detection of small variations in concentration for all six elements. The required sample volume of only 50 mL, the fast determination within one hour for all elements and the principle of a closed system are a clear advantage of the analytical procedure compared to many other methods and facilitates sample logistics for the determination of Ti, Zr, Nb, V, W and Mo in seawater.

3.1 Introduction

Trace metals investigated in this work can be grouped into particle-reactive trace elements (Ti, Zr, Nb and W) and redox-sensitive trace metals (V and Mo).

Although the abundances of Ti, Zr, Nb and W are high (15.7, 1809, 215, 8.16 $\mu\text{mol kg}^{-1}$)

in the Earth's crust (Taylor, 1964) they show concentrations in ultratrace range (pmol kg^{-1}) in seawater. Particle-reactive elements are expected to show a decrease in concentration with depth. However, the opposite behaviour is observed for Ti, Zr and Nb in the Pacific Ocean showing an increase in deeper waters (Firdaus et al., 2011, 2008; McKelvey & Orians, 1993; Orians & Boyle, 1990; Sohrin et al., 1998b). Molybdenum, which is present in the concentration range of nmol kg^{-1} , shows conservative profiles throughout the oceanic water column (Collier, 1985) although Mo is biologically essential (Mendel, 2005). Like Mo, V is present in the range of nmol kg^{-1} in seawater and shows nutrient-like profiles in the Atlantic and Pacific water column (Collier, 1984; Jeandel et al., 1987) which indicates that V might be controlled by the phosphate cycle. Moreover, V is used in various industrial processes such as steel industry, and therefore represents a potential parameter for anthropogenic input to the ocean (Moskalyk & Alfantazi, 2003). The detection of small variations in concentration is often difficult for elements at relatively high concentrations (nmol kg^{-1}), such as Mo and V, requiring a method with a very small standard deviation. Tracing variations in concentration in seawater may help to identify biological and other potential signals such as scavenging processes in Mo profiles and deviations from the nutrient-like pattern of V.

The analysis of trace metals in seawater faces two major problems: 1) determination of ultratrace concentrations requires preconcentration prior to analysis and 2) the salt matrix might produce interferences during analysis. A voltammetric method for direct determination of dissolved Ti in seawater was reported recently (Croot, 2011). For Zr, a single element method was presented using MnO_2 -impregnated filters to extract Zr from large seawater samples (Norisuye et al., 2000). This method consists of two extraction steps which requires in total several days. Co-precipitation with Fe(hydroxide) was reported to preconcentrate Zr and Hf in seawater (Boswell & Elderfield, 1988; Godfrey et al., 2008, 1996) prior to their analysis. Solid-phase extraction using the chelating resin Chelex 100 was applied to 1 L samples to determine Zr and Hf in seawater (McKelvey, 1994; McKelvey & Orians, 1998, 1993). A method for the simultaneous determination of Zr, Nb and W in seawater among other elements using a chelating adsorbent column for preconcentration was published by Firdaus et al. (2007). Sample preparation was performed off-line, though a closed system was used for preconcentration which decreases the risk of contamination significantly (Firdaus et al., 2007). They synthesized the stationary phase for solid-phase extraction, TSQ-8HQ, manually.

The redox-sensitive metals, V and Mo, are present in the range of nmol kg^{-1} in seawater. Dupont et al. (1991) reported the determination of V in seawater with ICP-AES after preconcentration using Chelex 100 resin and digestion of the resin prior to analysis (Dupont et al., 1991). Wang and Sañudo-Wilhelmy (2008) used the same chelating resin and eluted both redox species, V(V) and V(IV), sequentially with basic and acidic eluent prior to analysis with graphite furnace atomic absorption spectroscopy. Molybdenum was measured after preconcentration with Cobalt-APDC (ammonium pyrrolidine

dithiocarbamate) by thermal atomization - AAS (Collier, 1985). Another study reported the analysis of Mo redox species in seawater by GF - AAS using XAD 7HP as solid phase (Wang et al., 2009).

Voltammetric methods have the distinct advantage that undiluted seawater can be measured directly. Though, one could only gain information about one element. Multi-element methods such as solid-phase extraction (Firdaus et al., 2007; Norisuye et al., 2000; Orians & Boyle, 1993; Sohrin et al., 1998b) or co-precipitation (Godfrey et al., 1996; Raso et al., 2013) are less time-consuming compared to voltammetric determinations but most of these methods are performed off-line. Therefore, their application bears a high risk of contamination due to intensive sample pre-treatment, preparation of the applied chemicals as well as the synthesis of the adsorbing material. It is therefore an important advantage if commercially available pre-packed columns can be purchased.

We used the online-preconcentration system SeaFAST, which was originally developed for the analysis of rare earth elements in seawater (Hathorne et al., 2012). Furthermore, the SeaFAST was applied for the determination of the GEOTRACES key elements (Mn, Fe, Co, Ni, Cu, Zn) in seawater in a slightly modified version using syringe pumps instead of peristaltic pumps (Lagerström et al., 2013). These examples imply the wide applicability of the preconcentration system.

The objective of this paper is to present a new online-preconcentration method using the SeaFAST-system, with subsequent ICP-MS analysis for Ti, Zr, Nb, V, W and Mo in seawater. This solid-phase extraction procedure enables the detection of ultratrace concentrations for Ti, Zr, Nb and W as well as of small variations in concentration of Mo and V, facilitating detailed studies on the biogeochemical cycling of these elements in the ocean. We demonstrate the applicability of the presented method for Zr, Nb, W, V and Mo by the analysis of open ocean seawater samples from a water depth profile in the Atlantic Ocean.

3.2 Experimental

3.2.1 Chemicals

Sample acidification (pH 2) was performed with ultrapure HF (Roth) and HCl (Fisher Scientific), whereas a mixture of diluted HNO₃ and HF, both of ultrapure grade (Roth), was used for elution from the preconcentration column. For the preparation of acetate buffer, pH 6.05 ± 0.5, ultrapure glacial acetic acid (Roth) and suprapure ammonia (Merck) were selected. Sodium chloride of suprapure grade (Merck) was used for preparation of external calibration standards.

The sodium form of the chelating resin Chelex 100, 100 - 200 mesh particle size, was purchased from Bio-Rad Laboratories and the seawater reference standard, NASS-6, was purchased from NRCC, National Research Council Canada. Single element stan-

dards, 1000 mg L^{-1} , for Ti, Zr, Nb, V, W, Mo and In were obtained from Inorganic Ventures. While Ti, Zr, Nb, V, W and Mo are used for the preparation of a stock standard-mix, In serves as internal standard. The final standard-mix was prepared by dilution of the stock standard-mix on weight basis. All solutions and dilutions were prepared with de-ionized (DI) water from a Sartorius Arium 611 unit, and preparation of most solutions was performed in a clean-bench equipped with a HEPA-filter.

3.2.2 Online - preconcentration - method

We applied the commercially available SeaFAST (Elemental Scientific) for preconcentration following the solid phase extraction principle. The SeaFAST-device, which is directly connected to the inductively coupled plasma-mass spectrometry (ICP - MS), consists of a sample loop with defined volume, a pre-packed preconcentration column filled with chelating resin and two 6-port valves (Figure 3.1).

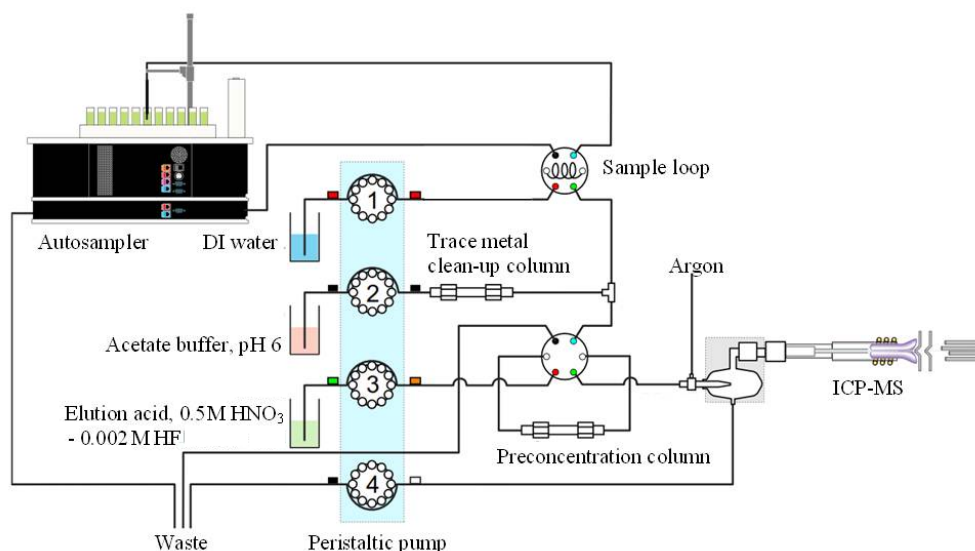


Figure 3.1: Schematic overview of the SeaFAST system, modified after Elemental Scientific (<http://www.icpms.com/pdf/seaFAST-Flier.pdf>).

The preconcentration column contains a chelating resin with two functional groups, ethylenediamine triacetic acid (EDTriA) and iminodiacetic acid (IDA), immobilized on a polymer backbone. The resin sorbs Ti, Zr, Nb, V, W and Mo on its surface while alkaline and alkaline earth metals pass the column. DI water, acetate buffer and elution acid were transported with a peristaltic pump, Perimax SPETEC AG, at different flow rates due to different inner-diameters of the tubes. The acetate buffer ($\text{pH } 6.05 \pm 0.5$) passes a clean-up column to remove trace metal impurities and is transported at a flow rate of 0.89 mL min^{-1} . DI water and the elution acid ($0.5 \text{ M HNO}_3 - 0.002 \text{ M HF}$) are transported at 0.80 mL min^{-1} and 0.23 mL min^{-1} , respectively, without passing a clean-up column. The

true volume of the 8 mL sample loop was measured and determined to be 8.28 ± 0.03 mL, $n = 8$. Rinsing and filling of the sample loop is controlled by the first 6-port valve whereas the subsequent valve controls rinsing of the resin, loading of the sample onto the resin and elution in counter current direction.

Measurements presented here were performed with an 8 mL sample loop. The autosampler, providing a vacuum-controlled sample introduction system, rinses and fills the sample loop within 30 s, consuming 25 mL sample volume. While the sample loop filling is processed the preconcentration resin is flushed continuously with a 1:1 mix of DI water and acetate buffer and maintained at pH 6. When the sample loop is filled, the valves switch their positions and the DI water-acetate buffer mix flushes through the sample loop pushing the sample onto the resin at a flow rate of 1.31 mL min^{-1} . Within 608 s the sample is loaded on the resin and rinsed with DI water-acetate buffer mix. During this process, the main part of the seawater matrix is removed from the resin while the elements of interest are concentrated on the resin. Meanwhile, the nebulizer is continuously rinsed with the elution acid by-passing the preconcentration column. In counter current direction the preconcentrated sample is eluted from the column at a flow rate of 0.23 mL min^{-1} with elution acid (0.5 M HNO_3 - 0.002 M HF). The elution process includes the data acquisition (detection of the peak eluted from the column) and subsequent rinse of the preconcentration column with elution acid, which is necessary to prepare the resin for the next measurement. We measured Ti, Zr, Nb, W in one run as their concentrations are within the same range (pmol kg^{-1}) and they require a similar time frame for data acquisition (1.25 min). The complete elution process requires 10.50 min. The whole online-preconcentration procedure is started again beginning with the sample loading process to measure V and Mo in seawater in a separate run. The sample load and preconcentration process for V and Mo is equal to the process for the HFSE. However, V and Mo require more time for the elution process (23.32 min) due to their higher concentrations in seawater (nmol kg^{-1}). Hence, we adjusted the time frame for the elution process of V and Mo, which is the only difference to the online-preconcentration of Ti, Zr, Nb, and W. To conclude, the whole online-preconcentration process was performed twice resulting in two separate runs for the determination of all six elements. Titanium, Zr, Nb and W are processed within one run while V and Mo are determined in a subsequent run, which differs only in the required time for the elution process.

3.2.3 ICP - MS method

All measurements were performed with a quadrupole ICP - MS, ELAN 6000 DRC-e (Perkin Elmer); the operating conditions are shown in Table 3.1.

The performance of the instrument was checked daily using a sample introduction system which is directly connected to the nebulizer and which by-passes the preconcentration system. A tuning solution ($10 \mu\text{g kg}^{-1}$ containing Be, Mg, Co, In, Ba, Ce, Pb and U

in 0.16 M HNO₃) was used and the ICP - MS parameters were changed accordingly to reach a CeO/Ce oxide ratio of 0.03.

Parameter	Operating condition
ICP RF Power	1200 W
Nebulizer gas flow	0.97 L min ⁻¹
Auxiliary gas flow	0.99 L min ⁻¹
Plasma gas flow	15.00 L min ⁻¹
Nebulizer	Microflow PFA-ST for 400 µL min ⁻¹
Spray chamber	Cyclonic spray chamber
Sweeps	1
Readings	72 (for Ti, Zr, W and Nb), 500 for (Mo and V)
Replicates	1
Dwell time	55 ms (for Ti, Zr, W and Nb), 65 ms (for Mo and V)
Monitored Isotopes	²³ Na, ⁴⁷ Ti, ⁴⁹ Ti, ⁵¹ V, ⁹⁰ Zr, ⁹¹ Zr, ⁹³ Nb, ⁹⁵ Mo, ⁹⁷ Mo, ¹¹⁵ In, ¹⁸² W, ¹⁸³ W
Estimated time	1.25 min (for Ti, Zr, W and Nb), 11.22 min (for Mo and V)

Table 3.1: Operating conditions for ICP - MS

The column extraction method produces a transient signal for the elution from the pre-concentration column. The preconcentrated sample (0.29 mL) will be analysed within 1.25 min and data points are collected for Ti, Zr, Nb and W. The peak area is used for the calculation of the corresponding concentration (Figure 3.2).

The ratio between the initially introduced sample volume (8.28 mL) and the preconcentrated sample (0.29 mL) represents a preconcentration factor with respect to volume for Ti, Zr, Nb and W of 29. In seawater, V and Mo show higher concentrations in the range of one order of magnitude compared to Ti, Zr, Nb and W and a customized ICP - MS method with 11.22 min for data acquisition was used. The volume preconcentration factor for Mo and V is 3.2, as the initial sample volume is preconcentrated to 2.6 mL.

To summarize, online-preconcentration and analysis of Ti, Zr, Nb and W within the same analytical run take 22 min. In a separately performed run, V and Mo require 34 min (preconcentration, determination and subsequent rinse).

We used In as an internal standard to monitor correct filling of the sample loop and elution from the preconcentration column. Since In starts to elute simultaneously with the elements of interest from the preconcentration column, we assume similar adsorption and elution characteristics compared to Ti, Zr, Nb, W, V and Mo. Although In is not eluted quantitatively from the preconcentration column during the time frame of data acquisition in the HFSE - method (1.25 min), the elution process includes a rinsing step for the preconcentration column prior to the next measurement enabling the complete removal of In. Since the procedure is not changed during the analyses, the ratio between In and the analytes will remain constant.

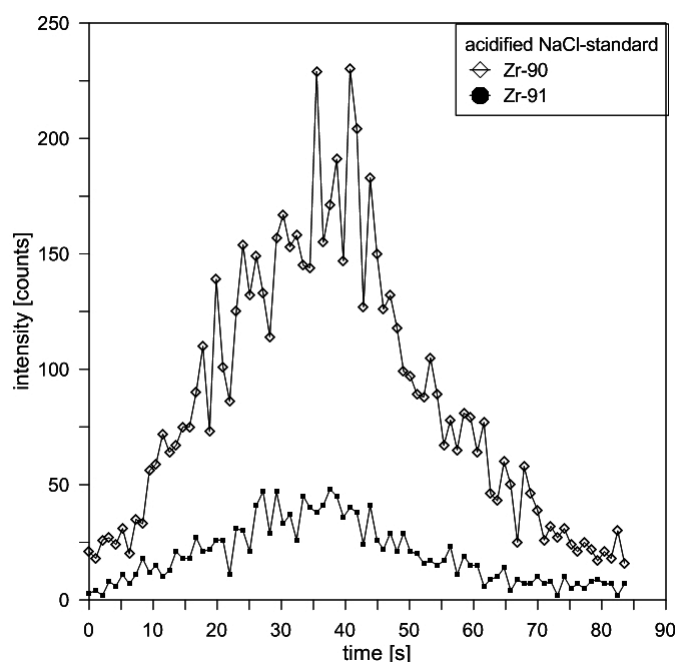


Figure 3.2: Transient signal of Zr in acidified NaCl-standard, 100 ng kg^{-1} ($0.6 \text{ M NaCl} - 0.02 \text{ M HCl} - 0.002 \text{ M HF}$).

The method for V and Mo determination includes a longer time for the elution process (23.32 min) enabling the quantitative removal of In. Although we applied two different time frames for the elution process in two separate analytical determinations, In can be used as internal standard due its similar adsorption behaviour compared to the six elements of interest. Data correction with In was applied to each sample and standard.

The matrix of calibration standards for an external 4-point-calibration was prepared as similar as possible to real seawater samples. Therefore, $0.6 \text{ M NaCl} - 0.02 \text{ M HCl} - 0.002 \text{ M HF}$ was applied to simulate seawater salinity of 35 g L^{-1} and acidification was performed in the same way as acidification of seawater samples. It was necessary to use a small amount of HF to keep the HFSE in solution (Münker, 1998). Addition of a higher amount of HF might cause the formation of less soluble CaF_2 , which in turn could lead to a loss of dissolved HFSE due to scavenging effects. We investigated the influence of different acidification approaches thoroughly and identified 0.002 M HF as the most suitable concentration for our purposes. The acidified NaCl-matrix was spiked with appropriate amounts of a standard-mix containing Ti, Zr, Nb, V, W and Mo. The calibration range varies for each element of interest according to its natural concentration in seawater.

Finally, approx. 60 min and 50 mL sample volume are required to preconcentrate and measure Ti, Zr, Nb, V, W and Mo in seawater within two separate analytical determinations.

3.2.4 Seawater samples

We used surface North Sea water for the evaluation of spike recoveries in the method development. Prior to the sampling campaign a 25 L high-density polyethylene (PEHD) container was systematically cleaned using 0.5 M HNO_3 - 0.01 M HF and allowed to stand for 48 hours at minimum. The acid-mixture was exchanged with DI water and after two more days the container was ready to use for subsequent sample collection.

During an expedition on research vessel Heincke in the German bight south of Helgoland in October 2011, North Sea water was collected. After filtration with 0.2 μm cellulose acetate filters, the seawater was immediately acidified to pH 2 with ultrapure HCl and HF resulting in final concentrations of 0.02 M and 0.002 M, respectively, to keep the HFSE in solution (Münker, 1998). The samples were spiked with the internal standard In resulting in 0.44 nM final concentration.

3.3 Results and discussion

3.3.1 Influence of elution acid

At first, the affinity of Ti, Zr, Nb, V, W and Mo to the resin material and to different elution acids was evaluated, aiming at optimizing the loading and elution process of a standard.

A standard was prepared in 0.02 M HNO_3 containing 100 ng kg^{-1} of Zr, Nb, W and Mo. Within a first approach, 0.5 M HNO_3 was applied as elution acid. The standard was loaded onto the column and measured, followed by acid blank (0.02 M HNO_3) measurements. These were performed by loading 0.02 M HNO_3 , representing the matrix of the previously measured standard, on the column and elution with 0.5 M HNO_3 , the previously used elution acid, was applied. The values of the acid blank measurements decreased with each subsequent measurement reaching values comparable to values prior standard measurement only after several blank measurements. This indicates that the elution process was not performed quantitatively as the elution acid was too weak to elute the elements of interest completely from the column.

Within a second approach we loaded a standard, 100 ng kg^{-1} (0.5 M HNO_3), on the column and used different concentrations of HNO_3 (0.5, 0.75 and 1.0 M) for elution. This approach was also applied to acid blanks (0.5 M HNO_3) representing the matrix of the standard loaded before. Higher intensities for acid blank measurements were observed for the elution with 1.0 M HNO_3 compared to 0.5 M HNO_3 , and we assume these result from the use of a higher acid concentration (Figure 3.3). Although we applied acids of ultrapure grade, traces of the elements of interest might be present which produce a specific concentration-dependent signal on the corresponding masses during ICP-MS analysis. It is therefore important to correct the intensities of the eluted standards (0.5 M HNO_3) with the corresponding intensities of acid blanks eluted under the same conditions.

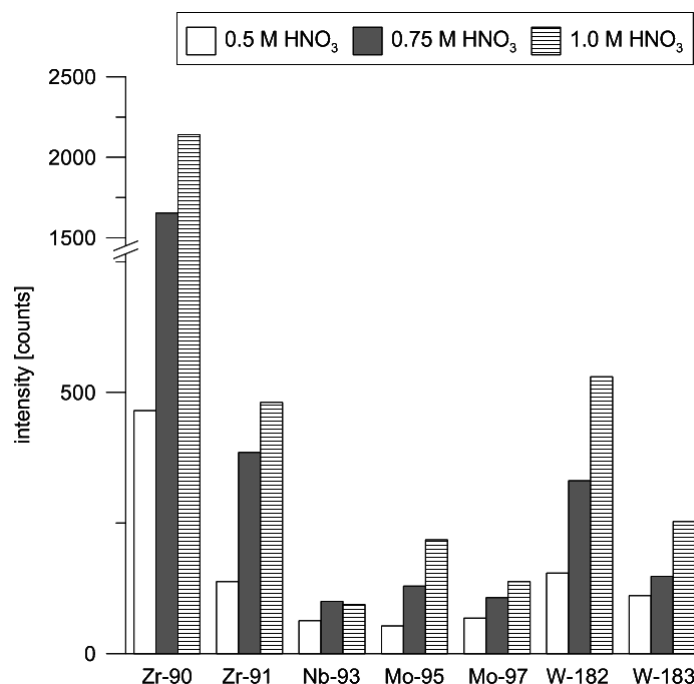


Figure 3.3: Comparison of ICP - MS intensities for acid blank (0.5 M HNO₃) measurements eluted with 0.5 M, 0.75 M and 1.0 M HNO₃.

Only Zr showed a significant increase in intensity with increasing concentration of HNO₃ after correction with the according acid blank values. This indicates an improvement for the elution process of Zr, while Nb, W and Mo are not affected to the same extent as Zr and their intensities increase only slightly for increasing concentrations of HNO₃ as elution acid (Figure 3.3).

We continued the optimization process by adding HF to the elution acid as the HFSE are known to form strong complexes with fluoride anions, F⁻ (Münker, 1998). This approach included elution acid mixtures of 0.5, 0.75, 1.0 and 1.5 M HNO₃ with a constant proportion of 0.001 M HF. A significant signal increase was observed for Zr while W increased only slightly. In contrast, Nb and Mo were not affected significantly by changing the composition of the elution acid (Figure 3.4).

The elution step, 10.50 min for Ti, Zr, Nb, W and 23.32 min for Mo and V, consists of the elution of the elements of interest and subsequent rinse of the preconcentration column. This relatively long rinse process is necessary to remove the fraction of elements which was not eluted within the adjusted time frame for data acquisition. The quantitative elution of a 100 ng kg⁻¹ standard (0.5 M HNO₃) was enabled by the addition of 0.001 M HF to the elution acid and proved by subsequent acid blank (0.5 M HNO₃) measurements which showed low values similar to the ones before. Further tests were performed with respect to the influence of increasing concentration of HF in elution acid. No significant differences in intensities for Zr, Nb, W and Mo were observed for elutions using 0.5 M HNO₃ - 0.001 M HF or 0.5 M HNO₃ - 0.002 M HF.

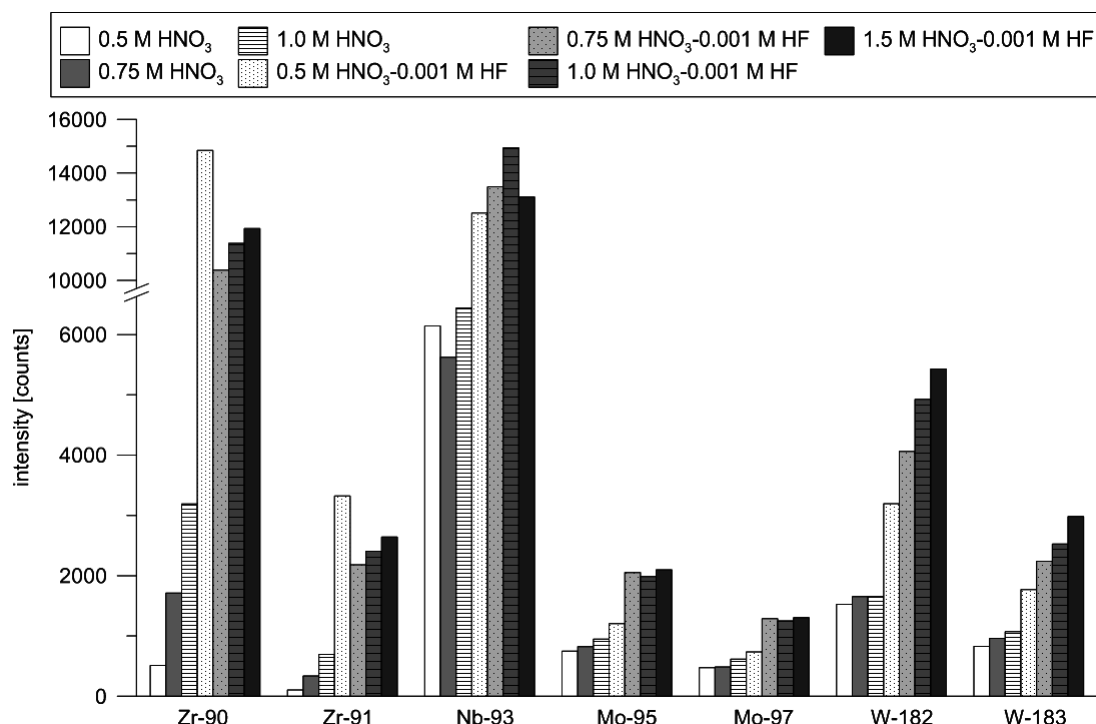


Figure 3.4: ICP-MS intensities for elution of a 100 ng kg⁻¹ standard (0.5 M HNO₃). Comparison between elution with different concentrations in HNO₃ (0.5 M, 0.75 M, 1.0 M) and mixtures of increasing concentration in HNO₃ with constant proportion of HF.

As it is intended to apply this online-preconcentration method to seawater samples which were acidified with 0.002 M HF, we decided to use 0.5 M HNO₃ - 0.002 M HF in the following method development as elution acid. This provides the same HF acid content for samples and elution acid.

3.3.2 Column yield

A quantitative evaluation was aimed at by introducing the determination of the column yield for each element of interest. A standard was loaded onto the resin and two fractions were collected in pre-weighed beakers. One contained the fraction of the standard passing the column during the loading process of the standard and subsequent rinse while the other fraction was collected during elution of the preconcentrated standard. Both fractions were evaporated on a hotplate and re-dissolved in the corresponding elution acid. These fractions were measured against external calibration standards prepared of the corresponding elution acid. Column yield determination with standard prepared in 0.5 M HNO₃ and eluted with 0.5 M HNO₃ - 0.002 M HF resulted in high recoveries for Zr and Nb, 88 and 78 %, respectively. In contrast, W and Mo were recovered with 48 and 58 %, respectively. Although the elution process was performed quantitatively, the loading process of the standard onto the preconcentration column is obviously not quantitatively processed, especially for W and Mo. We assume that almost 50 % of W and 40 % of Mo

pass the preconcentration column without getting retained.

In a next step, the acidification procedure of the designated samples (0.02 M HCl - 0.002 M HF) was applied to standards containing Ti, Zr, Nb, W and Mo since the autosampler was covered with a hood equipped with a HEPA - filter (ESI Scientific) enabling the determination of Ti. The hood was necessary, since Ti values were not reproducible due to the ubiquitous abundance of Ti in the environment, such as in wall paint (Al-Kattan et al., 2013). Column yield experiments using 100 ng kg⁻¹ standard (0.02 M HCl - 0.002 M HF) and the optimized elution acid showed high recovery rates of 93, 116 and 99 % for Ti, Zr and Nb. Tungsten and Mo were recovered to 64 and 65 %, respectively. These results are similar to results obtained with a standard prepared of 0.02 M HNO₃, demonstrating no significant influence of the acidic matrix of the loaded standard.

The standard matrix was furthermore adjusted to the matrix of acidified seawater samples using an acidified NaCl matrix (0.6 M - 0.02 M HCl - 0.002 M HF). A 100 ng kg⁻¹ standard was prepared accordingly and the column yield was determined. This approach revealed the influence of the salt matrix on the processes during loading the standard onto the column, rinsing the column after loading and elution of the preconcentrated sample, especially for W and Mo. Recovery rates for both elements decreased from 64 and 65 % to 35 and 43 %, respectively, when an acidified NaCl matrix is used. Measurements of appropriate acid blanks (0.02 M HCl - 0.002 M HF) after measurement of the standard showed no increased results, indicating that almost 65 and 57 % of W and Mo, respectively, pass the column without retention. It is therefore essential to adjust the standard matrix as close as possible to seawater matrix, enabling similar conditions for Ti, Zr, Nb, W and Mo in standards and samples during the preconcentration process. The use of matrix-matched calibration standards is indispensable due to differing retention behaviour of Ti, Zr, Nb, W and Mo in different matrices. A comparative overview is provided in Figure 3.5 for the evaluation of an appropriate standard matrix and elution acid.

Hence, 0.6 M NaCl simulating seawater matrix acidified with 0.02 M HCl - 0.002 M HF serves as a standard matrix for external calibration standards while 0.5 M HNO₃ - 0.002 M HF are used as elution acid. We determined the blank values for the standard matrix (0.6 M NaCl - 0.02 M HCl - 0.002 M HF) and observed high concentrations for Zr and Ti compared to their natural concentrations in seawater. In order to decrease the blank concentrations, a cleaning of the 2 M NaCl stock solution was inevitable. We applied the chelating resin Chelex 100, which provides iminodiacetate as functional groups immobilized on a styrene divinylbenzene copolymer. Using 5 g Chelex 100 resin filled in a PE-column, the trace metal impurities were retained by the functional groups of the chelating resin and the pre-cleaned NaCl stock solution that had passed the resin was collected in a pre-cleaned PE-bottle. The corresponding blank (0.6 M NaCl - 0.02 M HCl - 0.002 M HF) decreased significantly after the cleaning procedure was performed. All elements of interest, except Mo, showed column yields between 92 and 106 %.

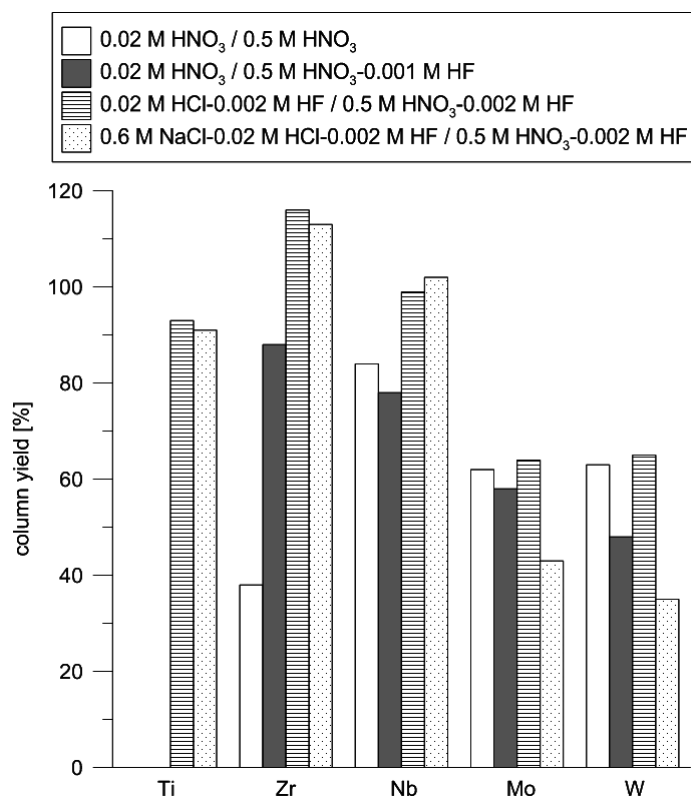


Figure 3.5: Overview of column yields for a 100 ng kg^{-1} standard in different matrices and corresponding elution acids.

The recovery rate for W increased from 35 to 93 % for an unknown reason and we assume that removal of trace metal impurities from the salt matrix provides more potential sorption sites for W during the loading process on the preconcentration column. This demonstrates that Ti, Zr, Nb, V and W attach almost quantitatively under the described conditions to the preconcentration resin and are furthermore quantitatively eluted. Mo shows a different behaviour as its recovery rate is only $45 \pm 4 \%$ (Table 3.2).

Element	Concentration of spike [pmol kg^{-1}]	Column yield [%]
Ti	1045	97 ± 13 (n = 4)
Zr	548	106 ± 2 (n = 4)
V	147000	92 ± 3 (n = 4)
Nb	27	100 ± 3 (n = 6)
Mo	65000	45 ± 4 (n = 4)
W	272	93 ± 5 (n = 4)

Table 3.2: Concentrations of spiked 0.6 M NaCl - 0.02 M HCl - 0.002 M HF - solution and column yield

Subsequent blank measurements do not display increased concentrations of Mo induced by residual Mo on the column. Accordingly, 45% of the total amount of Mo sticks to the resin while the remaining fraction passes the column.

The rather small fraction of retained Mo might be caused by the pH of the DI water-acetate buffer mix maintaining the pH of the preconcentration column. Since the pH conditions have a significant influence on the characteristics of the resin, investigation on this parameter might lead to a higher column yield of Mo.

This incomplete loading process does not affect the determination of Mo in seawater since even 45 % of its natural concentration, $97 - 105 \text{ nmol kg}^{-1}$, are sufficient for preconcentration, achieving signals well above the detection limit, and since the fraction retained on and eluted from the column is constant and the standard deviation of the column yield is low (Table 3.2).

3.3.3 Procedure blank and limit of quantification, LOQ

Since the salt matrix has a significant influence on the loading and elution process as well as on the measured intensities during ICP - MS analysis as demonstrated in the several column yield approaches we suggest the acidified NaCl matrix (0.6 M NaCl - 0.02 M HCl - 0.002 M HF) as the procedure blank for the presented method. This matrix is most similar to the seawater sample matrix and we expect similar intensities for similar concentrations. Applying an acid matrix as procedure blank would mislead data evaluation as the detected intensities would not show correct concentrations. The procedure blank was calculated by applying standard addition procedure, spiking the acidified NaCl matrix with Ti, Zr, Nb, W, V and Mo. The acid blank was determined applying standard addition to the acid matrix (0.02 M HCl - 0.002 M HF). Results for the procedure blank and the acid blank for the element of interest are summarized in Table 3.3.

Element	Blank matrix	
	0.6 M NaCl - 0.02 M HCl - 0.002 M HF ^{(a)(b)} [pmol kg ⁻¹]	0.02 M HCl - 0.002 M HF ^(a) [pmol kg ⁻¹]
Ti	635 ± 93 (n = 4)	219 ± 25 (n = 6)
Zr	14.5 ± 3.0 (n = 17)	34.7 ± 1.3 (n = 4)
V	9790 ± 1660 (n = 15)	1530 ± 50 (n = 4)
Nb	1.35 ± 0.42 (n = 8)	0.578 ± 0.094 (n = 8)
Mo	5610 ± 910 (n = 22)	800 ± 30 (n = 4)
W	10.2 ± 2.57 (n = 21)	7.18 ± 0.28 (n = 4)

(a) Mean ± SD, (b) Acidified NaCl-blank serves as procedure blank.

Table 3.3: Blank concentrations for correction of calibration standards and samples

Results for Zr, Nb and W in acid blanks are low due to the use of acids in ultrapure grade for acidification. Hence, no significant contamination results from the ultrapure HCl and HF, respectively. Moreover, acid blanks for Nb and W are in the same range as their procedure blanks indicating no significant contamination from NaCl. We calculated even smaller concentrations for Zr in the acidified NaCl matrix compared to the acid blank. We assume that the NaCl matrix affects the behaviour of the dissolved metals during

the preconcentration process which indicates the necessity of matrix-matched calibration standards providing similar characteristics as the samples, and matrix-matched corrections need to be considered as well.

Sodium chloride contributes mainly to the procedure blank for Ti, V and Mo. Natural concentrations in seawater exceed these procedure blank concentrations except for Ti. In this study North Sea water containing $1333 \pm 168 \text{ pmol kg}^{-1}$ Ti was used for the method development, which is significantly higher compared to open ocean seawater concentrations of 6 - 260 pmol kg^{-1} (Bruland & Lohan, 2003). This online-preconcentration method can therefore be applied to seawater samples containing higher Ti concentrations than open ocean water, e.g. coastal and estuarine samples. Within future optimization of the method it will be essential to decrease the procedure blank for Ti and thus enabling the determination of Ti in open ocean seawater (Al-Kattan et al., 2013). Comparison of the natural concentrations of Ti, Zr, Nb, V, W and Mo in our North Sea sample with the corresponding procedure blank reveals that the natural concentrations exceed the procedure blank concentrations significantly (Table 3.4).

Element	Conc. North Sea [pmol kg^{-1}]	Ratio: Natural concentration / Procedure blank
Ti	1333 ± 168 (n = 7)	2.1
Zr	107 ± 16 (n = 12)	10
V	23100 ± 2900 (n = 12)	3.7
Nb	3.52 ± 0.34 (n = 13)	2.4
Mo	90900 ± 3800 (n = 12)	3.7
W	79.2 ± 5.1 (n = 13)	5

Table 3.4: Measured trace metal concentrations in North Sea seawater and ratio between natural concentration and procedure blank

The limit of detection (LOD) was calculated to be three times the standard deviation of the procedure blank while the limit of quantification (LOQ) was taken as nine times standard deviation. Comparison of natural concentrations of Zr, V, W and Mo with the LOQ leads to ratios of 5.7, 2.3, 2.2 and 11, respectively, indicating the applicability of the proposed method to seawater samples (Table 3.5).

The ratio calculated for Nb gives a value of 0.8. As the natural concentration of Nb in open ocean seawater is very low, 3.1 pmol kg^{-1} , small variations during preparation of calibration standards or samples result in high percental variation for the final result and the corresponding standard deviation. This clearly demonstrates the importance to consider the surrounding laboratory environment to the method development as each single preparation step may have a substantial influence on the determination while working in ultra-trace concentration ranges. Due to the very low concentration of Nb in seawater it might be useful to load a higher sample volume on the preconcentration column to receive a higher concentrated sample after elution and an increase in the ratio between sample concentration and LOQ.

Element	LOD ^(a) [pmol kg ⁻¹]	LOQ ^(b) [pmol kg ⁻¹]	Ratio: Natural concentration / LOQ
Ti	297	836	1.6
Zr	9.10	27.3	5.7
V	4970	14920	2.2
Nb	1.27	3.82	0.8
Mo	2730	8190	11
W	7.72	23.2	2.2

(a) Limit of detection, 3 x SD, (b) Limit of quantification, 9 x SD.

Table 3.5: LOD and LOQ

Hence, the proposed method in this form is applicable to Zr, V, W and Mo in seawater whereas the LOQ of Nb and the evaluation of ubiquitous contamination sources for Ti require further optimization if it is intended to work on open ocean seawater samples.

3.3.4 Calibration

We used North Sea seawater for the method development and compared results for standard addition to the determination of North Sea seawater using external calibration of spiked 0.6 M NaCl - 0.02 M HCl - 0.002 M HF. In general, these two approaches should lead to similar results assuming that external calibration can be applied for determination of Ti, Zr, Nb, V, W and Mo in seawater. Both determination techniques were performed using 4-point-calibration with appropriate spikes according to the natural concentrations of Ti, Zr, Nb, V, W and Mo in North Sea seawater. During method development it transpired that Ti concentration in North Sea (1333 ± 168 pmol kg⁻¹) exceeded the expected concentration for open ocean seawater and was therefore not covered by the calibration range, 84 - 418 pmol kg⁻¹. Assuming linear response for Ti the above mentioned calibration range was used for determination of Ti in the North Sea sample. For all elements of interest, results for standard addition and external calibration agree well within 1x standard deviation (SD) (Figure 3.6).

This reveals that the behaviour of the acidified NaCl calibration standards with respect to the preconcentration process is similar to real seawater samples. Hence, external calibration using 0.6 M NaCl - 0.02 M HCl - 0.002 M HF as calibration standards can be applied to determine Ti, Zr, Nb, W, V and Mo in seawater samples facilitating the analyses enormously compared to standard addition for each single sample.

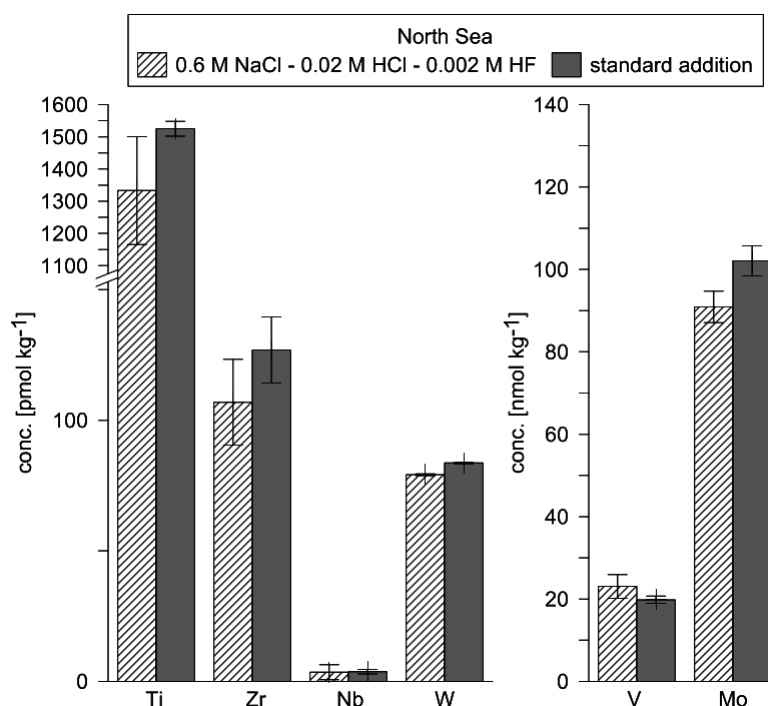


Figure 3.6: Concentrations of Ti, Zr, Nb, W, Mo and V in North Sea water determined by external 4-point-calibration ($n = 6 - 13$) using acidified NaCl-standards and 4-point-standard addition ($n = 2 - 4$), mean $\pm$ SD.

3.3.5 Recovery of spikes

The external calibration method was furthermore tested for the recovery of spikes. An appropriate amount of spike, with a concentration similar to the concentration ranges of Ti, Zr, Nb, V, W and Mo in North Sea seawater, was added to the North Sea sample and measured as described in sections 3.2.2 and 3.2.3. These spike experiments showed high recovery rates of $94 \pm 4\%$ for Ti, $104 \pm 5\%$ for Zr and $103 \pm 4\%$ for V (Table 3.6) and demonstrate that the natural fraction of elements behaves equally as the spiked elements on the resin.

Element	Repeatability [pmol kg ⁻¹]	Spike added [pmol kg ⁻¹]	Measured spiked sample [pmol kg ⁻¹]	Recovery [%]
Ti	1333 ± 168 ($n = 7$)	1236	2445 ± 150 ($n = 6$)	94 ± 4
Zr	107 ± 16 ($n = 12$)	134	237 ± 14 ($n = 9$)	104 ± 5
V	23100 ± 2900 ($n = 12$)	20900	48200 ± 2900 ($n = 4$)	103 ± 4
Nb	3.52 ± 0.34 ($n = 13$)	2.38	5.68 ± 0.3 ($n = 12$)	94 ± 6
Mo	90900 ± 3800 ($n = 12$)	92200	182000 ± 3000 ($n = 4$)	99 ± 2
W	79.2 ± 5.1 ($n = 13$)	66.5	140 ± 10 ($n = 12$)	97 ± 9

Table 3.6: Tests with North Sea seawater: Repeatability of sample concentration and recovery of spikes

Recovery of the spike for Nb showed $94 \pm 6\%$ emphasizing the applicability also for

these ultratrace concentrations although the LOQ is close to the natural concentration of Nb in seawater.

The spike for Mo was recovered to $99 \pm 2\%$. The high spike recovery confirms that the spiked Mo fraction behaves equally to the natural Mo fraction during the preconcentration process with 45 % of the total Mo load retained by the preconcentration resin. This spike experiment, performed in real seawater, demonstrates that Mo in calibration standards, North Sea water and spiked North Sea water shows the same sorption characteristics (45 % column yield) as the spike was recovered almost quantitatively.

As no appropriate certified reference material is available to control Ti, Zr, Nb and W determination in seawater, these spike experiments serve as a control and positive proof for the applicability of the developed online-preconcentration method to seawater samples.

3.3.6 Accuracy

A certified seawater reference standard, NASS-6 (National Research Council Canada, NRCC), was applied to determine V in seawater along with the expanded uncertainty of our analytical measurement, U. The standard water was collected in 2007 in the north-west Atlantic from Sandy Cove, Nova Scotia, 0.45 μm filtered and acidified with ultrapure nitric acid to pH 1.6 (NRCC, 2010). The expanded uncertainty of measurement provides an interval within which the concentration is believed to lie with a confidence interval of 95 %, in our case. We followed calculation procedures given by Ellison et al. (2000). Vanadium was determined to be $27.6 \text{ nmol kg}^{-1} \pm 12\%$ ($n=4$, 95 % confidence interval) with $U=12\%$ and recovered with $99 \pm 2.2\%$. Concentration of Mo serves only as information and not as a certified value in NASS-6. Comparing the available information for Mo with the determined result for Mo applying our online-preconcentration method, we achieved a recovery of $97 \pm 0.9\%$ (Table 3.7).

Element	Measured concentration [nmol kg ⁻¹] ^(a)	NRCC concentration [nmol kg ⁻¹]	Recovery [%] ^(a)
V	27.6 ± 0.60	27.9 ± 3.1	99 ± 2.2
Mo	98 ± 0.87	101	97 ± 0.9

(a) Mean $\pm$ SD of 4 replicates.

Table 3.7: Recovery of V and Mo in NASS-6

The quantitative recovery of Mo in NASS-6 supports the assumption that the NaCl matrix simulates seawater matrix sufficiently. Hence, the applicability of this method is verified by spike experiments for Ti, Zr, V, Nb, Mo and W as well as by measurement of NASS-6 for V and Mo. We also applied the presented preconcentration method to determine Zr, Nb and W in the seawater reference standard NASS-6 (Table 3.8).

Element	Concentration [pmol kg ⁻¹]
Zr	105.4 ± 2.0 (n = 4)
Nb	3.03 ± 0.17 (n = 5)
W	24.7 ± 0.8 (n = 4)

Table 3.8: Concentration of Zr, Nb, and W in seawater reference standard NASS-6

Raso et al. (2013) reported 249 ± 36 pmol L⁻¹ for Zr in NASS-6 determined by ICP - MS after co-precipitation with Fe-hydroxide, which is significantly higher compared to the concentration of Zr obtained in this study. This demonstrates the difficulty in the analysis of Zr in seawater and the importance of intercalibration efforts regarding the determination of Zr and other particle-reactive trace metals in seawater. The concentration of Zr in the northeast Atlantic have been reported to range between 70 - 180 pmol kg⁻¹ (Godfrey et al., 1996) while the sampling site for NASS-6 was located in the northwest Atlantic. Our data agree well with these results for the Atlantic despite the above mentioned discrepancy with published results on NASS-6.

3.3.7 Comparison with published preconcentration methods

An overview of selected off-line preconcentration techniques for Ti, Zr, V, Nb, Mo and W is provided in Table 3.9. Within this study, we present a fast on-line preconcentration technique, set up as a closed system, with a decreased risk of contamination. With our technique, only one hour is required for preconcentration and determination for Ti, Zr, Nb, V, W and Mo in seawater. Although we pre-cleaned the NaCl-stock solution with Chelex 100 resin, the calibration standards (0.6 M NaCl - 0.02 M HCl - 0.002 M HF) still contain trace metal impurities as their blanks give higher concentrations in Ti, Zr, Nb, V, W and Mo compared to acid blanks. The NaCl matrix will not be removed to full extent by the online-preconcentration method and a small fraction will enter the ICP - MS leading to higher procedure blanks (0.6 M NaCl - 0.02 M HCl - 0.002 M HF). Indeed, the most important fact is that samples and calibration standards are treated equally compensating this matrix effect provided that both matrices are similar. Hence, our online-preconcentration method requires intensive preparation of applied chemicals prior to their use and the pre-concentrated sample will enter the ICP - MS directly. In contrast, published studies necessitate processing of the preconcentrated samples in several individual steps off-line prior to analysis. While using solid-phase extraction the eluent matrix will be evaporated and re-dissolution in an appropriate acid matrix is necessary prior to injection into the analytical device (Firdaus et al., 2008, 2007; Sohrin et al., 2008). The blank matrix consists mostly of diluted acid leading to a lower procedure blank. However, off-line sample preparation is laborious, time-consuming and additionally carries a risk of contamination.

Although our proposed method gives higher results for the procedure blank compared to published off-line preconcentration methods the ratio between LOQ and natural con-

centration is still sufficient for Ti, Zr, V, W and Mo determinations. Even though the LOQ for Nb is close to its natural concentration in seawater the quantitative recovery of spikes in North Sea water proves the applicability of the proposed online-preconcentration method and subsequent ICP - MS measurement.

A few methods exist for the preconcentration of Zr, Nb and W in seawater, which are all off-line preconcentration methods (Firdaus et al., 2007; McKelvey & Orians, 1998; Norisuye et al., 2000; Raso et al., 2013). In some studies highly concentrated HF had to be used which is undesirable (Firdaus et al., 2008, 2007). In contrast, our method requires only highly diluted HF.

Analyts	Methods	Precision [%]	Procedure blank [pmol kg ⁻¹]	LOD [pmol kg ⁻¹]
Zr	solid phase	-	Zr 0.35	0.15
Nb, W ^(c)	extraction, TSQ-8-hydroxyquinoline		Nb 0.19	0.15
	ICP - MS		W 0.37	0.12
Zr, Nb ^(d)	MAF - 8HQ, HR - ICP - MS	< 10	-	-
Ti, V, W ^(e)	MAF - 8HQ, HR - ICP - MS	-	Ti 50.1 ^(a) V 35.3 ^(a) W 1.90 ^(a)	Ti 56.4 ^(a) V 64.8 ^(a) W 5.06 ^(a)
W, Mo ^(f)	XAD-4 resin loaded with Kelex - 100, catalytic current polarography	5	Mo < 500 ^(b) W < LOD	20 ^(b) 3 ^(b)
Ti ^(g)	TSK-8HQ, ICP - MS	7-10	-	5-10 ^(a)
V ^(h)	Chelex - 100, ICP - AES	-	< LOD	78500
V ⁽ⁱ⁾	Complexation by 8 - HQ, C ₁₈ , ICP - MS	-	11600 ^(a)	80300 ^(a)
Ti, Zr, Nb, V, W, Mo ^(j)	SeaFAST, ICP - MS	-	Ti 635 Zr 14.5 V 9790 Nb 1.35 Mo 5610 W 10.2	297 9.10 4970 1.27 2730 7.72

(a) Calculated from published results to [pmol kg⁻¹], (b) Concentration unit [pmol kg⁻¹], (c) Firdaus et al. (2007), (d) Sohrin et al. (1998a), (e) Sohrin et al. (1998b), (f) Sohrin et al. (1987), (g) Orians & Boyle (1993), (h) Dupont et al. (1991), (i) Abbasse et al. (2002), (j) this study.

Table 3.9: Comparison of the method used in this study with published preconcentration methods

Due to the high concentrations of V and Mo in seawater only some preconcentration methods are published. Some studies describe the use of organic compounds to form metal-organic complexes and subsequent solid phase extraction (Abbasse et al., 2002;

Wang et al., 2009) while other workgroups apply solid-phase extraction to seawater directly (Dupont et al., 1991). More often, these elements as well as Ti are determined in single-element methods without preconcentration (Croot, 2011). Our method enables determination of V and Mo within one analytical measurement while Ti, Zr, Nb and W are determined in a separate one. The determination of higher concentrated elements such as Ti in combination with lower concentrated elements, Zr and Nb, in seawater within the same analytical run is advantageous and represents a promising approach to extend the method to additional elements in seawater.

3.3.8 Application to open ocean seawater

We applied our new online-preconcentration method to seawater samples collected on a GEOTRACES research cruise, M81/1 in February 2010. The vertical distribution of V and Mo is presented for an open ocean seawater station (Figure 3.7), TM 12 (9.49°N, 20.50°W), located off the west African coast in the eastern basin of the Atlantic Ocean. Variations in concentration with depth exceeded the SD of the presented method for V (RSD 1 - 3 %) and Mo (RSD 1 - 7 %).

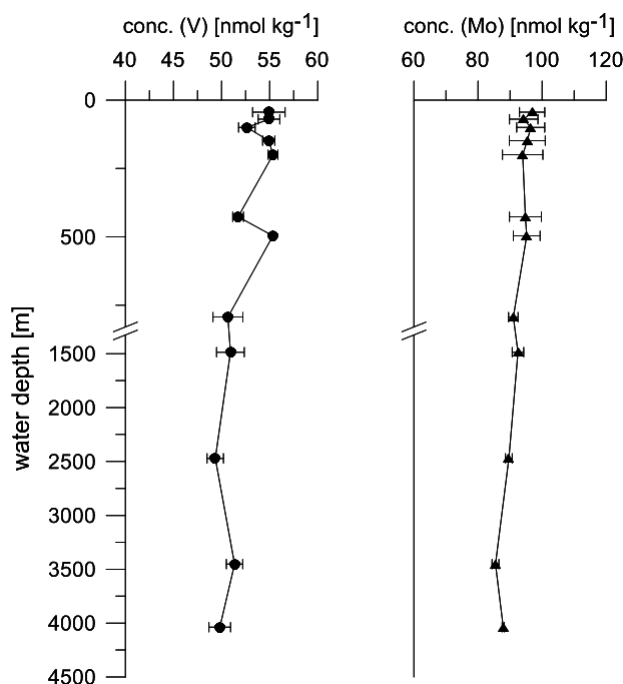


Figure 3.7: Water depth profiles of V and Mo at station TM 12 (9.49°N, 20.50°W), mean $\pm$ SD.

Both metals showed a slight decrease in dissolved concentration with depth. Morris (1975) reported dissolved concentrations of Mo ranging from 91.1 - 135.5 nmol L⁻¹ in the North Atlantic Ocean which agree with our data. We report dissolved V concentrations which are slightly higher compared to previously published data reporting 35 ± 2.5 nmol kg⁻¹ (Jeandel et al., 1987) and 31.8 - 33.9 nmol L⁻¹ (Middelburg et al., 1988)

in the Atlantic Ocean. Potential input from Saharan dust might cause these elevated concentrations providing trace metals to surface water layers.

Determination of Nb resulted in 3 - 14 % RSD and W was measured within 2 - 9 % RSD for station TM 20 (7.17°S, 31.33°W) located in the western basin of the Atlantic Ocean. For Zr, only single measurements per sample were possible, due to a problem with the Chelex column for pre-cleaning the NaCl stock solution.

While Zr shows a strong increase and Nb a slight increase in concentration with depth, W decreases below the surface water layer which probably reflects its interaction with biological cycles and removal from the water column (Figure 3.8).

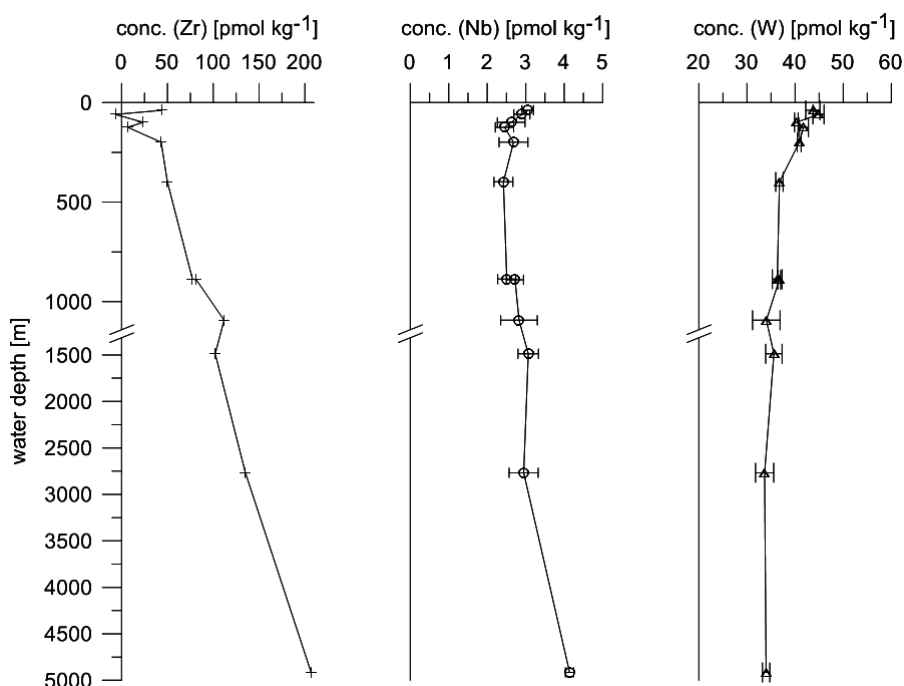


Figure 3.8: Water depth profiles of Zr, Nb and W at station TM 20 (7.17°S, 31.33°W), mean $\pm$ SD.

Godfrey et al. (1996) reported for the northeast Atlantic dissolved concentrations of Zr in the range of 70 - 180 pmol kg⁻¹ which agree with our presented concentrations whereas concentration data of dissolved Nb and W can only be compared to Pacific water profiles (Firdaus et al., 2008; Sohrin et al., 1987). We report slightly lower dissolved Nb concentrations compared to Pacific waters which might reveal differences in both oceanic basins. The concentrations of dissolved W are in the same range of concentration in the Atlantic and Pacific Ocean.

The same sample of station TM 12 (water depth 1485 m) was measured at different days for all six elements demonstrating the repeatability of our presented method (Table 3.10).

Element	Concentration [pmol kg ⁻¹] ^(a)	RSD [%]	Number of measurements
Zr	133.6, 131.6 ^(b)	-	2
Nb	2.99 ± 0.25	8	3
W	40.7 ± 3.4	8	3
V	48300 ± 1300	3	4
Mo	93900 ± 2100	2	4

(a) Mean ± SD, (b) two individual results.

Table 3.10: Concentration, SD, and RSD for one sample of TM 12 measured repeatedly

As the natural concentration of Ti in open ocean seawater is significantly lower than in North Sea water we could not determine Ti in these samples.

We demonstrated the applicability of our presented method to open ocean seawater for the other elements as the low SD of Nb, W, V and Mo concentrations enables the detection of small variations in concentration with depth for these metals and the method is sufficiently sensitive to detect picomolar concentrations. Interpretation and discussion of the specific patterns for Zr, Nb, W, V and Mo are beyond the scope of this study and will be presented elsewhere in combination with further water depth profiles collected in the framework of the GEOTRACES program.

3.4 Conclusion

This study presents a new online-preconcentration method which allows a combined two-step determination of Ti, Zr, Nb, V, W and Mo. We succeeded to determine ultratrace concentrations of Ti, Zr, Nb and W in seawater and trace concentrations of the quasi-conservative elements Mo and V. Our proposed method enables the detection of small variations in concentration for Mo and V due to the corresponding small standard deviation of the method. An acidified NaCl matrix (0.6 M NaCl - 0.02 M HCl - 0.002 M HF) is applied for external standard calibration of acidified seawater samples while In serves as internal standard. The preconcentration column is maintained at pH 6.05 ± 0.5 and the sample is eluted with 0.5 M HNO₃ - 0.002 M HF. More work needs to be done to decrease the procedure blank for Ti and Nb and the corresponding LOQ by optimizing pre-cleaning techniques and for Nb the use of a sample loop with higher sample volume might be auspicious.

The preconcentration and analysis of Ti, Zr, Nb and W in seawater takes about 22 min while Mo and V require 34 min in a separate analytical run. This method is time-saving compared to published solid phase extraction methods requiring several hours for column preparation and regeneration of the resin. It further reduces the consumption of aggressive chemicals such as HF to a minimum while the risk of contamination is decreased due to the principle of a closed system. With this method only 50 mL of sample volume

is needed for the determination of the six elements of interest in seawater, which facilitates sample logistics. Furthermore, the collection of more individual samples is possible as less volume and less time for laborious sample preparation per sample is needed for the analytical measurements. The preconcentration system might be decoupled from the mass spectrometry for the preconcentration on board a research vessel under clean conditions. This would facilitate transport of samples taken on research cruises back to the corresponding home-laboratories.

In conclusion, the presented online-preconcentration method provides an important new tool for seawater analysis of Ti, Zr, Nb, V, W and Mo with a low risk of contamination, time-saving preconcentration and low procedure blanks for Zr, V, W and Mo in comparison to natural concentrations of these metals in seawater. We showed the application of the presented online-preconcentration method to Atlantic water depth profiles. Small SD enabled the detection of small variations in concentration for Nb, W, V and Mo, while the determination of Ti requires further improvement due to its low concentrations in open ocean seawater compared to North Sea seawater. Reduction of required time could be achieved by the application of a smaller sample loop, e.g. 1 mL, for the analysis of V and Mo since both metals will be sufficiently preconcentrated due to their high concentrations in seawater (nmol L^{-1}).

The proposed online-preconcentration technique can be applied to the determination of other trace metals in seawater which also show a strong binding affinity to the column material. We investigated the applicability of this method to Hf and Ta but the natural concentrations of both metals under the described conditions were only slightly higher (factor 1 - 2) than the procedural blank. Since the column yield was below 40 % for both metals one should aim quantitative loading and elution procedures which consequently might increase the ratio between the natural concentrations and blank values. The resin is expected to retain Hf and Ta among other trace metals and application of the proposed method to a wider range of elements is worth striving for by adjusting the preconcentration and elution parameters as well as the time frame for the analytical detection.

Measurement of other matrices than seawater should be possible, but would require the revision of the parameters such as column yield and comparison between external calibration and standard addition. Hence, this online-preconcentration method provides a promising tool to assess the distribution of a wide range of trace metals not only in the oceanic water column but also in estuarine waters and freshwaters such as river and lake water, provided that the content of organic colloids that might block the preconcentration column is not too high.

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4 Depth profiles of Zr and Nb and the role of organic complexation

Title of publication

Depth distribution of Zr and Nb in seawater: The potential role of colloids or organic complexation to explain non-scavenging-type behaviour

Authors and affiliations

Sandra Poehle^{*1}, Andrea Koschinsky¹

^{*} Corresponding author. Tel.: +49 0421 2003261,

E-mail address: s.poehle@jacobs-university.de

¹ Department of Physics and Earth Sciences, Jacobs University Bremen

Campus Ring 1, 28759 Bremen, Germany

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Depth distribution of Zr and Nb in seawater: The potential role of colloids or organic complexation to explain non-scavenging-type behavior



Sandra Poehle^{*}, Andrea Koschinsky

Department of Physics and Earth Sciences, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany

Abstract

Dissolved zirconium (Zr) and niobium (Nb) are present in open-ocean seawater in low pmol/kg concentrations and studies for the Pacific Ocean reported an increase in concentration with depth although both metals are characterized as being particle-reactive. We analyzed dissolved Zr and Nb in 194 Atlantic seawater samples (0.2 μm filtered) collected at 16 stations located in the (sub)tropical Atlantic during GEOTRACES cruise M81/1 (GA11) and 6 Pacific samples (0.2 μm and 0.015 μm filtered) collected from a hydrothermal plume and the background seawater during SO229. Measurements were done using our newly developed online-preconcentration method for the SeaFAST-system with subsequent analysis by inductively coupled plasma - mass spectrometry. Our results showed an increase in dissolved Zr with depth with some distinct maxima at intermediate depths along a NE - SW transect (30°N to 12°S) in the Atlantic. Surface depletion was less pronounced along the Atlantic SE - NW transect (12°S to 8°N) and disappeared almost completely at the northernmost station at 8°N. Dissolved Nb was almost conservatively distributed except off West Africa where a surface depletion was observed. We suggest that dust deposited off West Africa scavenged Zr and Nb from surface waters and riverine discharge from the Amazon may represent a source to the West Atlantic. The correlation of Zr with Si hints to a coupling of Zr to the uptake and release on and from Si particles such as biogenic opal. Analysis of the size-fractionated Pacific samples ruled out a significant colloidal (0.015 μm - 0.2 μm) component as host for Zr and Nb. We suggest that dissolved Zr and Nb might be stabilized by organic complexation in deep waters because both elements form very stable complexes with organic molecules such as siderophores.

4.1 Introduction

Dissolved zirconium (Zr) and niobium (Nb) are present in seawater in very low concentrations in the range of pmol/kg and form neutrally or negatively charged hydroxide species ($\text{Zr}(\text{OH})_4$, $\text{Zr}(\text{OH})_5^-$, $\text{Nb}(\text{OH})_4$, $\text{Nb}(\text{OH})_5^-$) (Byrne, 2002). These species tend to strongly sorb onto particulate matter, e.g. sinking organic matter or mineral particles, which is why Zr and Nb are classified as particle-reactive elements. Based on this property a decrease in concentration with increasing water depth would be expected due to increased sorption onto particulate matter. Firdaus et al. (2011; 2008) observed the opposite behaviour for dissolved Zr and suggested a source for Zr in deep waters. The authors also reported a slight depletion in surface waters for dissolved Nb in the western North Pacific with largely constant concentrations at greater depth. These observations agree with a slight depletion compared to deep waters reported for dissolved Nb in the North Pacific (Sohrin et al., 1998a).

A linear relationship between dissolved Zr and Si has been reported for North Pacific waters (McKelvey & Orrians, 1993) with deviations in surface waters. Higher concentra-

tions of dissolved Zr relative to the Zr/Si -relationship have been observed indicating an atmospheric source for Zr. Godfrey et al. (1996) suggested a nutrient-like scavenging-regeneration behaviour of dissolved Zr in the northeastern Atlantic Ocean as one important process.

Dissolved Zr paired with hafnium (Hf) and dissolved Nb paired with tantalum (Ta) have been recently suggested as proxies for water masses (Firdaus et al., 2011). Hence, it is essential to understand the biogeochemical cycling of Zr and Nb and to reveal regional sources and sinks which will help to evaluate data on water masses. Data on Zr for the Atlantic are scarce and data on Nb have not yet been published. Thus, up to now it remains unclear whether the patterns observed in the Pacific Ocean (surface depletion and increase in concentration with depth) are a global feature or whether they might represent regional patterns.

Here, we provide data on dissolved Zr and Nb for 194 seawater samples collected at 16 different stations in the (sub)tropical Atlantic during GEOTRACES cruise M81/1 (GA11). We show that the Canary Islands as well as dust input off West Africa have a significant influence on the distribution of Zr and Nb in surface waters. River discharge from the Amazon is also assumed to have a distinct input on both trace metals. The Atlantic water depth profiles agree with published data for the Pacific with respect to the range of concentration and the distribution with depth. The analysis of size-fractionated components of deep Pacific waters collected at a hydrothermal plume during research cruise SO229 and at an appropriate seawater background location revealed a negligible role of the colloidal fraction (0.015 μm - 0.2 μm) in the dissolved concentrations of Zr and Nb. We suggest that organic complexation is a viable explanation for the ocean-wide increase of the particle-reactive elements Zr and Nb with water depth.

4.2 Materials and Methods

4.2.1 Sampling sites and sampling procedure

Within this study we analyzed seawater samples collected in two oceans 1) along two transects crossing the Atlantic and 2) in the Pacific Ocean in the proximity of hydrothermally active sites.

4.2.1.1 Atlantic Ocean

The cruise track of the GEOTRACES research cruise M81/1 (GA11, February 4 - March 8, 2010) covered an area in the (sub)tropical Atlantic and started at the Canary Islands to sail off the African coast along a transect at 20°W crossing the equator. The ship turned north at 11°S sailing off the Brazilian coast to end in the Caribbean (Figure 4.1).

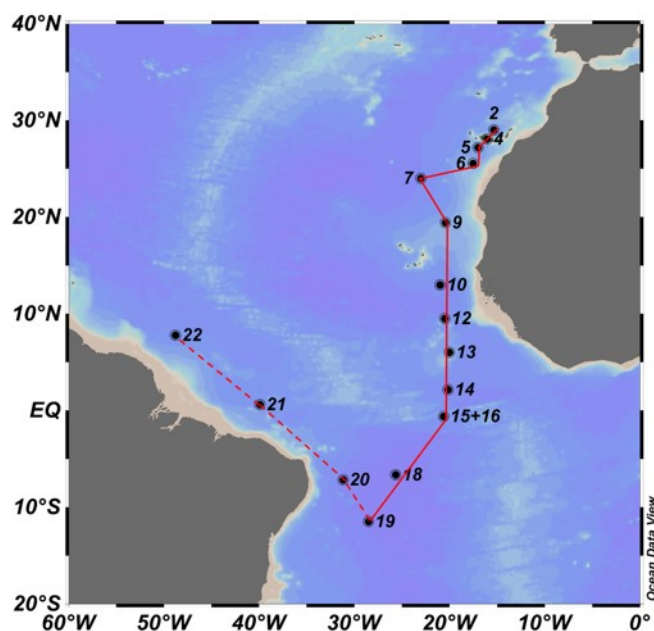


Figure 4.1: Stations sampled with the trace metal-clean CTD during GEOTRACES research cruise M81/1 in the (sub)tropical Atlantic Ocean. The solid red line connects stations used for section plots of the NE - SW-transect (Figures 4.4, 4.6 and 4.10), the dashed line for plots of the SE - NW-transect (Figures 4.5 and 4.7).

At 16 stations, each resolved with approx. 15 different depths, 194 seawater samples were collected with 24 12 L GO FLO water samplers mounted on a trace metal-clean conductivity-temperature-depth (CTD) - rosette provided by U.S. GEOTRACES partners together with a mobile winch and the corresponding Kevlar cable.

During downcast of the CTD the water samplers were open and the seawater was allowed to flush the sampling bottles. During upcast, the water samplers were closed in specific depths and hence flushed with the respective water mass before closure. After the CTD was lifted on deck the in- and outlet of the water samplers were immediately covered with plastic bags to avoid contamination and the samplers were brought to a clean laboratory container (U.S. GEOTRACES) for subsampling and filtration applying cellulose acetate filters (0.2 μm , Sartobran P-MidiCaps). The samplers were then emptied and only shortly before the next station was reached they were mounted again on the CTD - frame with covered in- and outlet.

The filtered 1 L subsamples, stored in high density polyethylene (PEHD)-bottles, were acidified with hydrochloric acid (HCl) and hydrofluoric acid (HF) to a final concentration of 0.02 mol/L HCl - 0.002 mol/L HF; both acids were of ultrapure grade (Roth). Until analysis in the home laboratory, the samples were stored under cool and dark conditions.

The PEHD-bottles for subsampling were cleaned in a three-stage process: (1) rinsed with deionized (DI) water, (2) filled with 0.5 mol/L HNO_3 - 0.01 mol/L HF and stored for 48 hours at 60°C, (3) rinsed and filled with DI water and stored for 48 hours at 60°C followed by a final rinse with DI water.

4.2.1.2 Pacific seawater samples

Since only 0.2 μm filtered samples were available from cruise M81/1, we used the opportunity of another cruise in the Pacific to filter water column samples with two different filter sizes in order to check for the role of colloids in Zr and Nb distribution.

During research cruise SO229, RV Sonne, in July 2013, the area east of the Vanuatu archipelago in the Pacific Ocean was investigated, which is known for its hydrothermal activity along the island arc (Figure 4.2).

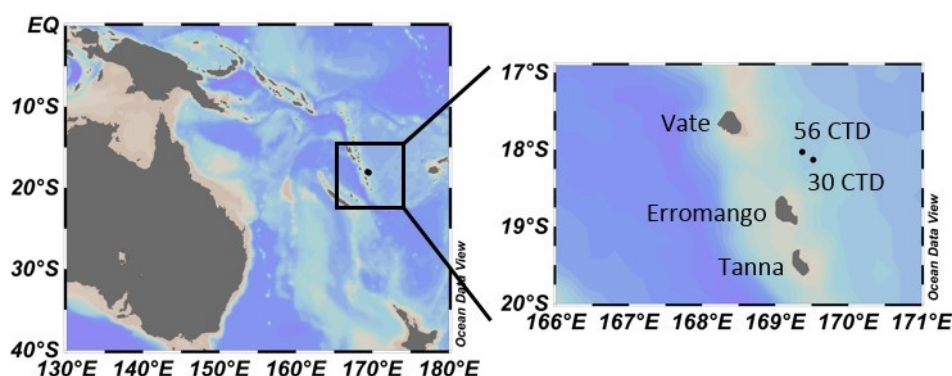


Figure 4.2: Sampling sites in the Pacific Ocean during research cruise SO229, in the Vanuatu Island Arc. The right map shows a close-up of the sampled stations; 56 CTD represents the seawater background site while 30 CTD represents the site where a hydrothermal plume was sampled.

At the Nifonea Ridge (18°S, 170°E) which is located southeast of the island Vate seawater samples were collected between 1500 m and 1700 m water depth where hydrothermalism was previously detected during this cruise by a Remotely Operated Vehicle, ROV Kiel 6000 (Haase et al., 2009). Sampling was performed with 24 NISKIN bottles, each with 10 L volume, which were mounted onto a rosette frame equipped with sensors for conductivity, temperature, depth and a turbidity meter (SBE 911, Seabird Electronics). The CTD-samplers were controlled from on board and closed during upcast of the CTD.

A recent study on Fe with samples from this site clearly identified the hydrothermal plume showing higher Fe concentrations in the plume compared to seawater not influenced by the plume (Kleint et al., 2016). Hence, the collected samples for the size fractionation approach were located in the hydrothermal plume (station 30 CTD).

A seawater background sample (station 56 CTD) was collected from 1600 m water depth at a location north of the hydrothermally active sites using the same sampling device. Prior to the sampling campaign a ship-board laboratory was equipped with adhesive mats and air filters to approach the requirements for handling seawater samples dedicated for trace metal analysis. Directly after the CTD was on deck subsampling and sequential filtration was applied to all samples using two different pore size filters, 0.2 μm (cellulose acetate, Sartorius) and 0.015 μm (polycarbonate, Sigma-Aldrich), performed under a clean bench in the prepared laboratory. The pore sizes were selected to par-

tition the dissolved phase of trace metals into the colloidal (0.015 μm - 0.2 μm) and the dissolved and small colloidal phase (< 0.015 μm). The samples were acidified with ultra-pure HCl and HF (both Roth) to final concentrations of 0.02 mol/L HCl - 0.002 mol/L HF and stored under cool and dark conditions until further analysis in the home laboratories.

4.2.2 Online-preconcentration method

We applied our newly developed online-preconcentration method with the system SeaFAST and subsequent ICP-MS analysis (Poehle et al., 2015). A short description is provided here. The system consists of three components: (1) sample loop, (2) preconcentration column and (3) two six port valves controlling rinsing and elution processes.

An 8 mL sample loop was filled via vacuum with the solution to be measured while the preconcentration column was maintained at pH 6 through rinsing with a 1:1 mix of DI water and ammonium acetate buffer (pH 6.05 ± 0.05). The column contained a pre-concentration resin characterized by two functional groups, iminodiacetic acid (IDA) and ethylenediaminetriacetic acid (EDTriA) immobilized on a polymer backbone. The sample to be measured was pushed through the sample loop by the DI - buffer mix to the column and loaded onto the resin. While alkaline and earth alkaline metals passed the resin most of the transition metals and metals from subgroups III and IV, e.g. Ga, In, Sn, Pb and Bi, were chelated by the functional groups and retained. A subsequent rinse with the DI-buffer mix removed the seawater matrix largely. In counter-current direction the sample was eluted quantitatively (Table 4.1) from the resin applying 0.5 mol/L HNO_3 - 0.002 mol/L HF as elution acid and the preconcentrated sample was directly transported to the nebulizer of the inductively coupled plasma - mass spectrometry (ICP - MS) and measured.

Indium served as an internal standard to monitor filling of the sample loop and the recovery from the preconcentration column and was added to all blank solutions, calibration standards and samples to a final concentration of 0.44 nmol/L. The intensities measured for Zr and Nb were corrected with a factor of the In intensity in the respective solution divided by the averaged In intensity of the NaCl blank measured in the same analytical run. Hereby, potential suppression of the ICP - MS signal as well as incorrect filling of the sample loop were corrected. In order to prepare the calibration standards similar to seawater with respect to the NaCl concentration we used a 0.6 mol/L NaCl solution. Quantification was performed via a 4-point external calibration with calibration standards prepared of 0.6 mol/L NaCl solution acidified following the procedure for the samples (0.6 mol/L NaCl - 0.02 mol/L HCl - 0.002 mol/L HF). Prior to the preparation of the calibration standards NaCl (suprapure, Merck) needed to be pre-cleaned to remove trace metal impurities.

	Zr [pmol/kg] ^(a)	Nb [pmol/kg] ^(a)
Column yield [%]	106 ± 2 (n = 4)	100 ± 3 (n = 6)
Procedure blank	14.5 ± 3.03	1.35 ± 0.42
0.6 M NaCl-0.02 M HCl-0.002 M HF	(n = 17)	(n = 9)
Acid blank	34.7 ± 1.3	0.578 ± 0.094
0.02 M HCl-0.002 M HF	(n = 6)	(n = 8)
LOD ^(b)	9.10	1.27
LOQ ^(c)	27.3	3.82
Spike experiment		
North Sea water	107 ± 16 (n = 12)	3.52 ± 0.34 (n = 13)
Spike added	134	2.38
Measured spiked sample	237 ± 14 (n = 9)	5.68 ± 0.60 (n = 12)
Recovery [%]	104 ± 5 (n = 5)	94 ± 6 (n = 12)
Calibration range	44 - 220	2.2 - 10.8
Natural concentration range	31 - 275 ^(d)	4.0 - 7.2 ^(d)

(a) Mean ± SD, (b) LOD = 3 x SD of the procedure blank, (c) LOQ = 9 x SD of the procedure blank, (d) Data taken from Firdaus et al. (2008).

Table 4.1: Important analytical figures of the applied online-preconcentration method

Therefore, 5 g Chelex 100 were filled into a PE-column and pretreated according to the manual (?). A 2 mol/L NaCl-stock solution was poured onto the Chelex-resin and the pre-cleaned NaCl solution was collected in a pre-cleaned PE-bottle. After dilution of the pre-cleaned 2 mol/L NaCl solution the calibration standards were prepared by adding appropriate volumes of a metal standard mix containing Zr and Nb in a concentration ratio similar to their natural ratio in seawater. We applied a 4-point external calibration adjusted to the natural concentration range of dissolved Zr and Nb in seawater (Table 4.1).

4.2.3 ICP - MS method

The measurements were performed with a quadrupole ELAN 6000 DRC-e (Perkin Elmer) instrument. The peak area of the transient signal was used for calculating concentrations of dissolved Zr and Nb in seawater. The intensity of the procedure blank of this method measured in 0.6 mol/L NaCl - 0.02 mol/L HCl - 0.002 mol/L HF is subtracted from intensities of the measured calibration standards. Since the seawater samples have been acidified with 0.02 mol/L HCl - 0.002 mol/L HF the intensity of this acid blank is subtracted from the intensities of seawater samples (Table 4.1). Operating conditions of the ICP - MS analysis are given in Table 4.2.

Parameter	Operating condition
RF Power	1200 W
Nebulizer gas flow	0.97 L min ⁻¹
Auxiliary gas flow	0.99 L min ⁻¹
Time for data acquisition	1.25 min
Time for complete analysis (including preconcentration)	22 min

Table 4.2: Operating conditions for ICP - MS analysis (after Poehle et al., 2015)

4.2.4 Ancillary data, Atlantic Ocean

Temperature, salinity, dissolved oxygen

During M81/1 a conventional CTD (Seabird 911-plus) was deployed at the same stations as the trace metal-clean CTD and temperature, salinity and oxygen were recorded, except for station 21 where a normal CTD was not deployed. The concentration of dissolved oxygen was measured on board through Winkler titration and was used to calibrate the results for oxygen of the CTD-sensor. Since temperature, salinity and dissolved oxygen are expected not to be affected by the two different sampling devices we used the results obtained from the normal CTD-casts for correlation with dissolved Zr and Nb in seawater collected with the trace metal-clean CTD.

Nutrients (dissolved nitrate, phosphate and silicate)

Seawater samples collected with the conventional CTD during M81/1 were filtered on board (0.2 µm Sartobran P-MidiCaps) and stored frozen until the analysis at the GEOMAR Kiel (Frank Malien), Germany. Dissolved nitrate, dissolved phosphate and dissolved silicate were determined with a self-made autoanalyzer using the segmented flow analysis technique (SFA). The limits of detection for nitrate, phosphate and silicate were calculated to 0.03 µmol/L, 0.02 µmol/L and 0.03 µmol/L, respectively. A DI standard, which was adjusted to a seawater salinity of $S = 35$ containing 30.0 µmol/L nitrate, 2.50 µmol/L phosphate and 50.0 µmol/L silicate was used for calibration.

Reduction of dissolved nitrate on copper-coated granules which serve as a reductant in a heterogeneous system produced nitrite (Grasshoff et al., 1999). Total nitrite (initially present nitrite and reduced nitrate) was determined by the reaction with sulphanilamide and N-(1-naphthyl)-ethylenediamine dihydrochloride forming an azo dye. Its absorbance was measured at 520 nm wavelength. Subtracting the amount of initially present nitrite in the seawater sample from total nitrite resulted in the amount of dissolved nitrate.

A spectrophotometric method after Giedigkeit & Marquardt (2005) was applied to determine dissolved inorganic phosphate in the seawater samples. Phosphate reacts with trivalent antimony and acidified ammonium molybdate to a complex which was thereafter reduced with ascorbic acid at $\text{pH} < 1$. The absorbance of the intensely colored blue compound was measured at 880 nm wavelength.

Dissolved silicate in seawater reacts with ammonium heptamolybdate to a yellow β -silicomolybdic acid (Grasshoff et al., 1999). After sequential addition of oxalic acid and ascorbic acid which serves as a reducing agent a blue silicomolybdic complex was formed. The absorbance of this compound was measured at 660 nm wavelength.

Dissolved nitrate, phosphate and silicate showed the typical depth distribution of nutrients (Figure 4.3).

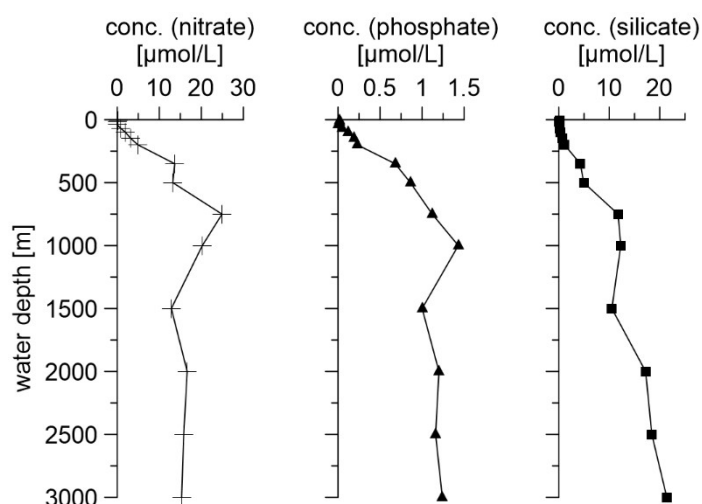


Figure 4.3: Vertical distribution of dissolved nitrate, phosphate and silicate at station 7. The samples were stored frozen until land-based analysis.

However, storage under frozen conditions until land-based analysis might have influenced the total concentrations in the seawater samples whereas the general pattern was not affected. In order to enable comparison of Si measured along the transects we decided to show the absolute values which are provided in the supplementary material (A2. Supplementary Data Table 2).

Dissolved Aluminum

On board analysis of dissolved Al was performed with most of the samples collected down to 500 m water depth and some deep water samples collected with the trace metal-clean CTD applying a fluorometric method (Hydes & Liss, 1976). Sixty ml subsamples were adjusted to pH 5 ± 0.05 with a sodium acetate-acetic acid buffer (Merck, suprapure), to perform a 4-point standard addition. Hence, three subsamples were spiked with an Al stock solution (500 $\mu\text{g Al/L}$, 0.05 mol/L HCl). After addition of 400 μl lumogallion solution (0.02 %, w/w, DI water) the subsamples were stored in a 70°C warm water bath for 90 min and were allowed to cool to room temperature afterwards. Excitation was performed at 465 nm and the fluorescence was measured at 555 nm (Koron SFM25 instrument). DI water adjusted to pH 5 with sodium acetate buffer served as a reagent blank. The reagent blank was determined separately for each analytical run applying a standard ad-

dition procedure. The average reagent blank was calculated to 7.57 ± 0.52 nmol/l (6.85 % RSD) and the limit of detection ($LOD = 3 \times$ standard deviation of the reagent blank) was 1.56 nmol/L.

The concentration of dissolved Al at the crossover station 7 (18.3 ± 8.0 nmol/L) is close to data provided by M. Hatta and C. Measures for this station (13 nmol/kg) within the GEOTRACES database (http://www.geotraces.org/sections/jpg/300dpi/GA03_e_Al_D_CONC_BOTTLE.jpg) in the upper 200 m of the water column. Measures et al. (2008) reported 17 nM at a station located at 24°N , 26°W sampled during a Climate Variability and Predictability (CLIVAR)-CO₂ Repeat Hydrography A16 N transect in June - August 2003. Small differences for Al between the studies are likely due to seasonal or hydrological differences.

4.3 Hydrography

A complex current system effects surface waters in the (sub)tropical Atlantic Ocean. The Azores current turns south at approx. 33°N and forms the Canary Current (CC) flowing southwestward along the west coast of the African continent (Mittelstaedt, 1991) and was observed at stations 2, 4, 5, and 6. The Canary Islands as a topographic barrier hinder the CC from unhampered flow southward and force the current to divide at the archipelago. The CC becomes detached from the continental margin between 25°N and 20°N (station 7) and turns into the North Equatorial Current (NEC) flowing westwards (Stramma & Schott, 1999). Further south at 10°N the North Equatorial Counter Current (NECC) dominates the surface waters of the eastern tropical Atlantic Ocean (stations 12 and 13). This wind-driven current system influences the distribution of surface water masses in the East Atlantic. Between 70 and 500 m water depth the upper ocean is occupied by North Atlantic Central Water (NACW). It is saltier, warmer and contains less dissolved oxygen than the corresponding South Atlantic Central Water (SACW) (Stramma & Schott, 1999). Mixing between NACW and SACW is assumed to occur at 20°N (station 9) since the detected water mass characteristics do not match unambiguously either those of NACW or SACW (Figure 4.4). In the western basin the boundary between NACW and SACW was detected at 8°N (station 22, Figure 4.5).

Antarctic Intermediate Water (AAIW) is formed in the Antarctic Polar Frontal Zone through subduction processes and flows northwards in the Atlantic Ocean. It is characterized by its low salinity and high oxygen concentrations (Stramma & England, 1999) and can be traced until approx. 20°N between 500 to 1200 m water depth (Figure 4.4b). The signature of AAIW is most distinct in the western basin (stations 19, 20, 21 and 22) with low salinities ($S < 34.55$) combined with high oxygen concentrations (Figures 4.5b and 4.5c).

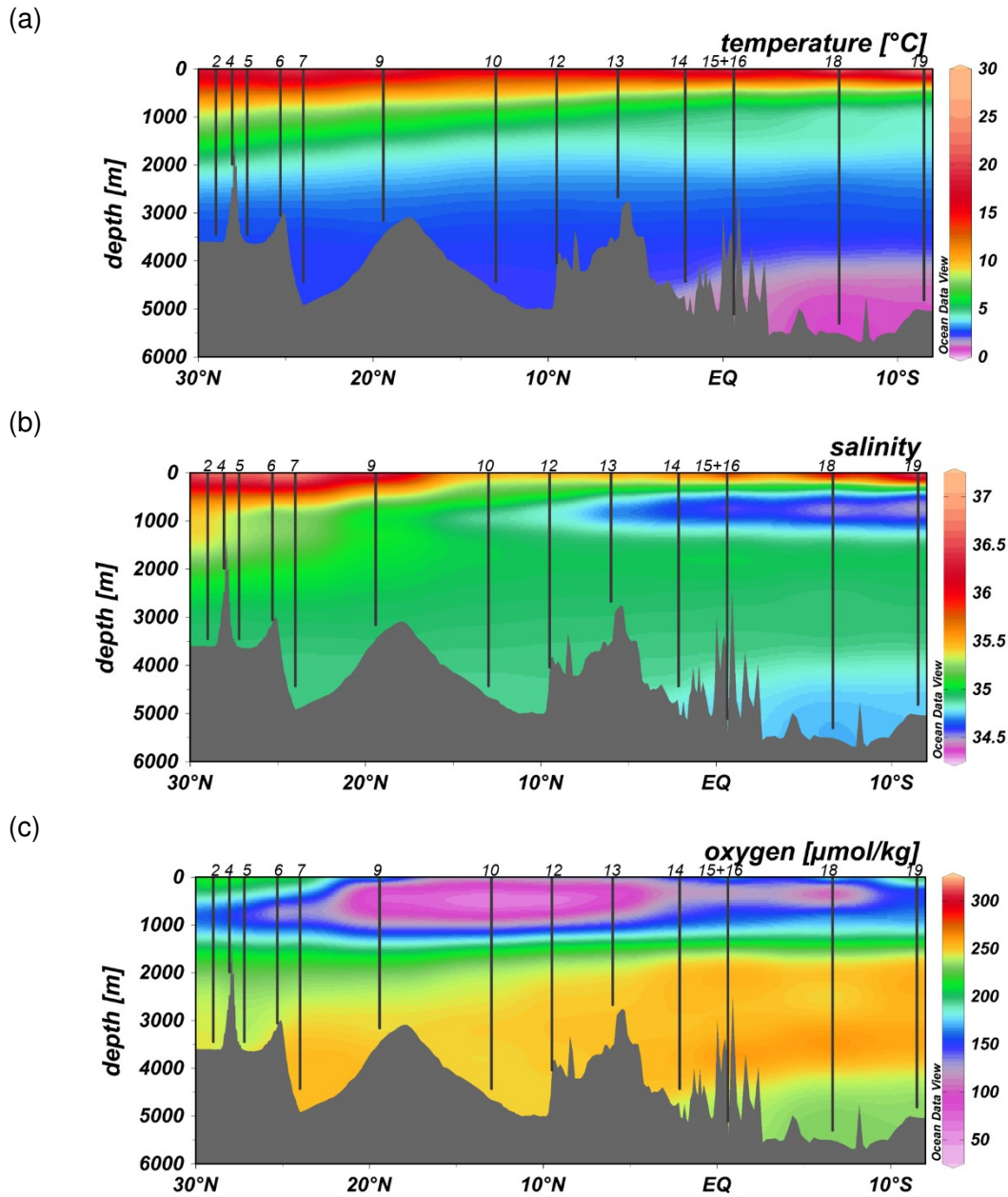


Figure 4.4: Section plots of (a) temperature, (b) salinity and (c) oxygen derived from the conventional CTD for the NE - SW transect from 30°N to 12°S. Station numbers indicated above the plot belong to trace metal-clean sampled stations which were performed at the same locations as the conventional CTD.

In the highly bioproduktive area off the African coast in the East Atlantic consumption of oxygen caused a pronounced Oxygen Minimum Zone (OMZ) (Figure 4.4c). Thus, AAIW can be traced by its low salinity ($S < 34.75$) until 7°N (stations 13, 14, 15+16, 18, 19). The observed increase in salinity at higher latitudes is probably due to admixing with southward moving more saline Mediterranean Outflow Water (MOW) (Figure 4.4b). To conclude, the characteristics of AAIW are more pronounced in the western than in the eastern basin.

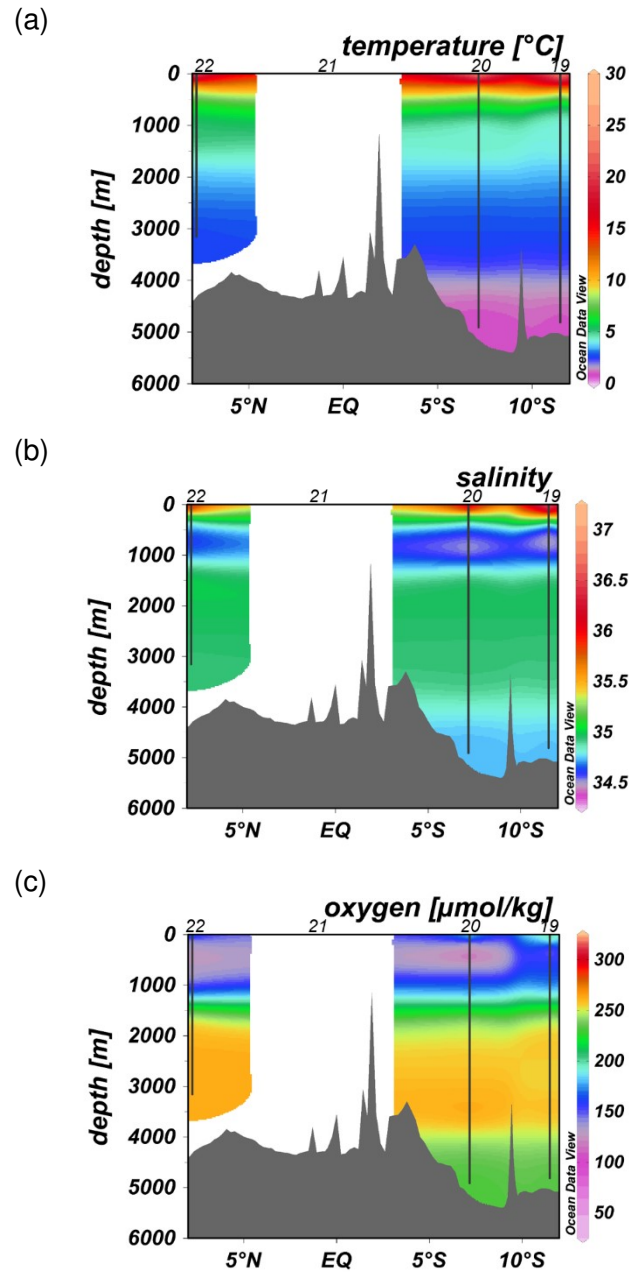


Figure 4.5: Section plots of (a) temperature, (b) salinity and (c) oxygen derived from the conventional CTD for the SE - NW transect from 8°N to 12°S. Indicated above the plot are the station numbers of the trace metal-clean sampled stations which were performed at the same locations as the conventional CTD. At station 21 a conventional CTD was not deployed.

North Atlantic Deep Water (NADW) flows southwards and originates from various regions such as the Labrador Sea and Greenland-Iceland-Norwegian (GIN) Sea, hence, showing different properties due to the individual source regions (Tsuchiya et al., 1994). According to Stramma and England (1999) the upper boundary of NADW in the tropical Atlantic was defined by the isopycnal $\sigma = 32.15$ and ranged between 1200 to 3800 m water depth in the area covered during M81/1 and was detected at all stations. NADW in the

Canary Basin (stations 2, 4, 5, 6, 7) is more saline and warmer ($\theta = 4.44^{\circ}\text{C}$, $S = 35.15$, $\text{O}_2 = 231.19 \mu\text{mol/L}$) due to mixing with southward flowing MOW compared to NADW detected in the Cape Verde Basin ($\theta = 3.57^{\circ}\text{C}$, $S = 35.00$, $\text{O}_2 = 229.25 \mu\text{mol/L}$). The core of Upper North Atlantic Deep Water (UNADW) was identified at 1700 m water depth for stations along the transect at 20°W from 10°N southwards in the East Atlantic Ocean (stations 12, 13, 14) and station 15+16 located above the Romanche Fracture Zone. In the western basin at 8°N UNADW was detected at 1600 m (station 22) and declines to 1800 m in the Brazil Basin (station 19).

The isopycnal at $\sigma = 45.90$ marks the upper boundary of Antarctic Bottom Water (AABW) in the western tropical Atlantic Ocean and was encountered at 3800 m water depth at a potential temperature near 1.74°C (stations 18, 19 and 20, Figures 4.4a and 4.5a); it is cooler, fresher and contains less oxygen than the overlying NADW. Only the densest part of the AABW, hence a relatively small fraction, enters the eastern basin from the Brazil Basin via the Romanche Fracture Zone and mixes with overlying NADW altering its characteristics. According to Tsuchiya et al. (1992) the isotherm $\theta = 2^{\circ}\text{C}$ defines the upper boundary of AABW in the East Atlantic, which deepens from 3925 m water depth at station 14 to 4055 m water depth at station 7 in the Canary Basin. AABW detected at station 10 in the Cap Verde Basin and further north originates from the Guyana Basin entering the eastern basin through the Vema Fracture Zone of the MAR and differs slightly in potential temperature ($\theta = 1.88^{\circ}\text{C}$), salinity ($S = 34.88$) and oxygen ($\text{O}_2 = 246.14 \mu\text{mol/L}$) from the AABW detected at lower latitudes ($\theta = 1.87^{\circ}\text{C}$, $S = 34.88$, $\text{O}_2 = 251.81 \mu\text{mol/L}$).

In general, the hydrographic characteristics are more strongly developed in the western Atlantic basin while the distinct features are altered in the eastern basin due to mixing with adjacent water masses.

4.4 Results

4.4.1 Atlantic Ocean

NE - SW transect

Along the NE - SW transect off the African coast Zr shows a surface depletion (approx. 80 pmol/kg) and increasing concentrations in deep waters with up to 200 pmol/kg (Figure 4.6a). Distinct maxima (284 pmol/kg, 300 pmol/kg and 360 pmol/kg) were observed in intermediate water depths at 1490 m at stations 4, 9 and 12, respectively, and in deeper waters at station 18 (359 pmol/kg, 3452 m).

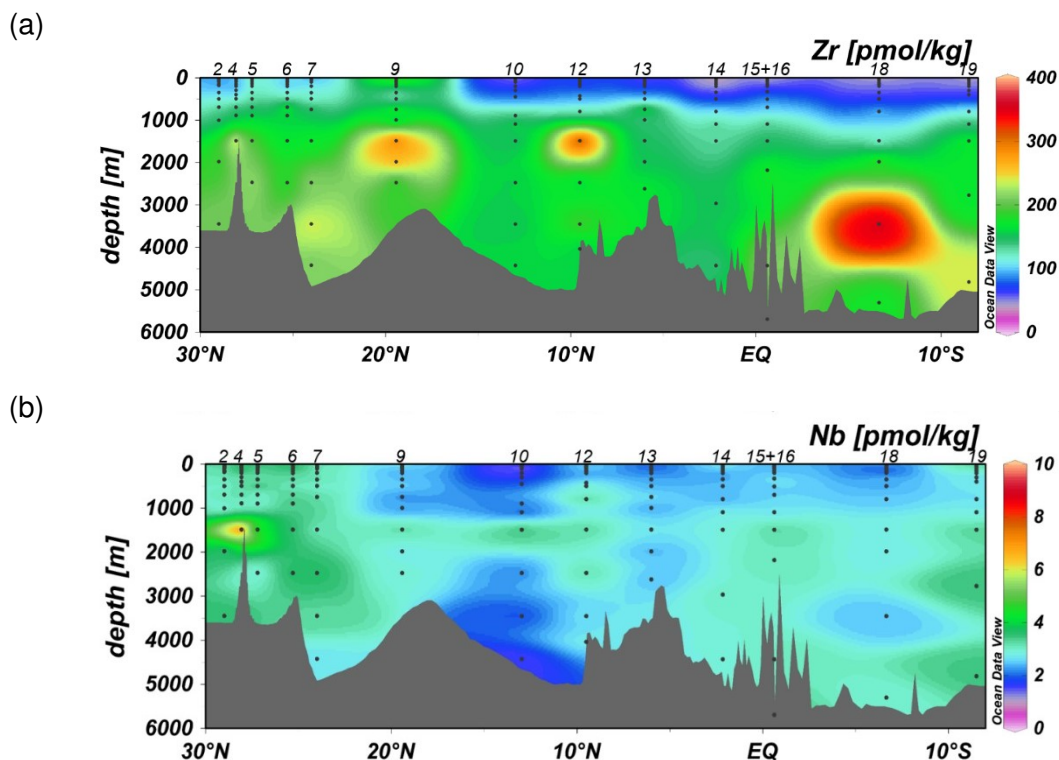


Figure 4.6: Vertical distribution of dissolved Zr (a) and Nb (b) along the NE - SW Atlantic transect between 30°N and 12°S.

In the Canary Basin (stations 2, 4, 5 and 6) Zr was detected at 103 ± 23 pmol/kg (upper 500 m) while the concentration in deep water layers was 182 ± 45 pmol/kg. At station 7 (24.0°N, 23.0°W) which is also located in the Canary Basin the concentration of Zr increased from 88.8 pmol/kg (39 m water depth) to 240 pmol/kg in bottom-near waters (3449 m). High variations in Zr concentration were observed at station 9 (19.4°N, 20.4°W). Surface waters contained 224 pmol/kg which decrease sharply to 99.7 pmol/kg (69 m water depth) followed by an increase to 324 pmol/kg in 100 m water depth. At the seafloor 160 pmol/kg Zr were detected in bottom-near waters (2472 m). The depth distribution of Zr along the transect at 20°W off the African coast between 14°N and 1°N (stations 10, 12, 13 and 14) resembles the profile described for the Canary Basin with a surface depletion and an increase in concentration with depth. The surface concentrations were lower (64 ± 20 pmol/kg) compared to the concentrations observed in the Canary Basin. The vertical profile of Zr above the Romanche Fracture Zone (station 15+16) was similar to the profiles observed between 14°N and 1°N and Zr increased from 29.1 pmol/kg (40 m) to 196 pmol/kg (5692 m).

Dissolved Zr increased with depth in the western Atlantic basin of the NE - SW transect between 1°S and 12°S (stations 18 and 19) from 54.3 ± 21.4 pmol/kg to 213 ± 37 pmol/kg, surface and deep water concentrations, respectively. At station 18 an intermediate maximum (359 pmol/kg) was observed at 3452 m water depth.

In summary, the general trend observed for Zr is lowest concentrations at the surface

and an increase with depth with some distinct maxima at intermediate depth.

Profiles of Nb showed in general less distinct features compared to Zr and were close to a conservative distribution.

In the Canary Basin (stations 2, 4, 5, 6 and 7) dissolved Nb was present at 3.33 ± 0.83 pmol/kg and was conservatively distributed with depth except a maximum, 8.49 pmol/kg, between Gran Canaria and Tenerife (station 4) at 1484 m water depth (Figure 4.6b) which coincides with the Zr maximum. Between 22°N and 11°N (stations 9 and 10) Nb was present at 2.02 ± 0.56 pmol/kg in the upper 1000 m of the water column and increased slightly to 3.40 ± 0.23 pmol/kg at 1487 m water depth. While at station 9 deep water concentrations of Nb were slightly higher (2.78 ± 0.09 pmol/kg) compared to concentrations in surface waters the concentration in deep waters at station 10 (1.81 ± 0.30 pmol/kg) was in the same range compared to surface waters. At lower latitudes (11°N - 1°S ; stations 12, 13, 14 and 15+16) Nb was depleted in surface waters (2.35 ± 0.33 pmol/kg) although the depletion was less pronounced compared to the area between 22°N and 11°N . The concentrations in deep waters were slightly higher than observed at stations 9 and 10.

In the western Atlantic basin (station 18; 6.65°S , 25.7°W) Nb was slightly depleted in surface waters (2.17 ± 0.28 pmol/kg, upper 500 m) compared to deep waters (2.85 ± 0.20 pmol/kg, 1500 - 5300 m water depth). The difference in concentration between surface and deep water concentrations exceeds the RSD of the applied method (9.7%, Poehle et al., 2015) and can therefore be considered significant. At station 19 (11.5°S , 28.5°W) surface waters were again slightly depleted (2.97 ± 0.43 pmol/kg, upper 500 m) compared to deep waters (3.39 ± 0.08 pmol/kg, 1500 - 4800 m water depth) but throughout the water column the concentrations were higher compared to station 18.

SE - NW transect

We observed a depletion of Zr in surface waters (47.0 ± 18.0 pmol/kg, upper 500 m) between 3°N and 12°S (stations 19, 20 and 21) which was most pronounced at station 20 with 23.4 pmol/kg in 99 m water depth (Figure 4.7a). With increasing water depth an increase in concentration was detected up to 200 pmol/kg. This pattern was less dominant at station 22 with 68 pmol/kg Zr in surface waters (68 m water depth) increasing to 161 pmol/kg in deep waters (3454 m water depth). The concentration of Zr varied significantly in the upper 500 m between 58.4 pmol/kg (99 m water depth) and 280 pmol/kg (149 m).

The average concentration of Nb along this transect off the Brazilian coast was 2.84 ± 0.56 pmol/kg (Figure 4.7b) and only small deviations were observed. At station 20 (7.17°S , 31.2°W) the concentration of Nb increased from 3.05 pmol/kg in surface waters (38.4 m) to 4.14 pmol/kg in deep waters (4915 m). We observed only slightly lower concentrations (2.24 pmol/kg, 20.7 m) in surface waters at station 21 (0.60°N , 39.9°W) compared to deep water concentrations (2.75 pmol/kg, 1487 m); this difference exceeds the

RSD of the applied method (9.7 %) only slightly. At the northernmost station 22 Nb was conservatively distributed throughout the water column ranging between 2.69 pmol/kg and 2.97 pmol/kg, surface and deep water, respectively.

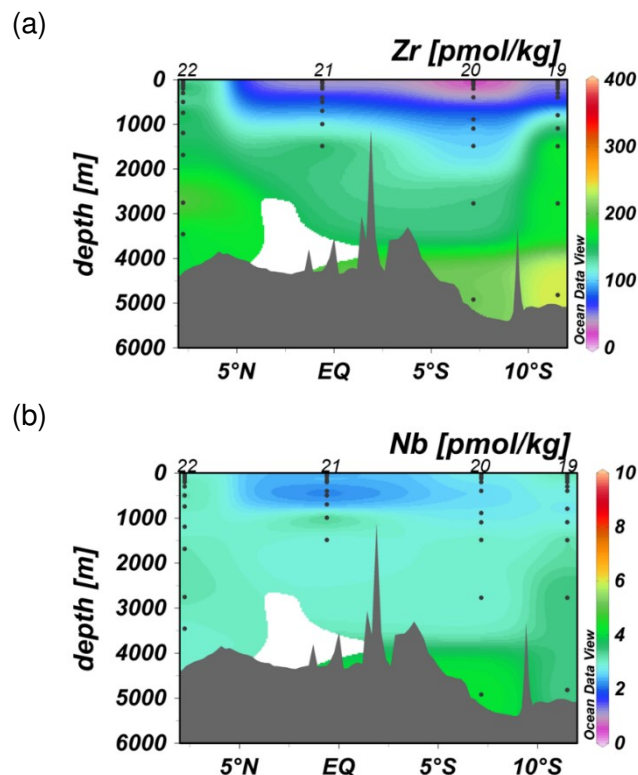


Figure 4.7: Vertical distribution of dissolved Zr (a) and Nb (b) along the SE - NW Atlantic transect between 8°N and 12°S.

4.4.2 Colloidal and dissolved Zr and Nb

The two stations in the Pacific Ocean were sampled in deeper waters (1500 m - 1700 m) and filtered with both pore sizes filters (0.2 μm and 0.015 μm) to investigate the role of colloiddally bound Zr and Nb. Colloidal and dissolved Zr (<0.2 μm) was present at 167 ± 7 pmol/kg in the hydrothermal plume between 1500 m and 1700 m sampling depth and no significant variation in this range was observed. The seawater background sample contained 178 pmol/kg dissolved Zr which is similar to the concentration observed at the hydrothermally active site (Figure 4.8). The average concentration of small colloidal and dissolved Zr (<0.015 μm) in the hydrothermal plume between 1500 and 1700 m water depth was 150 ± 3 pmol/kg. The concentration of small colloidal and dissolved Zr (<0.015 μm) in the seawater background sample was 191 pmol/kg which is slightly higher than the concentration of colloidal and dissolved Zr (178 pmol/kg). However, this difference is within the range of analytical uncertainty of this method (RSD = 15 %, Poehle et al., 2015).

Dissolved and colloidal Nb ($<0.2\mu\text{m}$) was present at $2.63 \pm 0.13\text{ pmol/kg}$ in samples collected in the hydrothermal plume and was distributed conservatively in the range of 200 m (Figure 4.8). The Nb fraction $<0.015\mu\text{m}$ was $2.80 \pm 0.11\text{ pmol/kg}$. Since the RSD of the applied method for the determination of dissolved Nb in seawater was calculated as 9.7 % (Poehle et al., 2015) the slight difference between measured dissolved and colloidal Nb lies within the uncertainty of the measurement.

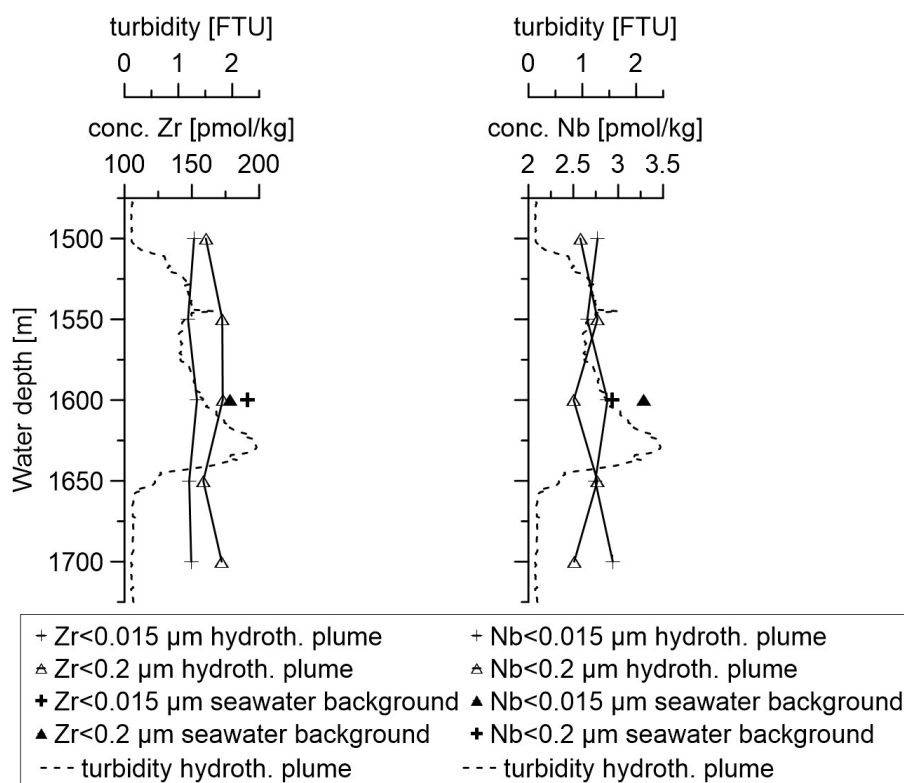


Figure 4.8: Distribution of dissolved ($<0.2\mu\text{m}$) and small colloidal and dissolved ($<0.015\mu\text{m}$) Zr and Nb in a hydrothermal plume between 1500 m and 1700 m and the size distribution of Zr and Nb in a seawater background sample at 1600 m water depth. The dashed line marks the turbidity signal during upcast of the CTD passing through the hydrothermal plume.

Dissolved ($<0.2\mu\text{m}$) and small colloidal ($<0.015\mu\text{m}$) Nb in the seawater background sample were present in similar concentrations, 2.94 pmol/kg and 3.29 pmol/kg , respectively, indicating no significant difference between the hydrothermal plume and the seawater background sample. The values for both Zr and Nb in these two Pacific sample sets were in the same range as the Atlantic samples from this depth range.

4.5 Discussion

4.5.1 Atlantic Ocean

NE - SW transect

The concentration of Zr in the upper 200 m of the water column upstream the Canary Islands (station 2) is similar to the concentration downstream (station 7) indicating that the observed concentration range of Zr in surface water might represent the Zr signature of southward flowing MOW which was detected between 30°N and 20°N and is characterized by its high salinity (Figure 4.4b). Zirconium is, however, a scarcely studied trace metal and data for the Mediterranean Sea have not yet been published.

Although highest variations in concentration of Zr were observed in the upper 500 m of the water column, which is part of the photic zone characterized by high biological activity, comparison of the depth distribution of Zr with nitrate and phosphate in the corresponding seawater samples revealed no correlation between these parameters. In contrast, comparison with Si revealed a correlation with coefficients ranging between 0.56 and 0.71 at stations 4, 5, 6 and 7 (Figure 4.9).

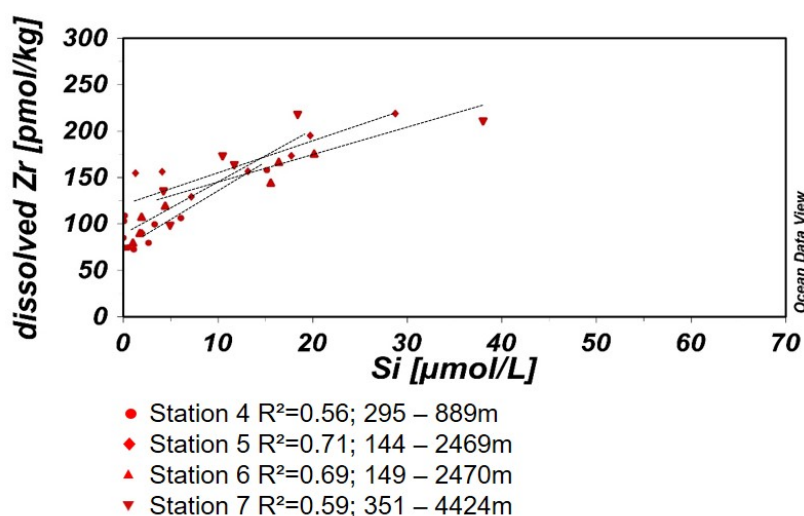


Figure 4.9: Scatter plot of dissolved Zr vs. dissolved Si for stations located in the Canary Basin (station 4, 5, 6 and 7) including the correlation coefficient R^2 . Data on dissolved Si are not available for station 2. The relationships are shown for the sampled depth range indicated after the coefficient factors.

Sorption onto or incorporation into silicate particles might have scavenged dissolved Zr in the vicinity of the Canary Islands. The observed increase in deeper waters is assumed to be due to release of Zr from silicate particles e.g. radiolarians. Deviations from the linear Zr/Si relationship were observed in surface waters, where we find higher Zr with respect to the linear correlation indicating atmospheric input of Zr or uptake of Si into radiolarians in the photic zone while Zr is not or to a lower extent affected by the biological

activities of these organisms. Our suggestion of an atmospheric source for Zr agrees with a study on dissolved Zr in the North Pacific Ocean (McKelvey & Orians, 1993). The authors suggested coastal sources of Zr, which led to deviations from the linear correlation between Zr and Si. We probably detect, however, the net effect of several processes, i.e. sorption onto or incorporation into silicates, sorption onto deposited mineral particles and release of Zr from deposited particulates, which cannot be distinguished at this stage of the study.

In deep waters at station 4, located between the islands Gran Canaria and Tenerife, the slight increase in concentration observed might have been caused by the direct proximity of an underwater rise to the sampled depth (1484 m water depth). A correlation with Si was obvious for waters down to 891 m water depth except in surface waters but Si data are not available for deeper waters to confirm our suggestion of Zr release from silicate particles.

Along the NE - SW transect highest surface concentrations of Zr were observed at station 9. Southward flowing MOW was detected in surface waters of the Canary Basin and further south at station 9 (Figure 4.4b). While waters in the Canary Basin might be influenced by at least two parameters: 1) MOW and 2) input from the volcanic islands in either dissolved or particulate form, no significant deposition of dust particles was observed at station 9 since dissolved Al, a tracer for dust deposition, showed low concentrations (Figure 4.10).

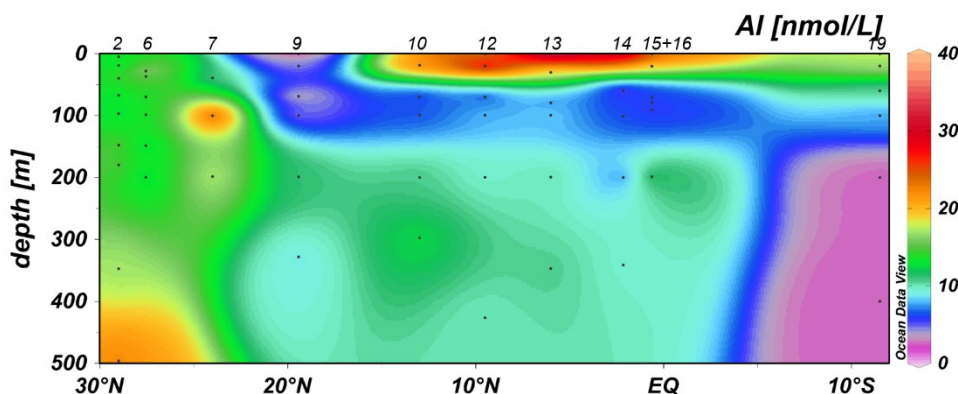


Figure 4.10: Distribution of dissolved Al in the upper 500 m of the water column along the complete investigated transect during M81/1 in the (sub)tropical Atlantic Ocean.

We assume that particles provided by the Canary Islands might represent sorption sites for dissolved Zr in the Canary Basin leading to lower surface concentrations in the proximity of the archipelago than detected at station 9.

A coupling between Si and Zr was not observed for water samples collected at station 9 indicating either minor scavenging onto silicate particles or a more pronounced release from particulate matter in comparison with the area investigated in the proximity of the Canary Islands. Since we do not have particulate samples an unambiguous allocation

cannot be provided.

Station 9, however, seems to be located in a transition zone between the region influenced by the Canary Islands and the transect further south influenced by Saharan dust input. During our sampling campaign a significant dust input was not observed but nevertheless dust deposition in this area is in general not negligible. Dissolved Al, which has been widely applied as a tracer for deposition of dust particles (Dammshäuser et al., 2011; Measures et al., 2008; Measures & Vink, 2000) showed elevated concentrations between 14°N and 5°S compared to Al in surface waters sampled at lower or higher latitudes of this transect (Figure 4.10). The residence time of particulate Al in surface water layers in the Atlantic was calculated to 3-22 days while dissolved Al can remain up to 3.8 years in surface waters (Dammshäuser et al., 2013). Hence, deposition of dust derived from Africa might have occurred prior to our research cruise. The elevated surface concentrations of Al coincide spatially with the most pronounced surface depletion of Zr (14°N and 12°S) supporting our suggestion of sorption of dissolved Zr onto particles in surface water layers. A scatter plot of dissolved Zr vs. dissolved Al approving their relation is not useful in this study since the sampling for the Zr analysis started in deeper waters than for the Al samples.

Although stations located in the proximity of the Canary Islands and stations between 14°N and 1°N are influenced by deposition of mineral particles the observed net effect on the distribution of Zr in surface waters is different. Particles deposited in both regions probably differ in their composition, size and their physico-chemical properties which might have led to lower surface concentrations between 14°N and 1°N compared to surface waters in the Canary Basin. This difference in distribution between the transect off West Africa and the Canary Basin has also been observed for dissolved W in samples collected during M81/1 (Poehle and Koschinsky, unpublished) with lower concentrations off West Africa.

Deep-water Zr concentrations between 14°N and 1°N are in a concentration range similar to deep waters sampled in the Canary Basin. Since the correlation coefficient between dissolved Zr and Si ranged between 0.68 and 0.85 for stations sampled between 14°N and 1°N a link in the geochemical behaviour of both elements appears reasonable (Figure 4.11). Higher Zr concentrations with respect to the linear relationship were observed for surface waters revealing that atmospheric sources e.g. mineral dust, might provide Zr to surface waters. Since deposited mineral particles have also been characterized as sorption sites for dissolved Zr off West Africa we assume that both processes might occur simultaneously and we observe a net effect. A correlation of Si with Zr between 100 and 2300 m water depth has been reported in the central North Pacific (McKelvey & Orins, 1993). The authors suggest that Zr is influenced by the internal cycling of Si including surface removal and regeneration in deep waters. A similar relationship was observed in the Pacific Ocean along 170°W and 160°W with an increase in concentration in coastal waters (Firdaus et al., 2011).

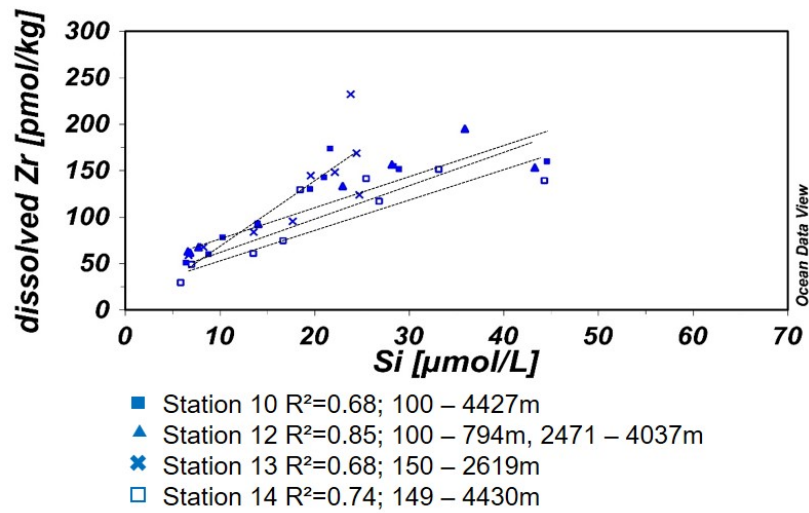


Figure 4.11: Scatter plot of dissolved Zr vs. dissolved Si for stations located between 14°N and 1°N (station 10, 12, 13, and 14) along the NE - SW transect including the correlation coefficient R^2 . The relationships are shown for the sampled depth range indicated after the coefficient factors.

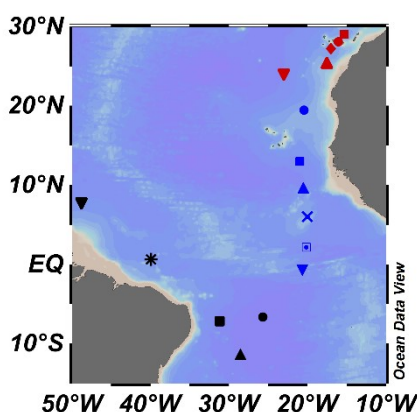
Dust input was also observed at the station located above the Romanche Fracture Zone at the MAR and might have caused the observed surface depletion as discussed for the transect between 14°N and 1°N. The water depth profile of Zr is similar to the vertical profiles observed at higher latitudes off the West African coast with no indication of hydrothermal input or scavenging. The similarity of Zr to the depth distribution of Si is less pronounced above the Romanche Fracture Zone than observed between 14°N - 1°N resulting in a correlation coefficient of only 0.47. Deviations of the linear relationship observed in surface water layers at this station were probably caused by deposited dust.

In the western Atlantic basin (1°S - 12°S) the typical Zr increase with depth was observed again with an intermediate maximum at 3452 m water depth at station 18 (6.65°S, 25.7°W) which was not observed at station 19 and we therefore assume that a water-mass dependent concentration for NADW is not probable since this water mass was traced at both stations between 1200 - 3800 m water depth (Figure 4.6a). Dissolved Al occurred at slightly lower concentrations between 5°S and 12°S than between 14°N and 5°S off the west African coast indicating a less pronounced dust input after long-range transport of Saharan dust which has been reported previously (Abouchami et al., 2013; Kumar et al., 2014; Mahowald, 2002; Prospero, 1999). However, the surface concentrations of Zr between 1°S and 12°S (stations 18 and 19) were similar to the concentrations detected in surface waters in the area influenced by Saharan dust and hence other parameters, e.g. the SACW characterizing surface water layers south of 8°N might also play a role. The temperature-salinity properties of the SACW revealed a higher resemblance to the properties of the Indian Central Water (ICW) than to the typical Subtropical Convergence in the Atlantic (Tomczak & Godfrey, 2001) indicating that a large portion of the

SACW is brought from the Indian Ocean to the Atlantic by the Agulhas Current. Hence, it is possible that the surface depletion observed between 1°S and 12°S may represent the signature of the SACW. Since our data do not allow to distinguish between the discussed different factors, sorption onto deposited dust particles and water mass specific signatures, a mixture of several influences may have caused the observed profiles in the western basin of the NE - SW transect (stations 18 and 19).

The concentrations, however, did not correlate with water masses (Figure 4.12) and hence the distribution of Zr alone does not serve as a proxy for water masses in the Atlantic Ocean.

(a)



(b)

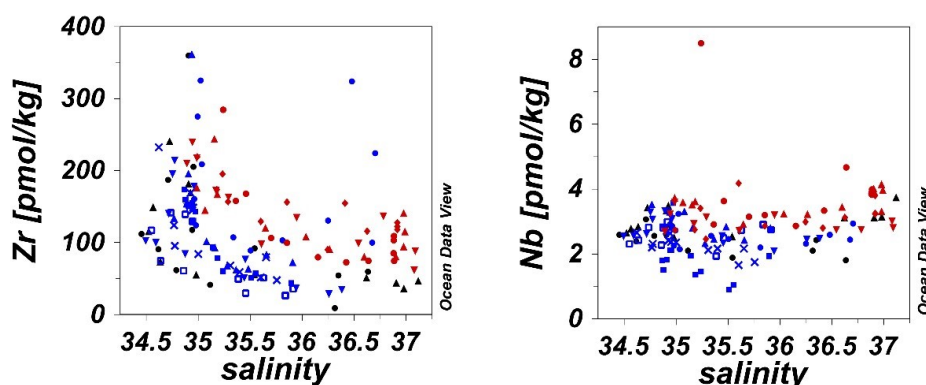


Figure 4.12: Symbols for all stations sampled during M81/1 used for scatter plots (a) and the scatter plots for the NE - SW transect (b) of dissolved Zr (left) and dissolved Nb (right) vs. salinity.

Niobium was uniformly distributed in the Canary Basin except a slight increase in concentration at station 4 located between the islands Gran Canaria and Tenerife, which coincides with increased Zr concentrations indicating a location-specific pattern e.g. release of both metals from underwater rock material of the volcanic islands.

The conservative depth distribution of Nb could be due to different reasons: 1) mixing with southward flowing MOW does not seem to have a major influence on the distribution

of Nb, 2) deposition of particles derived from the archipelago and subsequent release of Nb might overprint a potential signature of MOW transporting less Nb compared to surface waters not influenced by this water mass.

Surface waters at station 9 off the West African coast (19.4°N, 20.4°W) are not influenced by deposition of particles since dissolved Al does not indicate dust input in this distinct area and associated processes, e.g. dissolution of particles and/or sorption of dissolved Nb onto particles seem to be negligible. Surface waters are, however, influenced by southward moving MOW and the observed surface depletion might represent the signature of the MOW as discussed for Zr. Since this surface depletion was not observed in the Canary Basin we assume that deposited particles derived from the archipelago release Nb counteracting the lower concentrations of Nb in MOW and leading to a rather conservative distribution with depth.

The observed slight surface depletion between 14°N and 1°N as well as at the station located above the Romanche Fracture Zone may be attributed to sorption onto mineral particles derived from the African continent. Although both metals, dissolved Nb and Zr, are influenced by the same parameter, Saharan dust input, their distributions seem to be affected to different extents since a scatter plot of both metals showed only a small linear correlation (Figure 4.13). Influence of hydrothermal activity to deep water Nb concentrations was not observed at the station located close to the MAR, as for Zr.

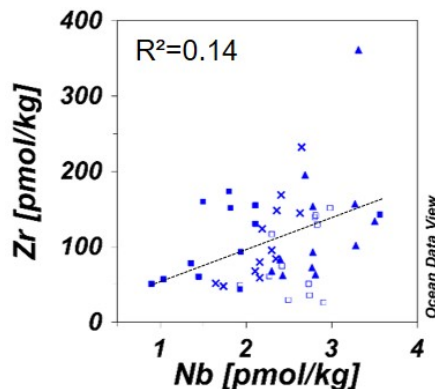


Figure 4.13: Scatter plot of dissolved Zr vs. dissolved Nb for stations 10, 12, 13, and 14 located between 14°N and 1°N along the NE - SW transect in the (sub)tropical Atlantic Ocean.

In the western Atlantic basin (station 18) Nb was slightly depleted in surface waters which might be due to sorption onto mineral particles deposited after long-range transport of Saharan dust as discussed for Zr. Surface concentrations at station 19 were higher compared to station 18, which might be due to a lower impact of sorption processes of dissolved Nb onto dust particles. Surface waters between 1°S and 12°S (stations 18 and 19) are influenced by SACW which might also play a role. It is, however, not possible with our dataset and the ancillary data to distinguish between these different parameters and to assess their relative effect on the distribution of dissolved trace metals.

Since deep water concentrations at station 19 were slightly higher compared to surface concentrations and to concentrations observed at station 18 potential release from the shelf sediment might be responsible.

Throughout the NE - SW transect comparison of Nb with dissolved nutrients (nitrate, phosphate and silicate) did not reveal a correlation indicating that the marine cycling of Nb is largely independent from biological element cycling.

Along the NE - SW transect the Si depth profile agrees with previous studies showing low surface concentrations, a sharp increase with depth towards approx. 1000 to 1500 m water followed by a slight increase in concentration towards the seafloor (Figure 4.14). In comparison to data provided by J. Swift (cruise GA03_e, October 2010, http://www.egeo-traces.org/sections/jpg/300dpi/GA03_e_SILCAT.jpg) for the area between 30°N to 22°N, we detected slightly lower concentrations throughout the water column which might be due to the previously mentioned storage under frozen conditions until land-based analysis. It should also be noted, that nutrient concentrations in general are lower in autumn compared to spring when the sampling campaign for this study was performed.

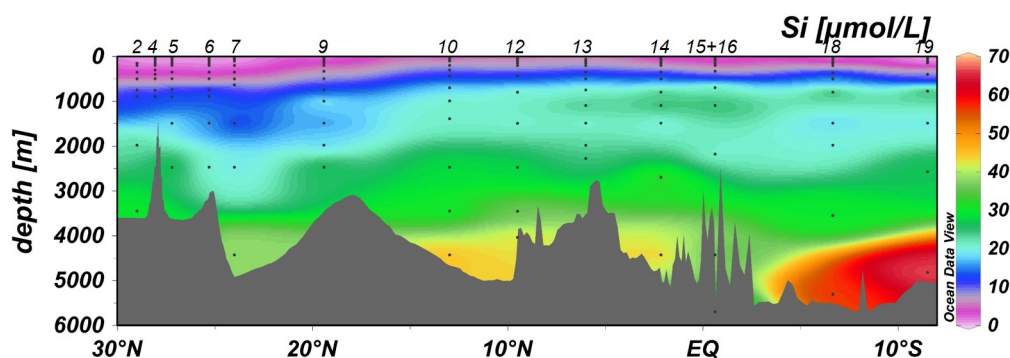


Figure 4.14: Vertical profile of dissolved Si along the NE - SW transect between 30°N and 12°S.

The Si distribution does not vary significantly between the stations along the NE - SW transect, which is different to the distribution of Zr showing distinct areas of lower concentrations off West Africa. The slopes for Zr vs. Si range between 2.78 and 3.36 except for stations 4 and 6 (5.76 and 5.52, respectively) in the Canary Basin and station 13 (6.58) off the African coast. Hence, the difference in slopes can be attributed to different Zr concentrations due to e.g. regional sources and/or scavenging mechanisms.

McKelvey & Orians (1993) observed a strong correlation between Zr and Si in the Pacific Ocean as well. We calculated the slope of the regression line for their data to be approx. 1.3, which is by a factor of 3 lower than the slopes presented in our study. This difference might be due to higher dissolved Si concentrations in the Pacific compared to the Atlantic (Levitus et al., 1993) since the concentration of Zr was in the same range in both studies.

SE - NW transect

The surface depletion of dissolved Zr between 3°N and 12°S was in the same concentration range as detected between 14°N and 1°S along the NE - SW transect. The concentration of dissolved Al at station 19 (Figure 4.10) agrees with data on dissolved Al determined during research cruise 74JC057 in March-April 2011 (Middag et al., 2015). Compared to the area under Saharan dust influence the concentration of dissolved Al was slightly lower indicating less pronounced dust input in the western Atlantic basin shortly before our sampling campaign. Nevertheless, deposition of Saharan dust after long-range transport needs to be considered as a parameter for the distribution of dissolved Zr in the West Atlantic in terms of providing sorption sites as discussed for the NE - SW transect (1°S - 12°S) or releasing Zr from deposited particles.

The higher concentrations in surface waters at station 22 (7.77°N, 48.8°W) compared to surface water layers sampled further south (3°N - 12°S) might be attributed to riverine discharge from the Amazon since the mean concentration of dissolved Zr in the Amazon was reported as 296 pmol/L (0.027 µg/L, Gaillardet et al., 2014) and a range of 110 - 2360 pmol/L for the Amazon and some tributaries close to the estuary (Schneider et al., 2015b) which is on average much higher than the mean concentration of dissolved Zr in the Atlantic (118 pmol/kg, this study). Release of Zr from riverine particles might also occur. Although based on salinity data this station was not located in the Amazon plume, which is expected to flow northeastwards in February (Chérubin & Richardson, 2007), and the sampling campaign was performed in the dry season it might be possible that we observed remnants of a previous high-discharge event in surface waters. The Amazon provides more than one-third of the freshwater discharge (Dai & Trenberth, 2002) to the Atlantic and transports a high load of particulate matter.

Surface waters (0 - 500 m) were also characterized by SACW which was detected at approx. 8°N extending further south during M81/1; this might also have affected the distribution of dissolved Zr in surface waters at all stations located along the SE - NW transect to a certain extent. Deep water concentrations were similar to those observed in the NE - SW transect and we assume that similar mechanisms stabilize dissolved Zr in deep waters throughout the (sub)tropical Atlantic Ocean.

A linear relationship between Zr and Si was detected for samples collected at station 19 while the correlation was even more obvious at station 20 (Figure 4.15). Potential dust deposition at station 19 might have led to deviations in surface waters as discussed for the area under Saharan dust influence leading to a higher intercept of the linear regression line for station 19 compared to station 20. Both lines display similar slopes revealing a comparable biogeochemical behaviour of dissolved Zr and Si with depth at both stations. Mixing with riverine freshwater might be an explanation for the absence of a Zr-Si-correlation at station 22.

The average concentration of Nb along this transect was similar to the average con-

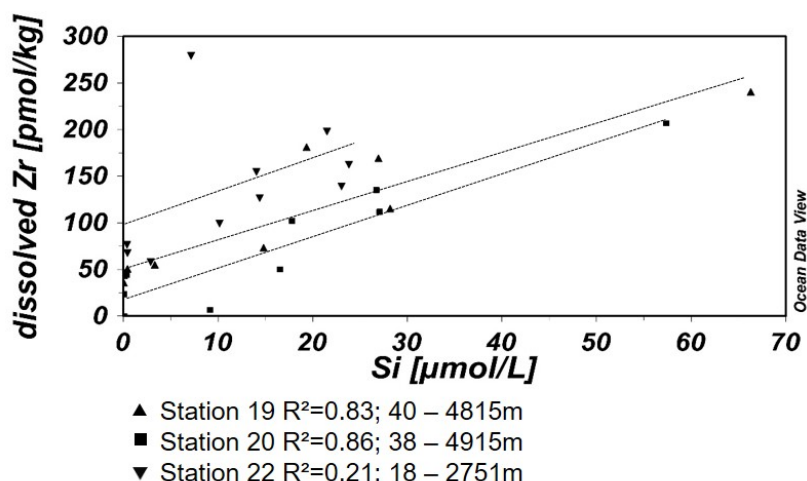


Figure 4.15: Scatter plot of dissolved Zr vs. dissolved Si for the SE - NW transect off the Brazilian coast between 8°N and 12°S (stations 19, 20, and 22) in the (sub)tropical Atlantic Ocean. The relationships are shown for the entire water column from surface to deep waters as indicated after the correlation coefficients.

centration reported for the NE - SW transect. Between 3°N and 12°S (stations 19, 20 and 21) the concentration increased slightly towards the seafloor which may be a signal of release from the shelf sediment.

Mixing with Amazon freshwater might explain the absence of a surface depletion at station 22, which was observed at lower latitudes (stations 20 and 21). The Amazon has been reported to be a source for Fe (Rijkenberg et al., 2014) and it seems probable that also other trace metals such as Nb and Zr are provided to the Atlantic by the Amazon River.

As observed for the NE - SW transect the distribution of Nb does not correlate with dissolved nutrients (silicate, nitrate and phosphate) indicating no strong coupling with biological activity, neither through sorption nor incorporation processes.

The distribution of Si along the SE - NW Atlantic transect shows low surface concentrations and an increase in concentration with depth which is more pronounced at stations 19 and 20 (up to 66 $\mu\text{mol/kg}$) compared to station 22 (21 $\mu\text{mol/kg}$, Figure 4.16).

This pattern agrees with data provided through GEOTRACES (http://www.egeotraces.org/sections/jpg/300dpi/GA02_SILCAT.jpg K. Bakker et al., GA02, June 2010) although they reported higher concentrations with up to 120 $\mu\text{mol/kg}$ Si between 8°N and 12°S. As already mentioned for the data from the NE - SW profile, the difference in concentration might be due to the sample handling until land-based analysis in this study and also seasonal differences have played a role.

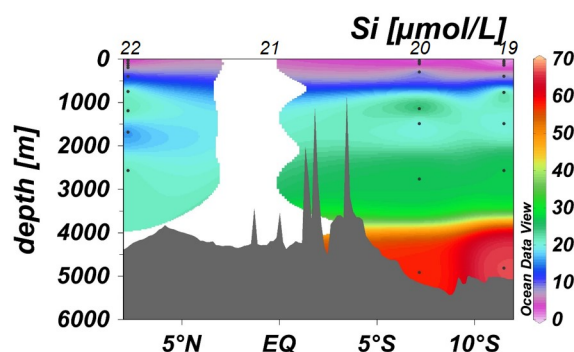


Figure 4.16: Vertical profile of dissolved Si along the SE - NW transect between 8°N and 12°S.

The slope of the Zr vs. Si regression lines ranges between 3.13 and 3.40 indicating a similarity in the biogeochemical behaviour of Si and Zr in this area.

4.5.2 Increase in dissolved Zr and Nb from surface to deep Atlantic waters – Coupling to the Si cycle and complexation with organic ligands as a potential explanation

We observed a general increase with depth of dissolved Zr and less pronounced also for Nb in the (sub)tropical Atlantic, which resembles the depth distribution of nutrient-type elements. A linear relationship between dissolved Zr and Si was detected for most Atlantic stations with some deviations observed for surface waters showing higher Zr concentrations relative to the linear relation while this correlation was not detected for dissolved Nb. We assume that Zr might be incorporated into or sorbed onto Si particulate matter, e.g. radiolarians. These particles dissolve in deep waters according to the Si cycle and probably release Zr. Although characterized as a particle-reactive element, Zr seems to stay in the dissolved phase ($<0.2\ \mu\text{m}$), shown by the higher concentrations in deep waters compared to surface waters. This contradicts the typical depth profile of a particle-reactive element.

A possible explanation for this unexpected water depth distribution of a particle-reactive trace metal could be complexation with organic ligands, e.g. siderophores in deep waters. Siderophores are low molecular weight organic molecules that serve as chelating agents in the marine environment and are produced and exuded by marine organisms in oxic seawater (Kraemer, 2004). Their major role is the mobilization of trivalent Fe, which is required by microorganisms at least in the range of $\mu\text{mol/L}$ (Kiss & Farkas, 1998). The production of siderophores is induced under low Fe concentrations (Neilands, 1995) and differences in the diversity and concentrations of siderophores have been reported in a study of nutrient-enriched Atlantic seawater (Mawji et al., 2011). Desferrioxamine B (DFOB) is a well-studied molecule of the siderophore group and has been reported to enhance the release of Fe and REE from volcanic ash in seawater incubation experiments (Bau et al., 2013). Stable complexes are also formed with other polyvalent metal

ions (Harrington et al., 2012a,b). Hence, release of Zr from silicate particulates or sinking particulate matter in general and subsequent stabilization through complexation with siderophores or siderophore-like molecules is a viable explanation why Zr continuously released from Si particles with depth remains in solution to a significant degree and does not sorb again on other particulate matter such as Fe oxides.

Zirconium associated with Si has also been observed in marine precipitates on the seafloor. A linear correlation between Si and Zr in ferromanganese (FeMn) - crusts collected from two chains of seamounts that cross the equator in the central Pacific from 4.6°N to 9.2°S has been found (Hein et al., 2004), indicating a similar control mechanism for Zr concentrations in seawater and in FeMn - crusts. Moreover, Zr is enriched in those samples ~34 % over its regional mean value, 921 mg/kg versus 613 mg/kg, respectively. Both Si and Zr are enriched in crusts in high primary productivity zones of equatorial upwelling and Zr in general correlates with elements typically considered to form the biogenic component of FeMn - crusts. FeMn - crusts are formed on sediment-free ridges in the deep ocean by precipitation of colloids of hydrated Mn and Fe oxides (Hein et al., 2013). They are characterized by a slow growth rate and high porosity allowing significant amounts of trace metals to sorb, with Zr being preferentially enriched in the FeOOH phase (Koschinsky & Halbach, 1995; Koschinsky & Hein, 2003). Due to the high amount of Zr in FeMn - crusts and nodules this may have an impact on dissolved concentrations of Zr in seawater (Koschinsky & Hein, 2003) and we suggest that the deep-water distribution of Zr is controlled by the chemical equilibrium between accumulation in FeMn - crusts and dissolved concentrations stabilized by organic complexation.

A selective leaching approach of FeMn - nodules and FeMn - crusts collected in the Pacific with the biogenic siderophore DFOB resulted in a release of large amounts of Zr and Nb (Mohwinkel et al., 2014) and indicated a high affinity of DFOB towards the tetravalent Zr and Nb based on the formation of stable complexes (Figure 4.17). The experiments were performed at pH 8 which is similar to the seawater pH. A recent study on Mid-Ocean Ridge Basalts (MORB) also reported that Zr was leached significantly with the siderophore DFOB (Kraemer et al., 2015). Hence, we suggest that besides other mechanisms also the so-called bioleaching of Zr and Nb with naturally occurring siderophores from sinking particulate matter, ocean floor basalts or sediment release and complexation of trace metals might be a viable explanation for higher concentrations of dissolved Zr and Nb in the deep water compared to surface water. These soluble complexes would contribute to the size fraction < 0.015 µm as observed in the sequentially filtered Pacific samples.

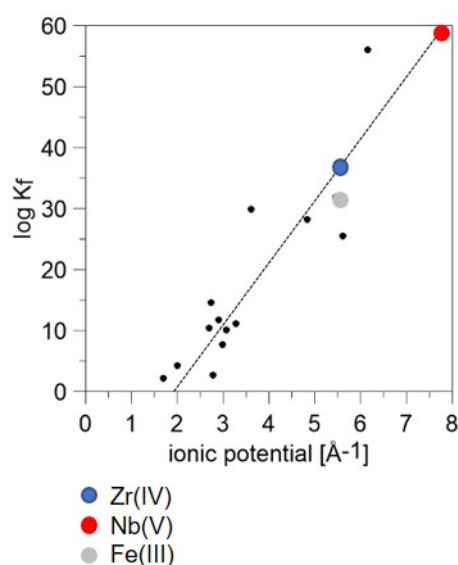


Figure 4.17: Scatter plot of the logarithmic stability constants ($\log K_f$) of metal-DFOB complexes ($M^{n+}HDFOB^{(2-n)-}$) vs. the ionic potential of metals modified after Kraemer et al. (2015). Black dots represent metal-DFOB relationships e.g. for Fe(III) highlighted by the grey dot and are taken from Martell & Smith (2001). The values for Zr(VI) and Nb(V) are calculated using the regression line.

Since the occurrence of organic molecules such as siderophores is not confined to specific ocean regions, but is a more general feature of seawater, we anticipate that sequential filtration of the Atlantic seawater samples would have given similar results with > 90 % of dissolved Zr and Nb being in the < 0.015 μm fraction of open ocean seawater.

An additional feature that could contribute to the observed higher dissolved concentrations of Zr at greater water depth is the lower abundance of particles in deep water compared to shallower water layers. In the world ocean the flux of e.g. Si particulates reaching the water-sediment interface is 78.8 Tmol/y which is only one third of the biogenic Si gross production in surface waters (240 Tmol/y; Tréguer & De La Rocha, 2013). Hence, less particle surface area would be available for trace metal sorption in deep water, which might also lead to a higher fraction of dissolved Zr in deep waters.

4.5.3 Distribution of Zr and Nb between the dissolved and colloidal fractions

At the hydrothermally influenced site and the background site in the Pacific Ocean the dissolved Zr pool constitutes to 91 ± 4 % of dissolved and small colloidal Zr, clearly dominating over the fraction between 0.015 μm and 0.2 μm . Assuming that this is not a specific feature of this site but a general one, the result of this size separation illustrates that dissolved Zr is present either in small complexes (< 0.015 μm) or in the truly dissolved state, which could be elucidated further by the application of ultrafiltration.

Within this study dissolved Zr in the hydrothermal plume was present in a similar con-

centration range compared to the background seawater and we assume, that either Zr emitted with the fluids is rather small or might be scavenged on Fe(oxy)hydroxides during mixing with ambient seawater since Zr is characterized as a particle-reactive trace metal. However, it also must be noted that at this stage in the plume the fluid is already diluted by seawater to a very large degree, which might make a possible hydrothermal signal indistinguishable from the background. This may also be true for the Atlantic station (15+16) above the Romanche Fracture Zone. Firdaus et al. (2011) detected a hydrothermal plume through anomalously high concentrations in manganese and methane but a corresponding signal in dissolved Zr and Nb was not observed. This agrees with the presented data in this study.

The $<0.2\text{ }\mu\text{m}$ fraction of Nb in the hydrothermal plume consisted to $99\pm2\%$ of Nb smaller than $0.015\text{ }\mu\text{m}$. As for Zr, the results show that dissolved Nb is present in small colloids ($<0.015\text{ }\mu\text{m}$) or in a truly dissolved form and no visible hydrothermal signal was found.

4.5.4 Interoceanic comparison of Atlantic and Pacific seawater data

Water depth profiles of dissolved Zr for the Atlantic are scarce while a few have been published for the Pacific Ocean. The general pattern of Zr in seawater showing a surface depletion and increase in deeper waters reported for the Pacific was also observed in Atlantic water depth profiles in this study. Our surface data agree with results for Pacific surface waters, 12 - 95 pmol/kg (McKelvey & Orians, 1993) and approx. 50 pmol/kg (Firdaus et al., 2011).

The export of biogenic silica and hence Zr from the euphotic zone depends on several parameters, e.g. surface coating of particulate matter, the morphology and structure of diatom frustules (Kamatani et al., 1980) and the food web structure (Buesseler, 1998). The mid-depth maxima observed in this study might be attributed to leaching from Si particulates and/or dissolution of biogenic silica depending on the specific regional and biological conditions.

Lower deep water concentrations have been observed in the Atlantic, approx. 196 pmol/kg below 2000 m water depth, compared to bottom waters in the North Pacific, 262 - 275 pmol/kg (Firdaus et al., 2011). This distribution correlates with the age of deep water masses revealing that leaching of Zr from particulate matter might be not as advanced in Atlantic deep water as in Pacific deep water which may also explain Zr maxima at mid-depth in some of the profiles.

Both oceanic basins also differ in their Si rain rate. While 0.02 mol/m^2 has been reported for the East Atlantic (Ragueneau et al., 2000) a higher Si rain rate was observed for the Pacific, $0.03 - 0.07\text{ mol/m}^2$ and 0.1 mol/m^2 (Dymond & Collier, 1988; Honjo et al., 1995), which might lead to higher deep water concentrations in the Pacific depending on the Si burial rate to the sediment. This might also be a reasonable explanation for the

observed higher Zr concentrations in deep Pacific waters compared to Zr data presented for the Atlantic in this study.

Data on dissolved Nb have not yet been published for the Atlantic Ocean. Our data in comparison with studies for the Pacific Ocean indicate a rather homogenous distribution of Nb in the world oceans. Firdaus et al. (2011) reported a slight increase in concentration from surface to deep waters, 1.5 pmol/kg and approx. 3 pmol/kg, respectively which agrees with data presented for the Atlantic Ocean in this study.

4.6 Conclusion

In this study we present first data on dissolved Zr and Nb in the (sub)tropical Atlantic Ocean and succeeded to elucidate general features and some of the factors controlling the oceanic distribution of both trace metals. Dissolved Zr and Nb showed water depth patterns with increasing concentrations with depth, especially for Zr, which contradicts their strongly particle-reactive nature.

Atmospheric input originating from the Canary Islands and the Saharan desert influenced dissolved Zr and Nb in surface waters in the Canary Basin and off West Africa. Depending on their origin deposited particles served as a source for Nb but also as sorption sites for both metals. Water mass-specific Zr and Nb concentrations were observed for the MOW in the East Atlantic while SACW is an important parameter for the surface concentrations in the West Atlantic. Mixing with Amazon freshwater richer in Zr and Nb than seawater might explain the absence of a Zr and Nb surface depletion as observed at lower latitudes in the West Atlantic. Hydrothermal signals of Zr and Nb were not detected.

Both elements do not correlate with nitrate or phosphate in their depth distributions. However, for most stations we observed a linear relationship with depth between dissolved Zr and Si indicating sorption onto or incorporation into silicate particles and release at depth except for surface waters. Such a correlation did not occur for Nb revealing that Nb is largely independent from nutrient cycling. The missing correlation of Zr and Si in surface waters indicates stronger atmospheric sources for Zr relative to Si or preferential uptake of Si during biogenic processes compared to Zr. During the biogeochemical cycle biogenic Si particles such as opal dissolve in deeper waters and probably release Zr to the dissolved phase, which appears to stay in solution despite its particle-reactive properties. A possible explanation may be the complexation with organic ligands such as siderophores which have been reported to mobilize not only Fe(III) but also Zr and Nb from particulate matter.

A sequential filtration approach to Pacific seawater samples revealed that almost all dissolved Zr and Nb ($< 0.2 \mu\text{m}$) are present in the size fraction $< 0.015 \mu\text{m}$, which indicates that colloids ($0.015 \mu\text{m} - 0.2 \mu\text{m}$) play a minor role in the increase of Zr and Nb with depth. Comparison with published data for the Pacific Ocean confirmed that the Atlantic water

depth profiles of dissolved Zr and Nb showed the same features. Hence, we suggest that the discussed processes for Zr and Nb distribution and cycling are not local phenomena but general features in the global oceans.

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5 Distribution of dissolved V, Mo, and W in the Atlantic

Title of publication

Sources, biogeochemical cycling and depth distribution of dissolved V, Mo, and W in the Atlantic Ocean

Authors and affiliations

Sandra Poehle^{*1}, Andrea Koschinsky¹

* Corresponding author. Tel.: +49 0421 2003261,

E-mail address: s.poehle@jacobs-university.de

¹ Department of Physics and Earth Sciences, Jacobs University Bremen
Campus Ring 1, 28759 Bremen, Germany

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Abstract

Dissolved concentrations of vanadium (V) and molybdenum (Mo) range in nmol/kg in seawater and both metals are essential trace elements for marine bioproductivity while the probably non-essential trace metal tungsten (W) ranges in pmol/kg in Pacific seawater. The vertical distribution of dissolved V, Mo and W has been studied widely in the Pacific Ocean and V has been suggested to show a nutrient-like pattern while conservative profiles have been reported for Mo and W.

The objective of this paper is to reveal the distribution of dissolved V, Mo, and W in 16 seawater profiles sampled during the GEOTRACES cruise M81/1 (GA11) in the (sub)tropical Atlantic elucidating regional sources and/or removal processes and compare these data with published data for the Pacific Ocean. Our study revealed deviations from the respective expected patterns of nutrient-type and conservative behaviour, respectively, which can be attributed to different regional sources. Tungsten showed slightly higher concentrations in the proximity of the Canary Islands compared to the average concentration in this study indicating that the volcanic rocks represent a significant source to the Atlantic while V and Mo did not seem to be influenced. Saharan dust was identified as a source for V and appears to provide sorption sites for Mo and W in the East Atlantic. In the Western Atlantic Basin, concentrations of V, Mo, and W appear to be partly influenced from the input from the Amazon river and sorption and desorption processes from particulate matter.

5.1 Introduction

The trace metals molybdenum (Mo), vanadium (V), and tungsten (W) occur in a wide range of concentrations from pM (W) to about 100 nM (Mo) in seawater. The distribution of dissolved V, Mo, and W is well studied in the Pacific Ocean (Collier, 1985, 1984; Firdaus et al., 2008; Jeandel et al., 1987; Sohrin et al., 1998a, 1987). Some studies focused on estuarine mixing zones and coastal waters (Dellwig et al., 2007; Rahaman et al., 2014, 2010; Strady et al., 2009) as well as anoxic basins (Albéric et al., 2000; Colodner et al., 1995; Emerson & Husted, 1991). However, only a few studies provided data on the distribution of V, Mo, and W in the Atlantic Ocean (Hartung, 1991; Jeandel et al., 1987; Middelburg et al., 1988; Morris, 1975; Riley & Taylor, 1972).

Dissolved V has been reported to show a slight depletion in Pacific surface waters (32.7 nmol/L) compared to deep waters 36.4 nmol/L, (Collier, 1984), while Jeandel et al. (1987) reported an average concentration of V at 36 ± 2.5 nmol/kg and observed no profound surface depletion in the Atlantic Ocean. The vertical distribution of V has been described as nutrient-like. The dominant redox species of V in seawater is V(V) which gets strongly hydrolyzed in seawater and is present as $\text{VO}_3(\text{OH})^{2-}$ (Byrne, 2002). Vanadium is an essential trace metal playing an important role for enzymes found in many

brown algae (Almeida et al., 2001) but is not a limiting trace metal due to its high concentration in seawater in the range of nmol/kg. In the Upper Continental Crust (UCC), V is relatively abundant with 2081 $\mu\text{mol/kg}$ (Hu & Gao, 2008). Weathering processes provide V to rivers and an average concentration of 0.014 $\mu\text{mol/kg}$ V was calculated (Gaillardet et al., 2014). Since the concentration in Atlantic seawater, 0.036 $\mu\text{mol/kg}$ (Jeandel et al., 1987), is higher compared to the average riverine concentration other sources such as atmospheric input probably provide V to the ocean. Not only mineral dust deposition from the African continent but also terrestrial input from islands in the Atlantic, e.g. the Canary Islands, might represent a potential source for V to the Atlantic Ocean.

Dissolved Mo has been reported to be conservatively distributed in the Pacific Ocean (107 ± 2.5 nmol/kg, Collier, 1985), and North Atlantic waters (112 nmol/L, Morris, 1975). Hexavalent Mo is the dominant redox species of Mo in oxic seawater (Sohrin et al., 1999) and is present as oxyacid MoO_4^{2-} (Byrne, 2002), which is highly soluble. Since the long oceanic residence time of Mo, 8×10^5 years (Emerson & Husted, 1991), exceeds ocean turnover time and considering the high solubility of Mo a conservative distribution in the world ocean is very probable. Deviations from the conservative patterns have been observed in anoxic basins (Albéric et al., 2000; Colodner et al., 1995) and estuarine mixing areas (Rahaman et al., 2014, 2010; Strady et al., 2009), which is often related to de- and adsorption processes with particulate matter or the formation of larger Mo enriched aggregates in sandy tidal flat areas (Dellwig et al., 2007). Nevertheless, deviations from the conservative distribution due to bioproductivity have not yet been reported although Mo is essential for enzymes and closely connected to the nitrogen cycle (Mendel, 2005). A possible reason might be that the applied methods might not have been sensitive enough to detect the corresponding small variations in concentration. Recently, Mo isotopes have been applied as proxies to trace global redox changes (Scott & Lyons, 2012; Xu et al., 2012). It is, however, essential to understand the biogeochemical behaviour of Mo in seawater since each reaction, e.g. dissolution and sorption processes, directly influences the distribution of the isotopes in the seawater column.

Dissolved W showed a conservative distribution with depth in North Pacific waters (Sohrin et al., 1987) while data for the Atlantic Ocean are not yet available. The dominant species in oxic seawater is the hexavalent WO_4^{2-} (Sohrin et al., 1999). A biological importance has not yet been reported supporting the observations of conservative distribution patterns. Dissolved W belongs to the same chemical subgroup of elements as Mo and physical and chemical similarities are expected. Although both metals are present in the UCC in a similar concentration range with 1.4 ppm (W) and 0.6 ppm (Mo) (Hu & Gao, 2008), 7.6 ± 0.5 $\mu\text{mol/L}$ and 6 ± 3 $\mu\text{mol/L}$, respectively, dissolved W is less abundant with 0.053–0.060 nmol/L (Sohrin et al., 1987) compared to dissolved Mo with about 105 nmol/L (Collier, 1985) in seawater. This implies that compared to Mo, W is preferentially bound to particulate matter in estuarine mixing zones and rapidly removed from the water column to the sediment (Sohrin et al., 1987). Hence, the biogeochemical

behaviour of W and Mo appears to differ under specific conditions despite their expected physico-chemical similarities. Studies on W in different environments, e.g. hydrothermal fluids (Kishida et al., 2004), showed deviations from the conservative pattern reported for the open ocean. The impact of mineral dust deposition or mixing with riverine freshwater on W distribution in the Atlantic has not yet been studied but might also lead to deviations from the conservative profiles.

The analysis of the elements of interest have been performed using several preconcentration techniques in previous studies, e.g. co-precipitation or solid-phase extraction, and different analytical determination methods have been applied. They all have in common that an offline-preconcentration step preceded the analysis. Jeandel et al. (1987) co-precipitated dissolved V with ferric hydroxide and determined V with atomic absorption spectrometry (AAS). Dissolved Mo was determined with AAS after co-precipitation with cobalt-APDC (ammonium pyrrolidinedithiocarbamate) at pH 4 (Collier, 1985). Dissolved V and Mo were concentrated simultaneously on a chelating ion-exchange resin prior to the determination with a flameless atomic absorption spectrophotometry (Morris, 1975). Sohrin et al. (1987) concentrated Mo and W using a XAD-4 resin mixed with Kelex 100 and determined both metals simultaneously with catalytic current polarography while both metals were measured with a high resolution-inductively coupled plasma-mass spectrometry (HR-ICP - MS) after preconcentration using a MAF-8HQ resin (Sohrin et al., 1998b).

These methods required an off-line preconcentration step which bears a certain risk of contamination during sample pretreatment in the laboratory. Recently, we developed a new method to determine dissolved V, Mo, and W among other metals by using the online-preconcentration system SeaFAST (Elemental Scientific) and subsequent ICP-MS analysis (Poehle et al., 2015) of filtered and acidified seawater samples. With this study, we provide concentration data of 16 water depth profiles with approx. 15 different depths per station for a transect across the Atlantic Ocean (RV Meteor M81/1, GA11 in February 2010). The objective of this work is to provide a detailed study on the distribution of dissolved V, Mo, and W in the Atlantic Ocean considering various sources such as weathering of volcanic rocks (Canary Islands), atmospheric dust input (Sahara), and riverine sources (Amazon) as well as corresponding regional removal processes.

5.2 Materials and Methods

5.2.1 Sampling sites

The GEOTRACES cruise M81/1 (GA11), February 2010, started at the Canary Islands heading south along the west coast of Africa, crossing the Mid-Atlantic Ridge (MAR) to the Brazil Basin and heading north along the coast of Brazil to end in Tobago (Figure 5.1).

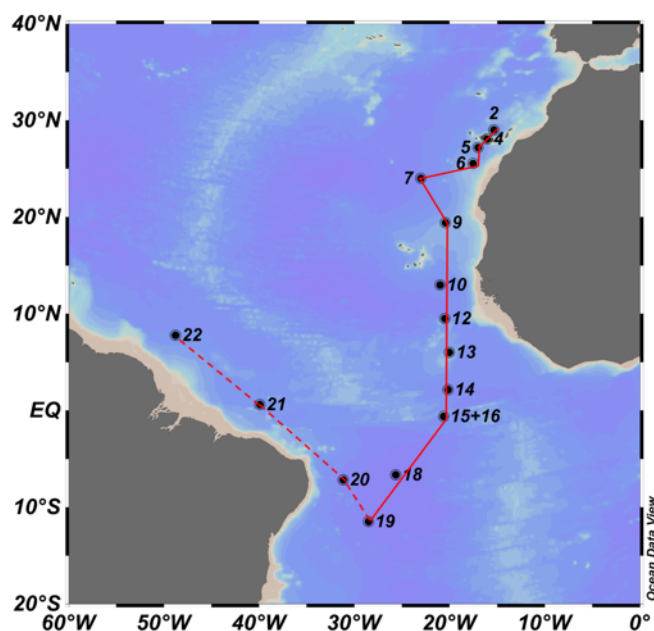


Figure 5.1: Trace-metal clean sampled stations during GEOTRACES cruise M81/1 (GA11); the solid red line represents stations used for Ocean Data View for a NE to SW transect (Figures 5.5, 5.7, 5.9, 5.10, and 5.14) and the dashed line includes stations used for a SE to NW section plot in the western Atlantic basin (Figures 5.6, 5.8, 5.15).

The cruise track covered areas with Saharan dust input, potential hydrothermal (MAR) and riverine sources (Amazon). In total, at 16 different stations 194 individual seawater samples were collected from the Atlantic Ocean, filtered ($0.2\ \mu\text{m}$), acidified ($0.02\ \text{mol/L HCl}$ - $0.002\ \text{mol/L HF}$) and stored under cool and dark conditions until further analysis of dissolved V, Mo, and W; hereafter referred as V, Mo, and W unless stated otherwise. Within the GEOTRACES program, we sampled at a cross-over station with the U.S. GEOTRACES cruise GA03 (station 7), which was conducted between October 15th and November 4th, 2010, and we will compare their concentrations of dissolved aluminum (Al) and nitrate with corresponding data presented in this study.

5.2.2 Sampling and sample pretreatment

Seawater samples were collected according to Cutter & Bruland (2012) with a trace metal-clean conductivity-temperature-depth (CTD)-rosette which was equipped with 24 individual 12 L GO-FLO water samplers lined with Teflon and coupled to a mobile winch by a Kevlar cable (provided by the U.S. GEOTRACES program). The CTD was controlled from on board and the seawater samples were collected during upcast of the CTD. Directly after the CTD was on board the water samplers were brought into a clean laboratory container (U.S. GEOTRACES program) and filtration was performed using $0.2\ \mu\text{m}$ cellulose acetate filters (Sartobran P-MidiCaps). Subsamples were collected in 1 L high density polyethylene (PEHD)-bottles, which have been pre-cleaned in a 4-step

process. Firstly, the bottles were rinsed with deionized (DI) water, filled with 0.5 mol/L HNO_3 - 0.01 mol/L HF and stored at 60°C for 48 hours at minimum. The acid mixture was exchanged with DI water and the bottles were allowed again to stand for 48 hours at 60°C. After a thorough final rinsing step with DI water the bottles were ready for trace metal clean sampling.

Acidification of the filtered subsamples was necessary to keep V, Mo, and W in solution. Although hydrochloric acid (HCl) would have been sufficient to stabilize dissolved V, Mo, and W until further analysis we decided to use a mixture of HCl and hydrofluoric acid (HF) resulting in final concentrations of 0.02 mol/L HCl - 0.002 mol/L HF since we intended to analyze more trace metals such as Ti, Zr and Hf in these samples, which form strong complexes with fluoride anions. The small HF content however does not cause any interferences during the determination of V, Mo, and W.

Trace metal-clean sampled seawater from surface water layers and some deep waters was also used for the determination of dissolved Al on board. In addition, contamination-free sampling of surface waters was performed with a towed fish (GEOMAR) for the determination of Al. The sampling device was equipped with a Teflon introduction system and deployed on the starboard side in approx. 5 m distance from the ship. Samples were collected in 2 m water depth. A membrane pump (ALMATEC) transported the seawater into a clean laboratory container where subsampling was performed.

During M81/1 a conventional CTD-rosette, Seabird 911-plus, equipped with 24 Niskin bottles (each 10 L) was deployed alternating with the trace metal clean CTD and at the same positions. Filtered subsamples were stored frozen for the land-based determination of nutrients (nitrate, phosphate, silicate) while other aliquots served the determination of dissolved oxygen on board. These oxygen data were used to calibrate the sensors mounted at the frame of the rosette of the normal CTD. Since the locations of both CTD casts, trace metal-clean and conventional, were identical we will use oxygen, salinity and temperature data obtained from the normal CTD for evaluation of the water masses.

5.2.3 Online preconcentration method and ICP - MS analysis of V, Mo, and W

We applied the online-preconcentration system, SeaFAST, and subsequent ICP - MS (Perkin Elmer, ELAN 6000 DRC-e) analysis for the determination of V, Mo, and W in seawater. A brief description of the preconcentration process and important analytical figures are provided here while details of the applied method are given in Poehle et al. (2015).

The preconcentration system consists of 3 major components: (1) a 8 mL sample loop, (2) a preconcentration column and (3) two 6-port-valves (one controls loading and rinsing of the sample loop while the other valve controls the loading, rinsing, and elution processes of the preconcentration column).

While the sample loop was filled, the preconcentration column was flushed simultaneously with a 1:1 mix of DI water and ammonium acetate buffer ($\text{pH } 6.05 \pm 0.05$) and maintained at pH 6. DI water, provided by a Sartorius Arium 611 unit, pushed the solution to be measured from the sample loop to the preconcentration column. This pre-packed column contained a resin with two functional groups, iminodiacetic acid (IDA) and ethylenediaminetriacetic acid (EDTriA) immobilized on a polymer backbone. While alkaline and alkaline earth metals passed the resin most of the transition metals and metals from subgroups III and IV of the periodic table of elements were complexed by the functional groups and retained. A subsequent rinse with the DI-buffer mix (pH 6) removed the major proportion of the seawater matrix from the resin. The preconcentrated solution was eluted in counter current with 0.5 mol/L HNO_3 - 0.002 mol/L HF (both acids of ultrapure grade, Roth), directly transported to the spray chamber and introduced to the quadrupole ICP - MS. Peak areas of the detected transient signals were used to calculate concentrations of V, Mo, and W.

In order to monitor correct filling of the sample loop as well as the loading and eluting processes, indium (In, purchased from Inorganic Ventures) served as an internal standard and was added prior to the measurement to blank, standard, and sample solutions resulting in final concentrations of 0.44 nmol/kg. Indium was eluted completely from the resin within one analytical run and showed similar behaviour during the preconcentration process compared to V, Mo, and W.

Preparation of the solutions and dilutions was performed on weight basis and in a clean bench equipped with a HEPA-filter.

A 4-point external calibration with matrix matched calibration standards (0.6 mol/L NaCl - 0.02 mol/L HCl - 0.002 mol/L HF) was applied in this study.

Prior to the preparation of the calibration standards a pre-cleaning step of NaCl (suprapure, Merck) was necessary since first tests revealed high concentrations of V, Mo, and W in the acidified NaCl matrix compared to the natural concentrations of these three metals in seawater. Therefore, 5 g Chelex 100 resin, 100 - 200 mesh particle size (Bio-Rad Laboratories), were filled into a column, and a 2 mol/L NaCl stock solution was flushed through the resin. While trace metal impurities were complexed by the functional group IDA, which is immobilized on a styrene divinylbenzene copolymer, the pre-cleaned NaCl solution passed the resin and was collected in a pre-cleaned polyethylene (PE) bottle.

Different volumes of a spike of V, Mo, and W (Inorganic Ventures) in 0.5 M HNO_3 were added to the calibration standard matrix (0.6 mol/L NaCl - 0.02 mol/L HCl - 0.002 mol/L HF) to prepare the calibration standards.

Acidified NaCl matrix was given the preference to natural seawater for preparation of the calibration standards, since the application of the same preparation and pre-cleaning procedure provided reproducible blank concentrations with 17 %, 16 % and 25 % RSD for V, Mo, and W (Table 5.1) and ensures a constant quality of the calibration.

	V [nmol/kg] ^(a)	Mo [nmol/kg] ^(a)	W [pmol/kg] ^(a)
Procedure blank 0.6 mol/L NaCl - 0.02 mol/L HCl - 0.002 mol/L HF	9.79 ± 1.66 (n = 15)	5.61 ± 0.91 (n = 22)	10.2 ± 2.6 (n = 21)
Acid blank 0.02 mol/L HCl - 0.002 mol/L HF	1.53 ± 0.05 (n = 4)	0.80 ± 0.03 (n = 4)	7.18 ± 0.28 (n = 4)
LOD ^(b)	4.97	2.73	7.72
LOQ ^(c)	14.9	8.19	23.2
NASS-6 Certified	27.9 ± 3.1	101	
Measured	27.6 ± 0.60 (n = 4)	98 ± 0.87 (n = 4)	
Recovery [%]	97 ± 0.9	99 ± 2.2	
Spike experiment North Sea water	23.1 ± 2.9 (n = 12)	90.9 ± 3.8 (n = 12)	79.2 ± 5.1 (n = 13)
Spike added	20.9	92.2	66.5
Measured spiked sample	48.2 ± 2.9 (n = 4)	182 ± 3	140 ± 10 (n = 12)
Recovery [%]	103 ± 4	99 ± 2	97 ± 9

(a) Mean ± SD, (b) LOD = 3 x SD of the procedure blank, (c) LOQ = 9 x SD of the procedure blank.

Table 5.1: Important analytical figures of the applied online-preconcentration method; modified after Poehle et al. (2015)

In contrast, a natural seawater sample is a limited source and its use for calibration standards might have exceeded the linear range of the applied method, since V and Mo are present in high concentrations (nmol/kg).

A standard addition procedure was applied to determine concentrations of V, Mo, and W in 0.6 mol/L NaCl - 0.02 mol/L HCl - 0.002 mol/L HF (Table 5.1), which served as the procedure blank. Its intensities were used to correct intensities of the calibration standards.

Since the seawater samples have been acidified with 0.02 mol/L HCl - 0.002 mol/L HF after their collection, the corresponding acid blank, which was determined by standard addition, was subtracted from all measured sample values (Table 5.1).

The applied online-preconcentration method provides sufficiently low limits of detection (LOD) and limits of quantification (LOQ).

In order to show the accuracy of the presented method we measured the certified seawater reference standard NASS-6 (National Research Council Canada, NRCC) and recovered V and Mo almost quantitatively comparing our measured concentrations to the concentrations of both metals provided in the certificate (Table 5.1). Since no certified reference standard is available for W in seawater we added a W spike to North Sea water and recovered this spike with 97 ± 9 %.

We showed with our tests that the resin preconcentrates V, Mo, and W, which are present as negatively charged oxyanions in seawater (H_2VO_4^- , MoO_4^{2-} and WO_4^{2-} , respectively). The preconcentration process was performed at slightly acidic conditions (pH 6) possibly leading to the protonation of the carboxyl groups ($-\text{COOH}$) and the imino group ($-\text{NH}^+$) of IDA. We suggest that the oxyanions interact with positively charged IDA leading to a distinct complexation of V, Mo, and W. In contrast, the neutrally or negatively charged EDTriA may not contribute to the retention of oxyanions during the preconcentration process. Hence, the online-preconcentration method is pH-dependent, requiring stable pH conditions during the preconcentration of blanks, standard or sample solutions.

As the concentration of W in seawater ranges in pmol/kg while V and Mo are present in nmol/kg, two separate methods for the preconcentration process as well as for the analytical detection were inevitable. Hence, V and Mo were preconcentrated and measured simultaneously in one run while the analysis of W was processed in a separate run.

Precision of the applied method for the determination of V, Mo and W in seawater

Replicate measurements were performed with samples collected at station 12 and 20 (Poehle et al., 2015). The concentration of V at station 12 (9.50°N , 20.50°W) ranged between 49.3 nmol/kg (minimum) and 55.3 nmol/kg (maximum) providing a natural variation of 6 % throughout the water column while the replicate analysis of V resulted in a low relative standard deviation (RSD) of 1 - 3 %. Hence, variations of the natural concentrations between lowest and highest concentration exceed the determined RSD for the analysis of V (Figure 5.2a). This was also observed for Mo (station 12) with a natural concentration range between 85.4 nmol/kg to 96.9 nmol/kg (7 % variation) and a RSD of 1 - 7 % (Figure 5.2a).

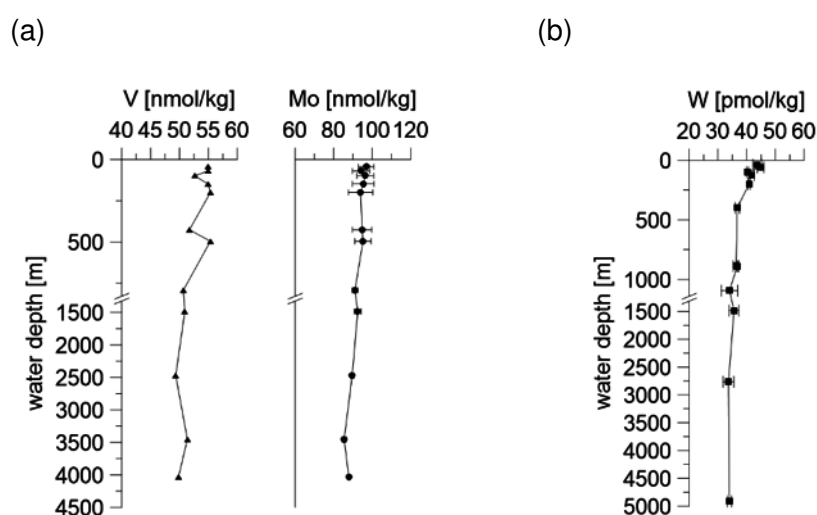


Figure 5.2: Depth distribution of dissolved V and Mo (a) at station 12 (9.50°N , 20.50°W) and of dissolved W (b) at station 20 (7.17°S , 31.17°W). Figure from Poehle et al. (2015).

Dissolved W was determined repeatedly in seawater samples of station 20 and the variation of the natural concentrations (33.7 pmol/kg - 44.9 pmol/kg, 14 % variation) exceed the low RSD (2 - 9 %) of the applied method (Figure 5.2b).

One distinct seawater sample of station 12 was measured repeatedly and the low RSD shows the precision of the applied method (Table 5.2).

	V	Mo	W
	[nmol/kg]	[nmol/kg]	[pmol/kg]
Conc. ^(a)	48.3 ± 1.3	93.9 ± 2.1	40.7 ± 3.4
(1485 m water depth, station 12)	(n = 4)	(n = 4)	(n = 3)
RSD [%]	3	2	8
(a) Mean ± SD			

Table 5.2: Replicate measurements of sample collected at 1485 m water depth at station 12 (Poehle et al., 2015)

5.2.4 Ancillary data

Salinity, temperature and dissolved oxygen

Salinity, temperature and dissolved oxygen data were obtained from casts of the conventional CTD (Seabird 911-plus) by sensors. The oxygen sensor was calibrated with values of dissolved oxygen obtained by Winkler titration performed on board.

Analysis of nutrients

Subsamples of seawater collected with the conventional CTD were filtered on board and stored frozen until land-based analysis of nutrients at the GEOMAR, Kiel, Germany (Frank Malien).

Nitrate, phosphate, and silicate were determined with a self-made autoanalyzer using the segmented flow analysis technique (SFA). The limit of detection for nitrate, phosphate, and silicate was 0.03 µmol/L, 0.02 µmol/L and 0.03 µmol/L, respectively. A standard prepared of DI water and adjusted to a salinity similar to seawater, $S = 36$, containing 30.0 µmol/L nitrate, 2.5 µmol/L phosphate and 50.0 µmol/L silicate was used for calibration.

Nitrate was determined after reduction to nitrite applying copper-coated Cd granules as reductant in a heterogeneous system (Grasshoff et al., 1999). Nitrite (reduced nitrate and originally present nitrite) reacts with sulphanilamide and N-(1-naphthyl)-ethylene-diamine dihydrochloride forming an azo dye and its absorbance was measured at 520 nm wavelength. The amount of nitrate in the sample was calculated after subtracting the fraction of initially present nitrite.

A spectrophotometric method after Giedigkeit & Marquardt (2005) was used to determine dissolved inorganic phosphate. Trivalent antimony, acidified ammonium molyb-

date and phosphate react to a complex, which is then reduced with ascorbic acid at a $\text{pH} < 1$ to an intensely colored blue compound. The absorbance of the reduced phosphomolybdenum complex was measured at 880 nm wavelength.

The spectrophotometric method to determine silicate included the formation of the yellow β -silicomolybdic acid with ammonium heptamolybdate (Grasshoff et al., 1999). Oxalic acid was added followed by the addition of ascorbic acid which serves as a reducing agent. The blue silicomolybdic complex was measured at 660 nm wavelength.

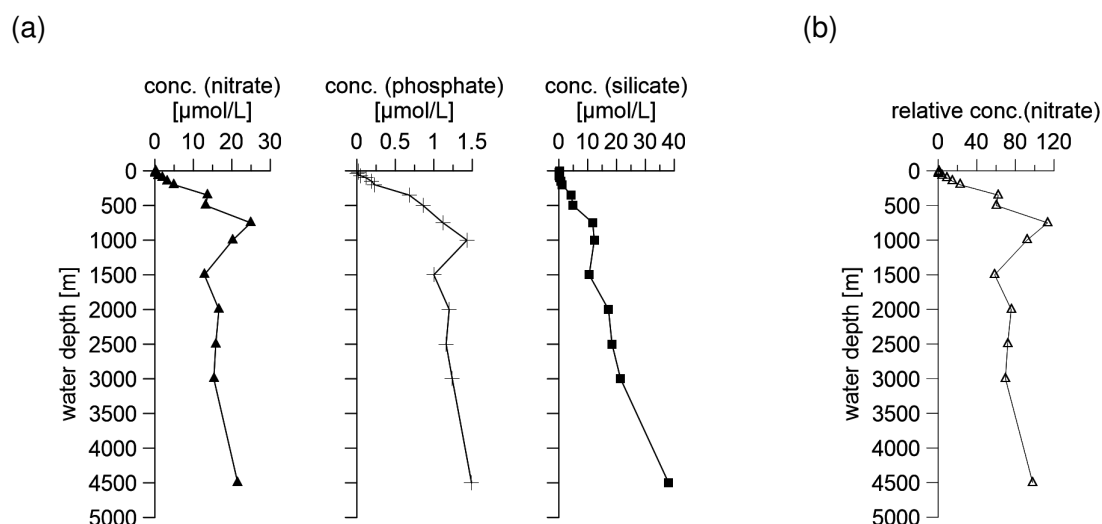


Figure 5.3: Distribution of (a) dissolved nitrate ($\blacktriangle$), phosphate (+), and silicate ($\blacksquare$) with depth at the crossover station 7 (M81/1, 24°N , 23°W) and (b) relative changes in nitrate concentration with depth at station 7, normalized to surface concentration.

Sample storage under frozen conditions might have influenced the total concentrations of nitrate, phosphate, and silicate although the relative changes have not been affected and resemble the typical depth distribution of nutrients in seawater (Figure 5.3). We therefore use only the relative changes with depth, concentration in specific depth divided by concentration in the respective surface sample, for correlation with the concentrations of dissolved V, Mo, and W in this study and provide these data in the supplementary material (B2. Supplementary Data Table 2).

Determination of dissolved Al

A fluorimetric method was applied to determine dissolved Al on board (Hydes & Liss, 1976; Schüßler et al., 2005) in the trace metal-clean collected seawater samples ($0.2 \mu\text{m}$ filtered). Data were provided by Xiaoliang Tang and Michael Ostendorf from the University of Bremen.

Four 60 mL subsamples were adjusted to $\text{pH } 5 \pm 0.05$ with a sodium acetate-acetic acid buffer (suprapure, Merck). Three subsamples were spiked with an Al stock solution ($500 \mu\text{g Al/L}$ in 0.05 mol/L HCl) to perform a standard addition. After the addition of

400 μ L lumogallion solution (0.02 % w/w in DI water) to all subsamples they were stored for 90 min at 70°C in a water bath. They were allowed to cool to room temperature and after excitation at 465 nm the fluorescence was measured at 555 nm (Koron SFM25 instrument).

The calculated concentrations of Al in seawater were corrected for the reagent blanks (DI water adjusted to pH 5 with sodium acetate buffer) determined by standard addition and individually calculated for each analytical run. The average blank concentration was 7.57 ± 0.52 nmol/L (6.85 % RSD) and the detection limit of the fluorometric method was determined to 1.56 nmol/L (LOD = 3 x SD of the reagent blank). The Al concentration data are given in the appendix (B3. Supplementary Data Table 3).

Comparison of the detected vertical distribution of dissolved Al at station 7 with data by Measures et al. (2014) for this crossover station revealed a similar water depth profile. We detected a surface water concentration of 10.3 nmol/L (39 m water depth), while 9 - 11 nmol/L were reported by Measures et al. (2014). Between 900 and 2500 m water depth dissolved Al ranged between 16.8 to 18.6 nmol/L and increased in bottom near waters to 24.4 nmol/L during M81/1. Measures et al. (2014) reported Al concentrations of 20 nmol/L between 1000 - 3000 m and a slight increase in concentration to 30 nmol/L below 3000 m. Hence, the distribution of dissolved Al agrees for both cruises and confirms the applicability of the used method on board.

5.3 Hydrography

The Azores current turns south at approx. 33°N and forms the Canary Current (CC) flowing southwestward along the west coast of the African continent (Mittelstaedt, 1991) and was observed at station 2, 4, 5, and 6. The Canary Islands as a topographic barrier hinder the CC from unhampered flow southward and force the current to divide at the archipelago. The CC becomes detached from the continental margin between 25°N and 20°N (station 7) and turns into the North Equatorial Current (NEC) flowing westwards (Stramma & Schott, 1999). Further south at 10°N the North Equatorial Counter Current (NECC) dominates the surface waters of the eastern tropical Atlantic Ocean (stations 12 and 13). This wind-driven current system influences the distribution of surface water masses in the East Atlantic. Between 70 and 500 m water depth the upper ocean is occupied by North Atlantic Central Water (NACW). It is saltier, warmer and contains less dissolved oxygen than the corresponding South Atlantic Central Water (SACW) (Stramma & Schott, 1999). Mixing between NACW and SACW is assumed to occur at 20°N (station 9) since the detected water mass characteristics do not match unambiguously either those of NACW or SACW. In the western basin the boundary between NACW and SACW was detected at 8°N (station 22).

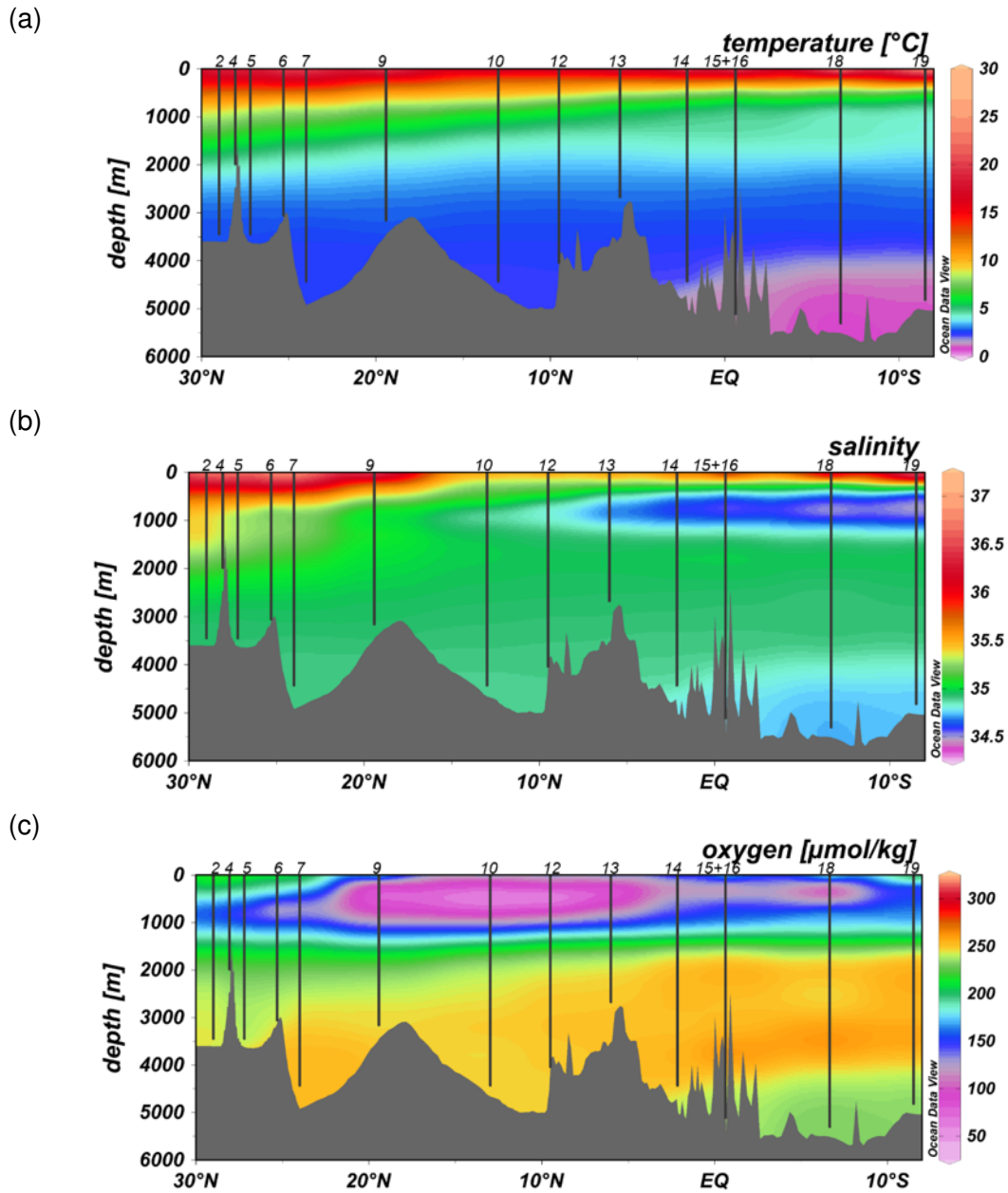


Figure 5.4: Section plots of (a) temperature, (b) salinity, and (c) oxygen derived from the conventional CTD for the NE-SW transect from 30°N to 12°S. Station numbers indicated above the plot belong to trace metal-clean sampled stations which were performed at the same locations as the conventional CTD.

Antarctic Intermediate Water (AAIW) is formed in the Antarctic Polar Frontal Zone through subduction processes and flows northwards in the Atlantic Ocean. It is characterized by its low salinity and high oxygen concentrations (Stramma & England, 1999) and can be traced until approx. 20°N between 500 to 1200 m water depth (Figure 5.4b). The signature of AAIW is most distinct in the western basin (stations 19, 20, 21 and 22) with low salinities ($S < 34.55$) combined with high oxygen concentrations (Figures 5.5b and 5.5c). In the highly bioproductive area off the African coast in the East Atlantic con-

sumption of oxygen caused a pronounced Oxygen Minimum Zone (OMZ) (Figure 5.4c). Thus, AAIW can be traced by its low salinity ($S < 34.75$) until 7°N (stations 13, 14, 15+16, 18, 19). The observed increase in salinity at higher latitudes is probably due to admixing with southward moving more saline Mediterranean Outflow Water (MOW) (Figure 5.4b). To conclude, the characteristics of AAIW are more pronounced in the western than in the eastern basin.

North Atlantic Deep Water (NADW) flows southwards and originates from various regions such as the Labrador Sea and Greenland-Iceland-Norwegian (GIN) Sea, hence, showing different properties due to the individual source regions (Tsuchiya et al., 1994). According to Stramma & England (1999) the upper boundary of NADW in the tropical Atlantic was defined by the isopycnal $\sigma = 32.15$ and ranged between 1200 to 3800 m water depth in the area covered during M81/1 and was detected at all stations. NADW in the Canary Basin (stations 2, 4, 5, 6, 7) is more saline and warmer ($\theta = 4.44^{\circ}\text{C}$, $S = 35.15$, $\text{O}_2 = 231.19 \mu\text{mol/L}$) due to mixing with southward flowing MOW compared to NADW detected in the Cape Verde Basin ($\theta = 3.57^{\circ}\text{C}$, $S = 35.00$, $\text{O}_2 = 229.25 \mu\text{mol/L}$).

The core of Upper North Atlantic Deep Water (UNADW) was identified at 1700 m water depth for stations along the transect at 20°W from 10°N southwards in the East Atlantic Ocean (stations 12, 13, 14) and station 15+16 located above the Romanche Fracture Zone. In the western basin at 8°N UNADW was detected at 1600 m (station 22) and declines to 1800 m in the Brazil Basin (station 19).

The isopycnal at $\sigma = 45.90$ marks the upper boundary of Antarctic Bottom Water (AABW) in the western tropical Atlantic Ocean and was encountered at 3800 m water depth at a potential temperature near 1.74°C (stations 18, 19 and 20, Figure 5.4a); it is cooler, fresher and contains less oxygen than the overlying NADW. Only the densest part of the AABW, hence a relatively small fraction, enters the eastern basin from the Brazil Basin via the Romanche Fracture Zone and mixes with overlying NADW altering its characteristics. According to Tsuchiya et al. (1992) the isotherm $\theta = 2^{\circ}\text{C}$ defines the upper boundary of AABW in the East Atlantic, which deepens from 3925 m water depth at station 14 to 4055 m water depth at station 7 in the Canary Basin. AABW detected at station 10 in the Cap Verde Basin and further north originates from the Guiana Basin entering the eastern basin through the Vema Fracture Zone of the MAR and differs slightly in potential temperature ($\theta = 1.88^{\circ}\text{C}$), salinity ($S = 34.88$) and oxygen ($\text{O}_2 = 246.14 \mu\text{mol/L}$) from the AABW detected at lower latitudes ($\theta = 1.87^{\circ}\text{C}$, $S = 34.88$, $\text{O}_2 = 251.81 \mu\text{mol/L}$).

In general, the hydrographic characteristics are more strongly developed in the western Atlantic basin while the distinct features are altered in the eastern basin due to mixing with adjacent water masses.

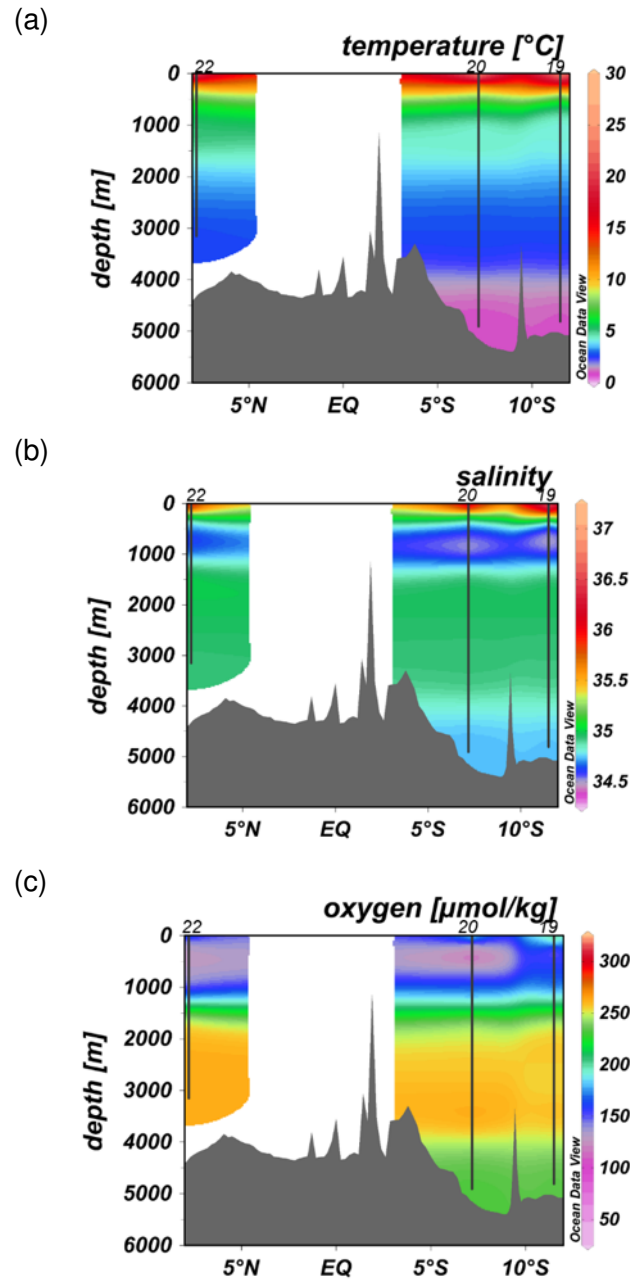


Figure 5.5: Section plots of (a) temperature, (b) salinity, and (c) oxygen derived from the conventional CTD for the SE - NW transect from 8°N to 12°S. Station numbers indicated above the plot belong to trace metal-clean sampled stations which were performed at the same locations as the conventional CTD. Only at station 21 a conventional CTD was not deployed.

5.4 Results

The presentation of the data is divided into two transects (Figure 5.1): (1) NE - SW (stations 2 to 19) and (2) SE - NW transect (stations 19 to 22). All concentration data on V, Mo and W presented in this study are provided in the supplementary material (B1).

Supplementary Data Table 1).

5.4.1 NE - SW transect

The average concentration of V along the NE - SW transect is 46.8 ± 5.5 nmol/kg which is higher than reported previously for the North Atlantic Ocean, 35 ± 3 nmol/kg (Jeandel et al., 1987) and 32.6 nmol/L (Middelburg et al., 1988). No profound surface depletion was observed but in contrast at stations 7, 12 and 14 slightly higher concentrations were observed in surface water (Figure 5.6a).

Upstream the Canary Islands (station 2; 29.0°N , 15.3°W) concentrations of V fall from 43.1 nmol/kg in surface waters to 33.5 nmol/kg in 2000 m water depth. Between the islands Gran Canaria and Tenerife V was present in slightly higher concentrations (49.5 ± 4.7 nmol/kg) compared to waters up- and downstream the Canary Islands. Downstream the archipelago (stations 5 and 6) V showed a conservative distribution with depth except a slight depletion (approx. 37 nmol/kg) in subsurface waters at 70 m and 150 m water depth. Elevated concentrations (approx. 55 nmol/kg) were observed in surface waters at stations 7 (25.0°N , 23.0°W) and 12 (9.5°N , 20.5°W) compared to the average concentration of V in seawater along this transect, while underlying waters showed concentrations of 44.4 ± 2.4 nmol/kg and 50.3 ± 0.8 nmol/kg and increase in bottom-near waters to 56.4 nmol/kg and 51.4 nmol/kg, respectively. Concentrations of V at 59 nmol/kg were found in intermediate waters (800 m and 1500 m water depth) at stations 14 (2.2°N , 20.2°W) and 19 (11.5°S , 28.5°W). At station 18 (7.5°S , 31.2°W), located in the western Atlantic basin, slightly higher concentrations in the range of 53 nmol/kg were observed at 3500 m water depth and in bottom-near waters. These slightly higher concentrations in deep water have also been observed at stations 7 and 14 compared to overlying water masses. In summary, there is no consistent trend of V concentrations with water depth but small maxima and minima were found in different water depths at different locations, indicating a variety of factors influencing V concentrations in the water column.

The average concentration of Mo along the NE - SW transect is calculated to 95.6 ± 5.6 nmol/kg which agrees with concentrations found off the Gironde estuary (95.5 ± 20.8 nmol/L, Strady et al., 2009), France, but are slightly lower than data reported for the North Atlantic Ocean (109.4 nmol/L, Morris, 1975). As for V, we found distinct minima and maxima at different depths compared to the average concentration of Mo along this transect, but no consistent trends with depth (Figure 5.6b).

Slight variations of Mo observed in the Canary Basin between 30°N and 25°N (stations 2 - 6) are lower than the RSD of the applied method and will thus not be discussed with respect to causes of these variations. At station 7, however, the highest concentrations of the whole transect were observed (102 ± 6 nmol/kg) with a slight surface depletion.

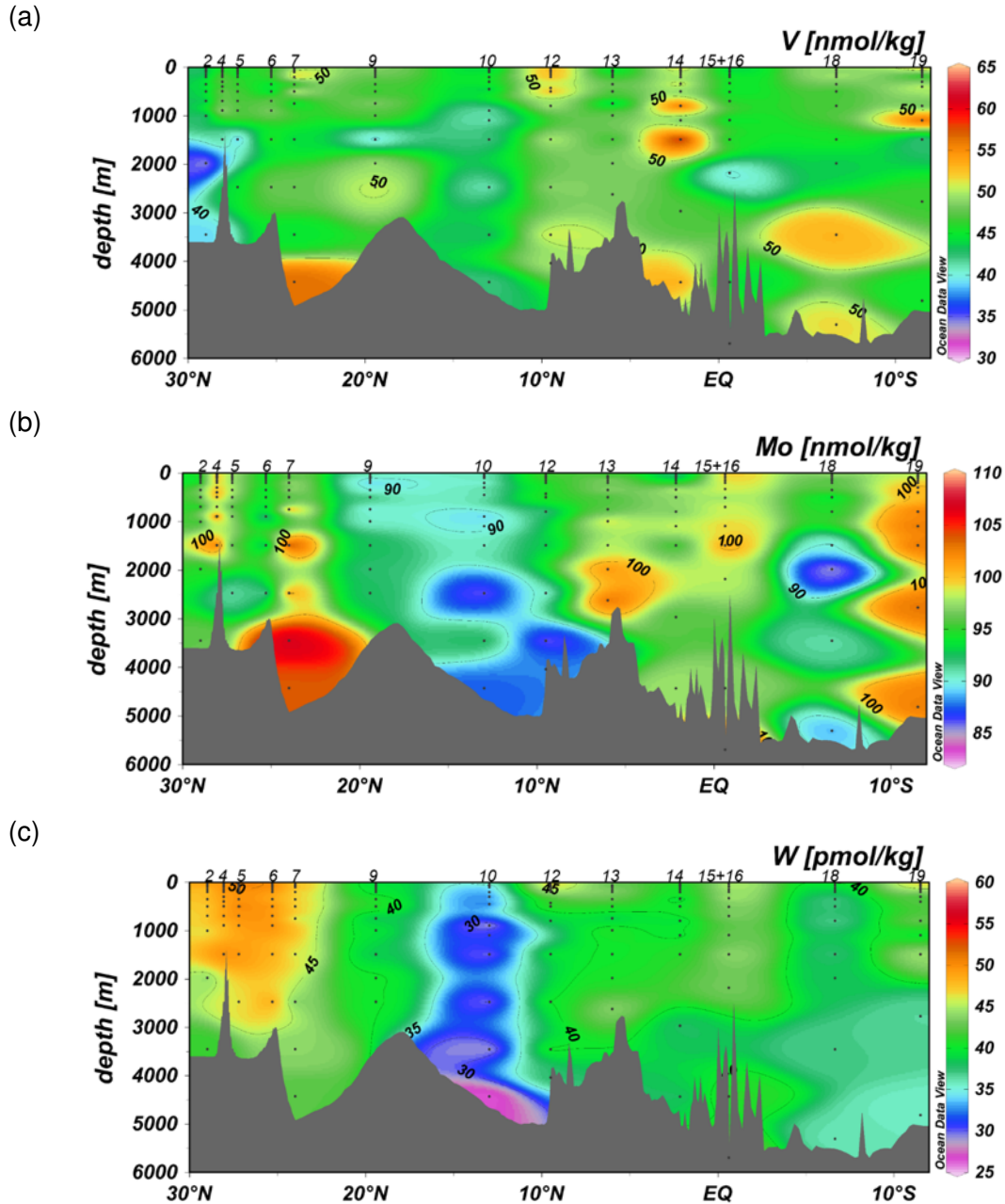


Figure 5.6: Section plot of (a) V, (b) Mo, and (c) W for the NE - SW transect from 30°N to 12°S. Station numbers are indicated above the plot.

We observed a distinct depletion of Mo between 20°N and 11°N (stations 9 and 10) in the upper 1000 m (92.5 and 90.4 nmol/kg, respectively) compared to the average concentration of Mo of this section. Between 14°N and 8°N (stations 10 and 12) the depletion appears to be subducted from surface to intermediate (2000 to 3000 m water depth) and to deep waters (3500 m) at station 12 (85.4 nmol/kg).

Between 8°N and 2°S (stations 13, 14, 15+16) Mo did not display significant variations in concentration with depth. In the western Atlantic basin (station 18; 7.5°S, 31.2°W) Mo displayed slightly lower concentrations of approx. 89 nmol/kg in intermediate (1485 m)

and deep (5304 m) waters while concentrations are higher throughout the water column (101 ± 2 nmol/kg) further south (station 19; 11.5°S , 28.5°W).

The average concentration of W (43.0 ± 5.9 pmol/kg) along the NE - SW transect is lower than reported for the North Pacific Ocean, 53-60 pmol/kg (Sohrin et al., 1987). To our knowledge only one study on W in the Atlantic has been published (Hartung, 1991).

Upstream the Canary Islands (station 2) W decreased slightly with depth from 51.0 pmol/kg in surface waters to 41.2 pmol/kg in deep waters (Figure 5.6c). Concentrations in surface waters sampled upstream the Canary Islands, between Gran Canaria and Tenerife and downstream the islands are similar at approx. 50 pmol/kg. Concentrations in deep waters upstream the islands are slightly lower (41.2 pmol/kg) compared to deep water concentrations downstream (approx. 46 pmol/kg) the archipelago. The difference in concentration between both investigated waters exceeds the RSD of the applied method for the determination of W in seawater only slightly. At 24.0°N , 23.0°W (station 7, located in the Canary Basin) W showed slightly lower values compared to waters collected in the direct proximity of the Canary Islands (stations 2, 4, 5 and 6) but similar to the average concentration of W along the NE - SW transect.

Significantly lower concentrations were observed between 14°N and 11°N (station 10; 13.0°N , 21.0°W); here, W decreased from 39.3 pmol/kg in surface waters (39.9 m) to 25.8 pmol/kg in deep waters (4427 m). A distinct maximum (50.0 pmol/kg) was observed in surface waters at station 12 (9.5°N , 20.5°W), which is comparable to concentrations observed in surface waters influenced by the Canary Islands. Underlying water masses showed concentrations of 42.1 ± 2.9 pmol/kg. Between 8°N and 2°S along the transect at 20°W (stations 13, 14 and 15+16) W showed a conservative pattern at 41.9 ± 2.8 pmol/kg. A decrease in concentration from surface to deep waters (43.0 to 36.0 pmol/kg, respectively) was again observed at station 18 (7.5°S , 31.2°W), which was slightly more pronounced further south at station 19 (11.5°S , 28.5°W) decreasing from 48.2 pmol/kg to 35.7 pmol/kg.

5.4.2 SE - NW transect

The average concentration of V is 45.6 ± 5.6 nmol/kg along the SE - NW transect in the Brazil Basin which is similar to the concentration range of V in the NE - SW transect.

Vanadium showed a distinct maximum (58.5 nmol/kg) at intermediate water depths (1091 m) at the southernmost station of the cruise while highest concentrations were observed in surface waters at station 20 (7.2°S , 31.2°W). Deep waters between 12°S and 5°S (stations 19 and 20) showed a conservative distribution of V at approx. 47 nmol/kg (Figure 5.7a) and slight variations in concentration at station 20 are within the RSD of the applied method.

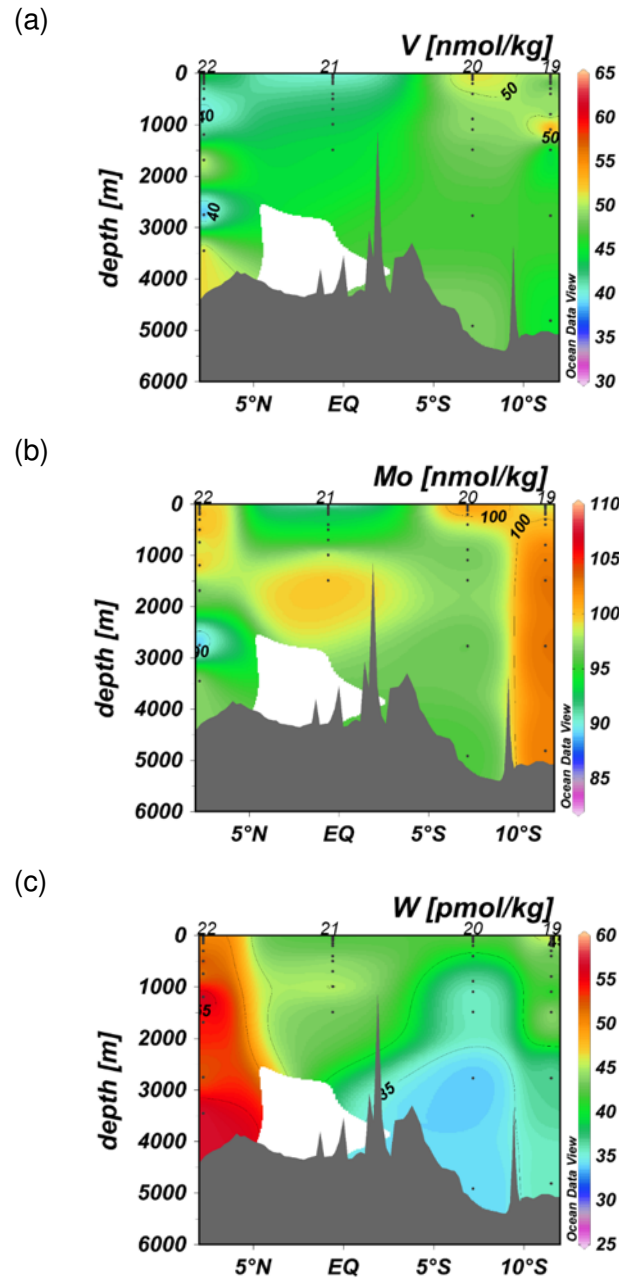


Figure 5.7: Section plot of (a) V, (b) Mo, and (c) W for the SE - NW transect from 8°N to 12°S. Station numbers are indicated above the plot.

Between 5°S and 5°N (station 21) V showed a nutrient-like distribution with a slight depletion in surface waters (38.6 nmol/kg) compared to deep water masses (44.1 nmol/kg). The northernmost station, station 22 (7.8°N, 47.8°W), is characterized by highest variations in concentration with depth. Surface waters sampled at 18 m water depth contained only 39.0 nmol/kg V while V was detected at 48.5 ± 2.1 nmol/kg between 38 m and 99 m water depth. This alternating pattern in concentration continues with increasing water depth to bottom-near waters, where the concentration was at 52.6 nmol/kg.

The average concentration of Mo in the SE - NW transect is 97 ± 5 nmol/kg which agrees

with concentrations we present for the NE - SW transect but is slightly lower than concentrations reported for the Pacific Ocean, 107 ± 2.5 nmol/kg (Collier, 1985). Highest concentrations of Mo (101 ± 2 nmol/kg) of this transect were observed at the southernmost station 19 (11.5°S , 28.5°W ; Figure 5.7b). Although the difference between the concentrations observed at station 19 and station 20 are within the uncertainty of the measurement a consistent trend have been observed for the vertical distribution of Mo at both stations. A slight surface depletion (98.6 ± 1.3 nmol/kg) and concentrations at 102 ± 0.8 nmol/kg in deeper waters were observed at station 19 while in contrast surface waters showed higher concentrations (101 ± 1 nmol/kg) compared to deeper waters (96.5 ± 0.5 nmol/kg; below 200 m water depth to bottom-near waters) at station 20. Between 5°S and 5°N (station 21) Mo was slightly depleted in surface waters (81.8 nmol/kg) compared to deep waters (100 nmol/kg, 1487 m water depth). At station 22 Mo showed slight variations between 88 and 94 nmol/kg with depth but the observed slight differences are within the RSD of the method.

The average concentration of W (44.0 ± 6.2 pmol/kg) along the SE - NW transect agrees with concentrations we report for the NE - SW transect. Between 12°S and 5°S (stations 19 and 20) W decreased slightly from approx. 48 pmol/kg in surface waters to 35 pmol/kg in deep waters (Figure 5.7c). Between 5°S and 5°N (station 21) the concentration of W varied within the RSD of the applied method at an average concentration of 43.1 ± 6.2 pmol/kg. The northernmost station, station 22 (7.8°N , 47.8°W), showed higher concentrations (52.2 ± 3.3 pmol/kg) throughout the water column compared to concentrations of seawater sampled at lower latitudes of this transect. Moreover, the concentration increased from 45.3 pmol/kg (18 m water depth) to 57.1 pmol/kg (3454 m water depth) at this station contrasting the decreasing patterns described for waters sampled further south.

5.5 Discussion

5.5.1 NE - SW transect

Vanadium does not show water mass-dependent signatures along the NE - SW transect, as can be deduced from the lack of correlation between V and salinity (Figure 5.8b-left) but the distribution of V rather appears to be influenced by various factors and processes since we observed distinct minima and maxima in concentration at different water depths.

Mediterranean Outflow Water (MOW) moves southward from the Strait of Gibraltar to the Canary Islands in the upper water layers of the water column. It is characterized by high salinities (Millot, 2009) compared to surrounding Atlantic waters and was detected from 30°N to 25°N flowing around the Canary Islands (Figure 5.4b). Surface waters flowing out of the Mediterranean Sea have been reported to show a slight depletion in V compared to Atlantic surface waters (Jeandel et al., 1987; Sherrell & Boyle, 1988).

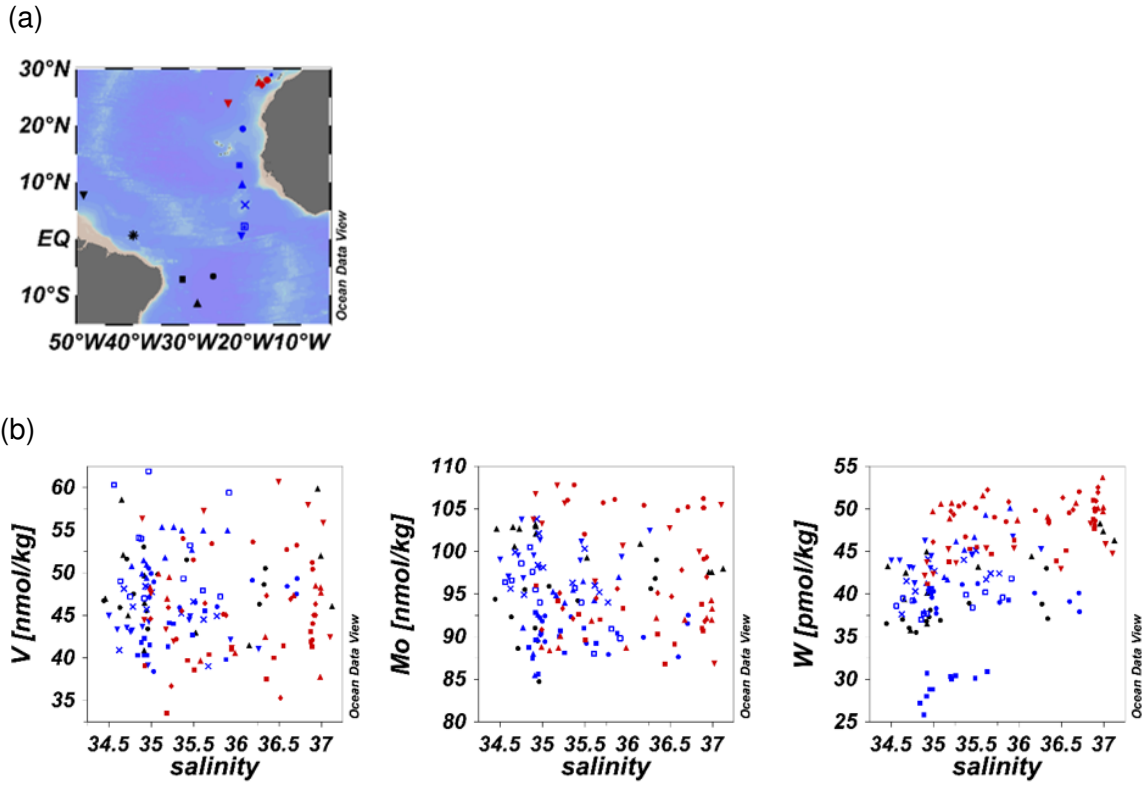


Figure 5.8: Symbols for stations of cruise track M81/1 (a) applied for a scatter plot of trace metal vs. salinity for all stations along the NE - SW transect (b): left - V, middle - Mo, right W.

Upstream the Canary Islands, dissolved V is similar to the average concentration of the NE - SW transect and hence no significant influence due to mixing with MOW was detected within this study. In deeper waters (2000 m) at stations 2 and 4 a slight depletion in concentration was observed which might be caused by sorption onto sinking particles. Since we did not detect a correlation between V and nutrients in this specific region, we suggest that mineral particles may dominate sorption processes compared to particulate organic matter, which leads to the observed decrease in concentration below 2000 m water depth.

The conservative depth distribution of V observed downstream the archipelago (stations 5 and 6) revealed that neither the MOW nor weathering processes from the Canary Islands had a significant influence on V south of the archipelago during our sampling campaign. Only at station 7 higher concentrations in surface waters were observed indicating potential atmospheric input either from the Canary Islands or from the African continent. A tracer for dust input is Al, which was conservatively distributed from surface waters to 500 m water depth except a slight maximum at 100 m. Since Al showed conservative depth patterns also at stations in the direct proximity of the Canary Islands atmospheric input might not be a reasonable explanation for the distinct V increase at station 7. We cannot provide a reasonable explanation for this observed feature with the data available from cruise M81/1 until now.

Slightly elevated concentrations of V were observed between 11°N and the equator (stations 12 and 14) and we assume that Saharan dust introduces V to the Atlantic Ocean. Aluminum is widely applied as a tracer for dust deposition (Dammshäuser et al., 2011; Measures et al., 2008; Measures & Vink, 2000). Aluminum enters the ocean mainly in particulate form while only 2.3% of particulate Al (pAl) dissolve in seawater (Spokes & Jickells, 1996). The solubility of aerosol dust particles depends on several factors, e.g. aerosol type, dry or wet deposition as well as pH conditions (Baker & Croot, 2010; Spokes & Jickells, 1996). Residence times of pAl in the Atlantic Ocean have recently been calculated to be 3-22 days while dissolved Al remain present in surface water layers up to several years (0.9-3.8 years, Dammshäuser et al., 2013). Main dust events derived from the African continent occur during June to October (Graham & Duce, 1979); research cruise M81/1 took place in February. Since no clear dust event occurred during our sampling campaign we assume that the observed high Al concentrations (up to 40.0 nmol/L) are remnants of former dust events (Figure 5.9), considering the long residence time of dissolved Al.

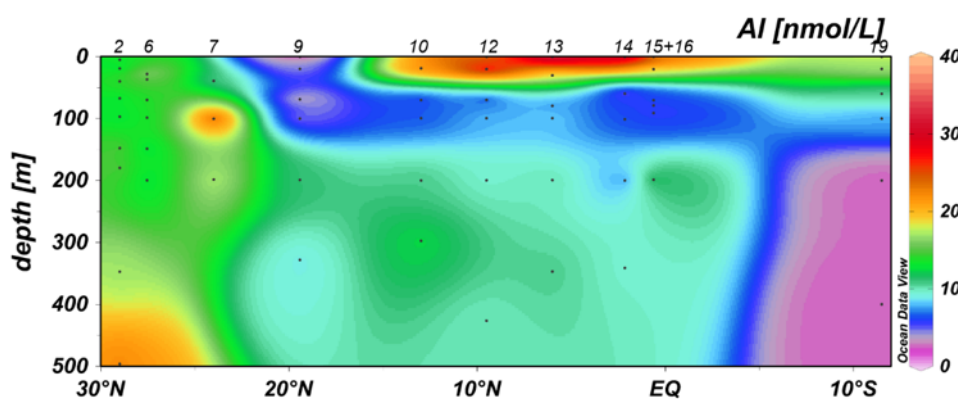


Figure 5.9: Section plot of Al for the upper 500 m of the NE-SW transect from 30°N to 12°S. Station numbers are indicated above the plot.

Our data agree with published data on Al in surface waters exposed to Saharan dust deposition reporting concentrations up to 40 nmol/L and 43 nmol/L (Dammshäuser & Croot, 2012; de Jong et al., 2007). Buck et al. (2010) reported that total aerosol V concentrations in air masses influenced by Saharan dust were higher compared to air masses sampled North and South this region. A recent study revealed that V together with Fe and Al correlates with the distribution of particles with less than 2.5 μm diameter (PM_{2.5}) sampled during Saharan dust events (Jiménez-Vélez et al., 2009). This indicates that V, Fe and Al originate from a similar source of origin, namely Saharan dust, confirming our suggestion of Saharan dust as a source for V.

The collection of seawater samples for the determination of V started at approx. 70 m water depth in which the signatures of atmospheric Al input are not detectable since dissolved Al accumulates in surface water layers. Hence, a direct comparison of both

parameters determined in this study to show the correlation between V and Al in ocean waters exposed to Saharan dust is not possible. Anthropogenically derived aerosols might also represent a minor source for V for the Northeast Atlantic since minerals deposited in winter in this region consist of Saharan dust and also of particles derived from the Sahel zone which is more affected by anthropogenic emissions (Patey et al., 2015). Aerosols, however, have not been collected during M81/1.

Vanadium is an essential element for enzyme processes (Almeida et al., 2001) and incorporation into organic matter might play a role. However, comparison with the nutrients nitrate, phosphate and silicate does not show a correlation (Figure 5.10) and contradicts the assumed similarity of V and phosphate (Jeandel et al., 1987).

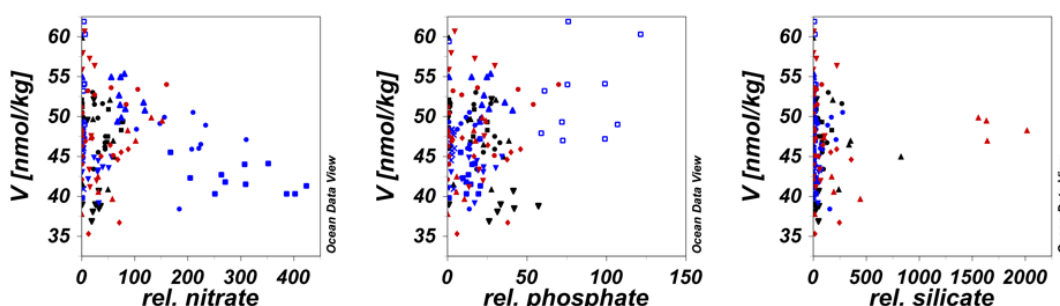


Figure 5.10: Dissolved V vs. nutrients: left - nitrate, middle - phosphate, right - silicate for all stations sampled during M81/1. For denotation of the symbols the reader is referred to Figure 5.8a.

Since V is present in high concentrations (nmol/kg) a small fraction consumed during bioproductivity might have been too low to reveal a possible correlation with nutrients. Moreover, the sampling campaign took place in February, which is not a period of high bioproductivity, and a biological importance of V might be more obvious in the high-productivity season later during the year.

The observed patterns of our V data deviate from a nutrient-like distribution and from published data on V in the Atlantic, which demonstrates that our knowledge on the biogeochemical processes controlling the distribution of V in the Atlantic Ocean is still incomplete. Co-precipitation of V with Fe(oxyhydr)oxides has been observed in the buoyant part of hydrothermal plumes (German et al., 1991). Although our profile taken at the MAR (station 15+16) did not show any clear signs of hydrothermal input (Figure 5.6a), a slight minimum of V above the ridge may possibly be referred to such a sorption process in the plume, and sorption on particles may also play a role to explain some of the observed decreases in concentration with depth, such as at station 2. Hence, our observations indicate that V distribution may also be influenced by other processes than only micronutrient cycling through the water column and may show deviations from nutrient-type distribution, depending on the dominating process involving V.

Although the high concentration of Mo in the range of nmol/kg and the long residence

time of 800 kyrs (Colodner et al., 1995; Morford & Emerson, 1999) which exceeds the time required for ocean turnover would support the conservative distribution of Mo in the world ocean, our study showed lower concentrations of Mo in the Atlantic compared to data reported for the Pacific Ocean, 107 ± 2.5 nmol/kg (Collier, 1985). Only a few stations in the Atlantic have been investigated for Mo but published results on a section covering several degrees of latitude or longitude showing the oceanographic significance is still missing.

As V, also Mo does not correlate with water masses along the NE - SW transect (Figure 5.8b-middle) which agrees with findings by Riley & Taylor (1972) reporting no correlation with major water masses or micronutrients but suggesting a biological origin to cause the patchy Mo pattern due to its biological role for enzymes. Deviations from conservative behaviour have also been reported in coastal areas during the breakdown of an algae bloom leading to the formation of Mo-enriched aggregates and to a simultaneous depletion of dissolved Mo in the water column (Dellwig et al., 2007). In estuarine mixing zones positive and negative deviations along the salinity gradient have been reported for dissolved Mo (Rahaman et al., 2014; Strady et al., 2009) possibly caused by de- and adsorption from and onto particulates such as Fe-Mn-oxyhydroxides. A decrease in concentration with depth was observed in anoxic basins such as the Black Sea (Emerson & Husted, 1991) which is controlled by removal of Mo from solution to the sediments. Hexavalent Mo, Mo(VI), is the dominant redox species of Mo in oxic seawater (Byrne, 2002). Pentavalent Mo was reported to contribute to 0 - 15 % to total dissolved Mo in Peconic River estuary, USA, in suboxic and anoxic waters (Wang et al., 2009). Since all samples collected during our sampling campaign showed oxic characteristics (Figure 5.4c and Figure 5.5c) we assume, that the contribution of the reduced species is negligible.

Soil erosion and weathering processes at the Canary Islands do not seem to represent a key source for Mo to the ocean since Mo is present in similar concentrations in surface and deep waters at stations sampled in the proximity of the archipelago (stations 2, 4, 5 and 6; Figure 5.6b). Concentrations of Mo observed at station 7 were highest of this transect (102 ± 6 nmol/kg) and we assume that this distinct area might represent an open ocean environment less affected by removal processes compared to the locations in the proximity of the Canary Islands or those investigated at lower latitudes along this transect. The concentrations at this position agree with concentrations reported for open ocean Atlantic and Pacific waters (Collier, 1985; Morris, 1975) confirming our suggestion.

Significant decrease in concentrations in surface and subsurface water layers (up to 1000 m water depth) was observed between 20°N and 11°N (stations 9 and 10; Figure 5.6b), which correlates in depth with the pronounced OMZ (Figure 5.4c). Since this distinct oceanic region is exposed to Saharan dust, dissolution of mineral particles providing the micronutrient Fe stimulates bioproductivity (Kim & Church, 2001) and leads to the observed pronounced OMZ. At least two key processes might cause the decrease in Mo concentration: (1) since Mo is essential for enzymes (Mendel, 2005) uptake by organisms

in surface water layers might lead to a measurable depletion of the high Mo background concentrations and (2) dissolved Mo may sorb onto sinking particulate organic matter and/or mineral particles provided by Saharan dust. Uptake into or sorption onto biogenic material would have caused an increase of Mo in deeper waters due to remineralization of organic matter, which was not detected and comparison with the distribution of nutrients indicated no correlation (Figure 5.11). Hence, we suggest sorption onto mineral particles to be the dominant factor controlling the distribution of Mo in this specific oceanic region.

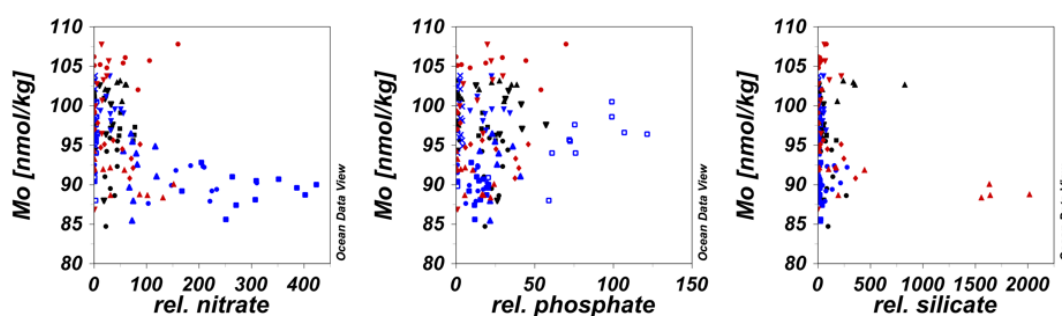


Figure 5.11: Dissolved Mo vs. nutrients: left - nitrate, middle - phosphate, right - silicate for all stations sampled during M81/1. For denotation of the symbols the reader is referred to Figure 5.8a.

Different factors have been suggested to control the distribution of Mo in different aquatic regimes. Our study revealed that Mo may deviate from a conservative distribution in areas characterized by high dust input to the marine environment. Scavenging through sorption onto mineral particles might have caused the observed depletion.

Throughout the presented section W did not correlate with major water masses (Figure 5.8b-right), which agrees with previously reported conservative characteristics of W in the Pacific Ocean. Nevertheless, our study revealed that the distribution of W may vary showing non-conservative patterns under specific conditions.

In the proximity of the Canary Islands (stations 2, 4, 5 and 6) the concentration of W was determined to approx. 50 nmol/kg which is highest along the NE-SW transect indicating the importance of the volcanic rocks as a source for W to the Atlantic Ocean. Weathering processes and subsequent transport of particulate and dissolved metals by rivers as well as dissolution of mineral particles in the marine environment may play a role providing metals to ambient seawater.

Between 14°N and 11°N (station 10; Figure 5.6c) a distinct depletion was observed throughout the water column matching spatially the depletion observed for Mo. As for Mo, we assume that W might be sorbed onto mineral particulates provided by Saharan dust since both metals belong to the same subgroup in the periodic table of elements and similar chemical properties can be expected. Since no particulate samples were collected, which could have assisted to confirm the above mentioned hypothesis, we

correlated the distribution of nutrients with the distribution of W (Figure 5.12).

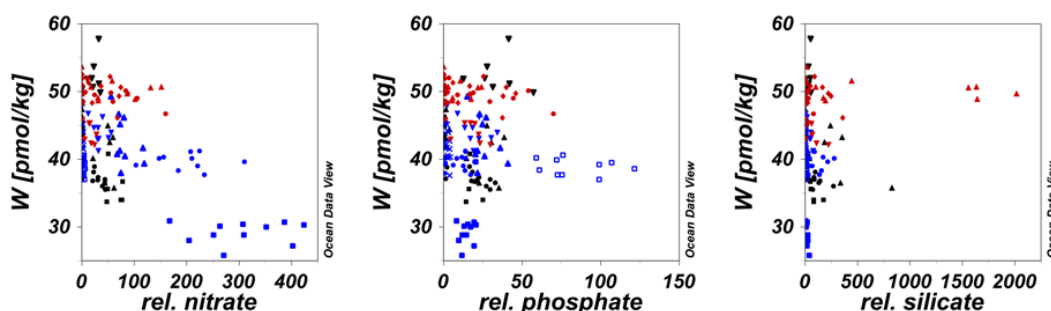


Figure 5.12: Dissolved W vs. nutrients: left - nitrate, middle - phosphate, right - silicate for all stations sampled during M81/1. For denotation of the symbols the reader is referred to Figure 5.8a.

We received a widely scattered image showing no correlation of W with nitrate, phosphate, or silicate and therefore suggest sorption onto mineral particulates being more important than sorption onto biogenic particles with respect to scavenging processes for W, as suggested for Mo.

Between 11°N and 12°S (stations 12, 13, 14, 15+16, 18, 19; Figure 5.6c) W was conservatively distributed at 42.5 ± 3.5 nmol/kg.

The correlation coefficient of $R=0.1$ between W and Mo (Figure 5.13) revealed that both metals display a largely different behaviour under the same regional influences which has been observed previously (Sohrin et al., 1999) except the observed similarities under Saharan dust input.

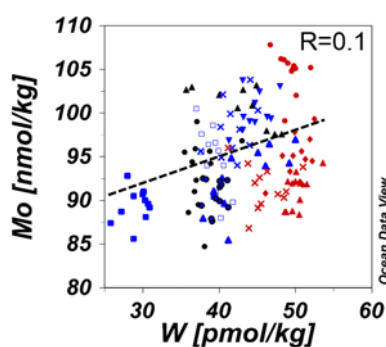


Figure 5.13: Scatter plot of dissolved Mo vs. dissolved W for stations sampled during NE - SW transect of M81/1.

5.5.2 SE - NW transect

Dissolved V at station 19 in the western Atlantic basin shows a distinct maximum at 1091 m water depth which corresponds with the location of AAIW (Figure 5.7a). Although AAIW was also identified further north V did not show a corresponding increase in concentration as observed at station 19. As evident from the black symbols in Figure 5.8b-

left, also in the West Atlantic V does not correlate with salinity, confirming that V does not serve as a tracer for water masses which agrees with our findings for the NE - SW transect.

The observed surface maximum in V concentration between 10°S and 5°S (station 20; Figure 5.7a) might be related to atmospheric input of mineral particles. Long-range transport of mineral dust from North Africa to the Amazon region and the southeastern United States has been reported (Formenti et al., 2001; Prospero, 1999). The composition of dust from North Africa has been investigated in several studies (Blanco et al., 2003; Caquineau et al., 2002; Falkovich et al., 2001; Formenti et al., 2003) and the source of dust particles can be determined since their composition reflects the average composition of the eroded areas. A study on dissolved Al, which serves as a tracer for atmospheric input, conducted in March/April 2011 during research cruise JCO57 in the same investigated area showed no elevated surface concentrations of dissolved Al (Middag et al., 2015). Nevertheless, a recent study reported African dust events occurring in winter to be directed to Brazil (Kumar et al., 2014) while dust from the African continent is mainly transported to the Caribbean in spring and summer. Since our research was conducted in February, we suggest to consider Saharan dust as a potential atmospheric source for V in the western Atlantic basin despite the lack of data on Al derived from cruise M81/1 for the SE - NW transect to confirm our suggestion.

Between 5°S and 5°N (station 21; Figure 5.7a) we observed a nutrient-like pattern of V which agrees with previously reported depth profiles for V in Atlantic and Pacific waters (Collier, 1984; Jeandel et al., 1987). However, comparison with nutrients such as phosphate did not reveal a correlation (Figure 5.10) as reported for the NE - SW transect and it seems unlikely that uptake of dissolved V into organic matter caused the slight depletion in surface waters.

A slight depletion in surface waters was also observed at station 22 which was located off the North Brazilian coast but is not within the Amazon plume according to the salinity data. The spatial extension of the plume depends on the season and was reported to direct northeastward in February while salinities in the Caribbean remain high (~36.0) (Chérubin & Richardson, 2007). Although we performed the sampling in the dry season and the Amazon discharge was expected to be low a distinct influence of Amazon freshwater cannot be excluded. Hence, the observed lower surface concentrations compared to deep waters between 5°S and 8°N might be caused by mixing with Amazon freshwater showing concentrations between 4.55 nmol/kg (Martin & Meybeck, 1979) and 13.8 nmol/L (Gaillardet et al., 2014) depending on the season, which is between 3 to 10 times lower than the average V concentration in the Atlantic observed in this study. Since the main part of V is transported by particulate matter to the ocean (Martin & Meybeck, 1979) desorption processes might be responsible for the observed increase in concentrations in subsurface (40 to 100 m) and intermediate waters (1683 m) while release from the shelf might have caused the slight increase in concentration in bottom-near waters.

The conservative distribution of Mo at 99.6 ± 2.7 nmol/kg between 12°S and 5°S (stations 19 and 20) in the western Atlantic basin represents a typical deep sea environment. Within the GEOTRACES program J.M. Godoy, Pontifical Catholic University of Rio de Janeiro, provided Mo data for the West Atlantic Ocean collected during cruise GA02-leg 3 (March 2011 - April 2011) from Punta Arenas, Chile, to Las Palmas, Spain (http://www.egeotraces.org/sections/GA02_Mo_D_CONC_BOTTLE.html). After a 1:20 dilution and determination with ICP-MS concentrations of 150 nmol/kg have been reported in surface waters to 200 m water depth between 12°S and 10°S while the concentration of Mo was observed at 140 nmol/kg in underlying water to deep waters. Between 10°S and the equator J.M. Godoy observed approx. 138 nmol/kg in surface waters while the concentration in deeper waters ranged between 128 and 135 nmol/kg. The general trend with slightly higher concentrations at 12°S compared to the area further north agrees with the pattern observed in our study although our reported variations lie within the RSD of our method. Since the RSD of the method applied by J.M. Godoy is not yet published we can hardly discuss whether the observed variations represent regional trends or lie within the RSD of the applied method. However, the reported concentrations provided by J.M. Godoy are up to 30 % higher than the concentration range we observed and cannot be explained at this point.

Between 5°S and 5°N (station 21) the surface depletion of Mo occurs at the same latitude as observed for V. Since no correlation with nutrients was detected (Figure 5.11) we suggest mixing with Amazon freshwater to cause the slight depletion as the Amazon transports only 4.3 nmol/kg Mo (Archer & Vance, 2008) which is approx. 20 times less than the average Mo concentration in the Atlantic. Hence, we expected a surface depletion due to mixing with riverine freshwater also at station 22. The concentration ranged between 88 nmol/kg in surface waters and 94 nmol/kg in deep waters and it should be noted, that these variations lie within the RSD of the applied method. However, besides simple physical mixing between river water and seawater other processes such as desorption from particulate matter might influence the distribution of Mo. Recently, Schneider et al. (2015a) observed positive deviations of Mo from the conservative mixing line at intermediate salinity probably caused by desorption processes during artificial mixing experiments using river water and seawater. Changes in salinity might induce changes in the surface charges of particles leading to ad- and desorption processes in estuarine mixing areas. Non-conservative mixing of Mo in the Gironde estuary (Strady et al., 2009) confirms these recent observations. Release of Mo during biogeochemical processes in the estuary and the shelf region, as observed for U, might also play a role (McKee et al., 1987). To conclude, several factors control the distribution of trace metals such as Mo during mixing between riverine freshwater and seawater and we observe the net effect of a few processes which cannot be distinguished easily.

The samples collected along the SE - NW transect showed no correlation between W

and salinity (Figure 5.8-right) or nutrients (Figure 5.12) as observed for Mo and V. The average concentration of W in seawater sampled during this transect (44 ± 6.2 pmol/kg) is slightly lower compared to concentrations reported for the Pacific Ocean (53 - 60 pmol/kg, Sohrin et al., 1987) but is by an order of magnitude lower than data reported for the North Atlantic Ocean (540 pmol/kg; Hartung, 1991). Anthropogenic sources might have contributed to the observed high concentrations in the North Atlantic waters while samples in our study are largely collected in open ocean seawater and we assume anthropogenic influences to play a minor role.

Between 12°S and 5°S (stations 19 and 20; Figure 5.7c) we expected a conservative pattern for W due to the absence of major riverine sources in the direct proximity of the investigated locations and sufficient distance from the Brazilian shelf. The observed decrease in concentration with depth might indicate mineral dust deposition, as previously suggested for V, and sorption of W. Deposition of mineral dust can explain the decrease in concentration of W due to sorption onto mineral particles as observed in the East Atlantic.

The conservative depth distribution between 5°S and 5°N (station 21) indicates no significant source of W and no significant incorporation into organic matter. The world riverine concentration of W was reported to be 54.4 nmol/L (Gaillardet et al., 2014), which is significantly higher than the concentration of W in seawater. We assume that the concentration of W in the Amazon river is also higher than concentrations in the Atlantic seawater which might be a reason for the slightly elevated concentrations observed for W at the last station of this transect at approx. 7°N . The increase of W with depth at this station may be due to desorption from soil particles introduced by the Amazon or from the shelf sediment.

A correlation between the distribution of W and Mo was not observed for the SE - NW transect (Figure 5.14), demonstrated by a correlation coefficient of 0.007. This transect, however, contains only four stations. Although both metals belong to the same subgroup of elements and similar geochemical properties can be expected, the observed differences in correlation between both transects imply that both metals partly react differently in the marine environment. The observed similar patterns of Mo and W cannot be artifacts of the applied method since their determinations were performed at different days applying different methods due to their significantly different concentrations in seawater (please refer to subsection 5.2.3).

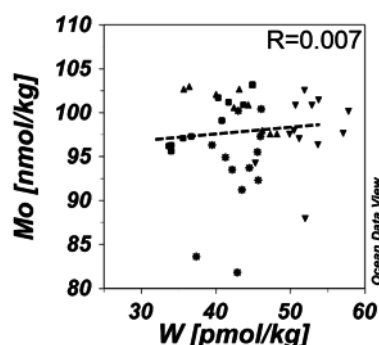


Figure 5.14: Scatter plot of dissolved Mo vs. dissolved W for stations sampled during SE - NW transect of M81/1.

5.6 Conclusion

With this study, we aim at elucidating key factors for the distribution of V, Mo, and W in the Atlantic Ocean, which might also be relevant for other oceanic basins. The distribution of dissolved V, Mo, and W in the Atlantic Ocean is controlled by various factors such as dust input, upwelling processes as well as (bio)geochemical processes in highly productive regions. Depending on the investigated area these processes vary with different sources and sinks dominating in this specific area and often influence the three elements in different ways.

A correlation between dissolved V, Mo, or W with salinity was not observed, showing that these three metals are not suitable as water mass tracers in the Tropical Atlantic and their distribution appears to be influenced rather by regional biogeochemical processes. The lack of a correlation between dissolved V, Mo, and W with nutrients indicates that sorption onto biogenic material or incorporation into organic matter with subsequent remineralization does not play an important role for the vertical distribution of V, Mo and W.

Although at least V and Mo are essential elements required for biological processes we assume that the fraction used for biological productivity might be too small compared to the total concentration in the range of nmol/kg and the impact might not be detectable, at least during the sampling period (February 2011).

Particles derived from volcanic rocks of the Canary Islands represented a source for W while sorption processes scavenged V from the water column. In contrast, Saharan dust was identified as a source for V to the Atlantic Ocean while mineral particles derived from the African continent represented sorption sites for dissolved Mo and W leading to a depletion off West Africa. Hence, Saharan dust serves as a source for V and as a sink for Mo and W.

In the West Atlantic between 8°N and 5°N a depletion of V and Mo was expected as the Amazon River is characterized by lower concentrations of V and Mo compared

to the average seawater concentrations but no distinct surface depletion was observed for these two metals in the Amazon outflow region. We assume that the slightly higher concentrations of V in subsurface and intermediate waters and the concentration range of Mo, which was higher than expected, might be due to the release of V and Mo from riverine particulate matter in the estuarine mixing area or biogeochemical processes in the shelf region, counteracting the dilution process. The increase in W concentration in that region might be due to mixing with Amazon freshwater, since based on world riverine concentration ranges at several nmol/kg W, concentrations in the Amazon can be assumed to be higher than average Atlantic Ocean concentrations.

Comparison of the results of V, Mo, and W obtained in this study with data for the Pacific Ocean reveals that we detected higher concentrations of V while Mo and W show lower concentrations than in the Pacific. Higher dust input probably causes lower concentrations of both metals in the Atlantic compared to the Pacific due to sorption on the particulate matter. In contrast, dust input appears to serve as a source for V, which might explain the observed higher concentrations compared to Pacific waters.

To conclude, the presented water depth profiles of dissolved V, Mo, and W are net effects combining various input and removal processes. These single features and parameters are difficult to distinguish from one another. In order to further investigate sources and sinks and to calculate e.g. oceanic residence times of V, Mo, and W in the Tropical Atlantic research on particulate matter and aerosol samples would be necessary, which is, however, beyond the scope of this manuscript. This study provides spatial and vertical distribution of V, Mo, and W in the Tropical Atlantic revealing element-specific sources and sinks. Molybdenum and W are traditionally described as conservative metals in the ocean but the deviations observed in this study show that both metals do not behave as conservative as previously assumed. Dissolved V did not show a nutrient-type pattern with depth but rather a variable distribution depending on regional influences. It would be interesting to follow up on these observations in future work to study seasonal variations of V, Mo, and W distributions because of the seasonally variable input of Saharan dust, bioproductivity effects, and flow rates of Amazon freshwater into the West Atlantic Basin.

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6 Chromium redox species in Pacific and Atlantic seawater

Title of publication

Significant abundance of Cr(III) in oxic seawater: implications of stabilization mechanisms

Authors and affiliations

Sandra Poehle^{*1}, Sylvia Sander^{2,3}, Andrea Koschinsky^{1,4}

* Corresponding author. Tel.: +49 0421 2003261,

E-mail address: s.poehle@jacobs-university.de

¹ Department of Physics and Earth Sciences, Jacobs University Bremen
Campus Ring 1, 28759 Bremen, Germany

² University of Otago, Department of Chemistry
Union Place West, Dunedin 9054, New Zealand

³ Present address: Marine Environmental Studies Laboratory, Division of IAEA Environment
Laboratories, Department of Nuclear Sciences and Applications, International Atomic Energy
Agency, Monaco, Principality of Monaco, E-mail address: s.sander@iaea.org

⁴ E-mail address: a.koschinsky@jacobs-university.de

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Abstract

Chromium (Cr) is present in seawater in two main oxidation states (+VI) and (+III), which control its physico-chemical properties, bioavailability and toxicity. Redox reactions of Cr in seawater have been shown to be influenced by different parameters, e.g. photochemical processes or hydrothermal activity.

Within this study Cr speciation under varying oxygen conditions was investigated at six stations; three water profiles were sampled in the South Pacific during GEOTRACES cruise GP13 in June 2011 (0.2 μm filtered seawater) and three were sampled in the Atlantic Ocean during GEOTRACES cruise M81/1 (GA11) in February-March 2010 (unfiltered seawater).

Cr(VI) largely dominated dissolved Cr(total) in the Pacific while Cr(III) was present at rather constant background concentrations. In the Atlantic, no consistent trend was observed in the distribution of Cr(VI) and Cr(III). Regional features e.g. dust deposition originating from the Sahara, or riverine freshwater discharge from the Amazon affected the Cr speciation in the (sub)tropical Atlantic. Substantial amounts of Cr(III) were observed in oxic and deep waters in both investigated areas, the South Pacific and the (sub)tropical Atlantic. In surface waters photoreduction producing Cr(III) might occur whereas complexation of Cr(III) with organic ligands might stabilize the particle-reactive species throughout the water column. Cr(III) consisted in both investigated areas almost quantitatively in its inert form Cr(III_unreactive), which confirms the suggestion of strong organic complexation stabilizing Cr(III).

Apparently, oxygen concentrations in the range of 50 - 250 $\mu\text{mol/kg}$ in the oceanic water column do not exert a significant influence on the Cr speciation indicating that other parameters e.g. sources, sinks, and the presence of organic molecules play a more important role in both oceans. Since the distribution of Cr into its redox species influences the isotopic composition of Cr, this result may be of relevance for studies on Cr isotopes, which have been applied to reconstruct the redox state of ancient seawater.

6.1 Introduction

Chromium is a trace metal in the ocean that has several sources, natural and anthropogenic, and its biogeochemical behaviour in seawater is related to redox conditions of the marine environment and particle-seawater interactions, among other factors.

The pool of total dissolved Cr, Cr(total), in seawater consists basically of the trivalent, Cr(III), and hexavalent, Cr(VI), species. The distribution of Cr(total) in open ocean seawater has been described as intermediate between conservative and nutrient-like type (Sirinawin et al., 2000) with residence times of 25,000 - 45,000 years (Campbell & Yeats, 1984). A slight depletion of Cr(total) in surface waters indicates either sorption onto deposited mineral particulates or sorption onto or incorporation into organic matter (Jeandel

& Minster, 1987) but also uptake into biological matter might play a role. A strong correlation between high carbon flux after bloom events and increase in Cr(total) flux to deeper waters has been observed in the Sargasso Sea, Atlantic Ocean (Connelly et al., 2006).

Deep waters of the Atlantic and Pacific Ocean differ slightly in dissolved Cr(total) concentrations with 3 nmol/kg in North Atlantic deep water compared to 5 nmol/kg in Pacific deep water (Jeandel & Minster, 1987).

The two dominant redox species in seawater, Cr(VI) and Cr(III), differ in their distinct biological, physical and chemical properties. Cr(III) is strongly hydrolyzed in seawater, $\text{Cr}(\text{OH})^{2+}$ and $\text{Cr}(\text{OH})_3^0$ (Byrne, 2002), and essential as a micronutrient (Anderson, 1989), showing low solubility and high particle reactivity (Boussemart et al., 1992). Cr(VI) is present as chromate species, HCrO_4^- and CrO_4^{2-} (Byrne, 2002) and known to be toxic at elevated concentrations. Cr(VI) is a human carcinogen and has the ability to cross cell membranes and act as an oxidizing agent (Nriagu & Nieboer, 1988). It is characterized by its high solubility and low particle reactivity (Geisler & Schmidt, 1992). This indicates that the more toxic redox species, Cr(VI), tends to stay in solution whereas Cr(III) might be easily scavenged from the water column through interaction with particulate matter.

Cr(VI) is reported to be the dominant species in open ocean seawater throughout the water column (Sirinawin et al., 2000) which agrees with thermodynamic calculations for oxic seawater (Elderfield, 1970), whereas Cr(III) occurred in significant concentrations in the oxygen minimum zone (OMZ) (Murray et al., 1983) as well as in surface waters (Berg et al., 1994). The substantial abundance of Cr(III) in oxic waters reveal probable reduction of Cr(VI) through chemical, photochemical or biological processes (Pettine & Millero, 1990; Pettine et al., 1991). Moreover, Cr(III) has also been detected in the water column of the North Fiji Basin and the Lesser Antilles indicating a distinct influence of hydrothermal activity (Sander & Koschinsky, 2000; Sander et al., 2003a). Besides the classification via the redox state Cr(total) can also be divided into Cr(reactive) and Cr(unreactive). Cr(VI) and Cr(III_reactive) combine to Cr(reactive), and the fraction of Cr(III_reactive) forms labile organic complexes. The fraction of Cr(unreactive) consists of unreactive trivalent Cr, Cr(III_unreactive), which forms stable complexes with organic or inorganic ligands. Such behaviour has been observed at hydrothermal sites where emitted Cr species may bind to organic compounds while mixing with seawater (Sander & Koschinsky, 2011). This property may lead to a decreased bioavailability of Cr(III) in seawater.

Redox reactions of Cr in seawater fractionate Cr isotopes (Paulukat et al., 2016; Scheiderich et al., 2015; Semeniuk et al., 2016). Cr isotopes have recently been applied to estimate atmospheric oxygen conditions in the past (Crowe et al., 2013) and to gain information about the composition of ancient seawater (Rodler et al., 2016) and the relationship to climate change (Frei et al., 2011; Pereira et al., 2016). It is thus essential to understand the biogeochemical cycling of Cr and its redox species in seawater with respect to the oceanic oxygen conditions. However, the lack of a basin wide study is still

outstanding in two oceans (Pacific and Atlantic).

This work aims to provide a better understanding of the marine redox speciation of Cr and may serve future studies e.g. on the isotopic composition of Cr.

6.2 Material and methods

6.2.1 Sampling sites and sampling procedures

Along a latitudinal transect at 32.5°S Pacific seawater samples were collected at three stations on the New Zealand leg of the GEOTRACES cruise GP13 in June 2011 (Figure 6.1).

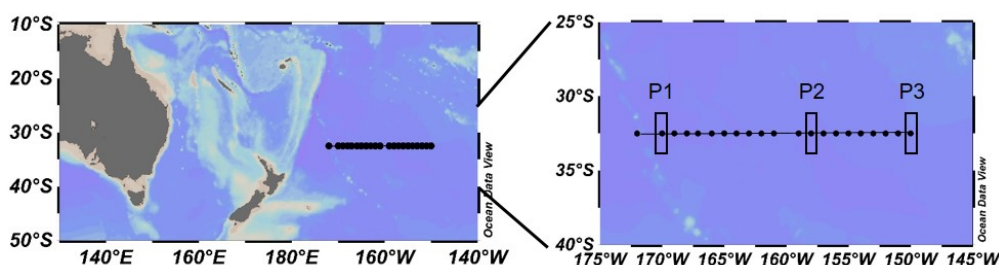


Figure 6.1: All stations sampled during GEOTRACES cruise GP13 (June 2011) are shown on the left side. Stations selected for Cr speciation (P1, P2, and P3) are indicated with a black frame in the close-up of all stations of GP13 (right).

Station P1 (32.5°S, 170.0°W) was located closest to the Kermadec Arc, an area characterized by submarine hydrothermal activity between the Australian and the Pacific Plate, while stations P2 (32.5°S, 158.0°W) and P3 (32.5°S, 150.0°W) were located further east. Each station was resolved with approx. 20 different depths samples. Sampling was performed during upcast of the trace metal-clean autonomous Rosette sampler (General Oceanics, USA) equipped with 12 Teflon coated NISKIN bottles. The NISKIN bottles were carried into a clean laboratory on board where filtration with 0.2 µm polycarbonate filter cartridges was performed. Filtered subsamples were filled into pre-cleaned 100 mL low-density polyethylene (PELD)-bottles. The samples were stored frozen at -20°C until analysis in the home-laboratory (Sander & Koschinsky, 2000).

Prior to the sampling campaign the PELD-bottles had been cleaned with a mixture of 0.5 mol/L nitric acid, HNO₃, and 0.1 mol/L hydrofluoric acid, HF, and allowed to stand for 72 hours at 60°C. The bottles were rinsed several times with deionized, DI, water and filled with 0.5 mol/L hydrochloric acid, HCl, for three days at 60°C. The sampling bottles were soaked for 24 hours in DI water and were ready for the sampling campaign after a final rinse with DI water and transported in sealable plastic bags.

Atlantic seawater samples were collected at three different stations during the GEOTRACES cruise M81/1 (GA11) in February 2010 (Figure 6.2).

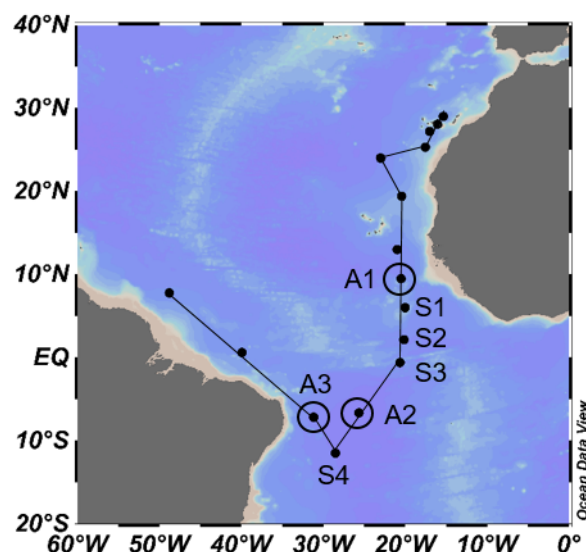


Figure 6.2: The black dots represent all stations sampled during GEOTRACES M81/1 (GA11) in February-March 2010. The stations A1, A2, and A3, for which Cr data are presented, are indicated with a black circle while supplementary stations used for section plot of temperature, salinity and dissolved oxygen (Figure 6.3) are indicated with S1 to S4. The map was created with Ocean Data View (ODV) provided by R. Schlitzer (Schlitzer, R., Ocean Data View, <http://odv.awi.de>, 2013).

Station A1 (9.5°N, 20.5°W) was located in the eastern basin in an area influenced by Saharan dust and 14 depth samples were collected, $n = 14$. The two subsequent stations, A2 (6.7°N, 25.7°W, $n = 16$) and A3 (7.2°N, 31.2°W, $n = 17$), represent typical deep-sea environments located in the West Atlantic.

Sampling was performed with a trace metal-clean CTD-rosette equipped with 24 Teflon coated GO-FLO samplers, each 12 L volume, with appendant mobile winch and 8 km rubber coated Kevlar rope, both property of Old Dominion University, USA. The water samplers were closed during upcast of the CTD-rosette and conductivity, temperature, depth and dissolved oxygen were recorded while salinity data were calculated. After the CTD-rosette was on deck again, the samplers were carried to a clean laboratory container (provided by Old Dominion University). Unfortunately Cr samples on this cruise were taken unfiltered into 100 ml PELD-bottles, immediately shock frozen at 80°C and later stored at -20°C. Samples of both cruises were thawed just before analysis in the home-laboratory.

6.2.2 Chemicals

All solutions were prepared with DI water provided by a Sartorius Arium 611 unit and most of the preparation was performed in a laminar flow cabinet equipped with a high efficiency particulate arrestance (HEPA)-filter.

Hydrogen peroxide, H_2O_2 , and hydrochloric acid, HCl , (both suprapure, Merck) were

used for UV-digestion of seawater aliquots. Diethylenetriaminepentaacetic acid (DTPA for complexometry, Fluka), glacial acetic acid, CH_3COOH , and ammonia solution (both suprapure, Roth) were used to prepare the 0.15 mol/L DTPA - 1 mol/L acetate buffer mixture. The DTPA buffer mixture was adjusted to pH 5.2 with either CH_3COOH or ammonia solution. Sodium nitrate, NaNO_3 (p.a., Sigma-Aldrich), served as catalyst. Trace metal-contamination in 5 mol/L NaNO_3 solution was removed by coprecipitation on iron hydroxide after oxidation of 10 mmol/L FeCl_2 ($\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$, p.a., Sigma-Aldrich) over-night. The precipitate was removed through filtration with 0.45 μm syringe filters and the filtrate was subsequently cleaned with the chelating resin Chelex 100 (Na-form, 100-200 mesh particle size, Bio-Rad Laboratories) to remove remaining trace metal impurities. The Chelex 100 resin, 5 g, was filled into a PE-column and pre-cleaned according the manual Bio-Rad-Laboratories_RevB. The NaNO_3 solution was poured onto the resin and the trace metal-clean eluate was collected in a pre-cleaned PE-bottle.

A 100 $\mu\text{g/L}$ Cr^{+6} standard (1.92 $\mu\text{mol/kg}$ Cr) was prepared weekly by dilution of 1000 mg/L standard (Inorganic Ventures) with DI water. For spike experiments a 100 $\mu\text{g/L}$ Cr^{+3} standard was prepared by dilution of a 1000 mg/L standard (Inorganic Ventures) with DI water.

6.2.3 Method

We determined Cr(total), Cr(VI) and Cr(reactive) in seawater following the method described in Sander and Koschinsky (Sander & Koschinsky, 2000). The catalytic adsorptive stripping voltammetry (CAAdSV) was performed with a 757 VA Computrace Analyser and a 747 VA Stand using a hanging mercury drop electrode (HMDE) as working electrode, a Ag/AgCl (3 mol/L KCl) reference electrode and a platinum auxiliary electrode.

For the determination of Cr(total) 50 μL 30 % HCl and 20 μL 30 % H_2O_2 were added to 10 mL sample volume in quartz glass tubes and treated for 60 min at 90 °C in a UV-Digester (Metrohm). Dissolved organic matter and organic material e.g colloids decomposed during UV-digestion, releasing Cr to the dissolved phase. Released Cr and reduced Cr species initially present in the seawater sample are oxidized to Cr(VI) during this procedure. After UV-irradiation, the sample was adjusted to pH 5.2 with 5 mol/L NaOH (suprapure, Merck). After addition of the DTPA-buffer mixture and NaNO_3 solution to final concentrations of 0.015 - 0.1 mol/L and 1 mol/L, respectively, the sample was purged with nitrogen gas for 3 minutes and the analysis was started (Table 6.1).

Prior to the determination of Cr(VI) the pH of the non-digested sample aliquot was adjusted to 5.2 with glacial acetic acid. After addition of DTPA-buffer-mixture and the catalyst NaNO_3 the sample was purged with nitrogen and a waiting time of 30 min started to allow complexation of Cr(III) and Cr(reactive) with DTPA forming electrochemical inactive complexes (Sander et al., 2003b). The voltammetric analysis started immediately afterwards following the method for Cr(total).

Parameter	Operating condition
Mode	Differential pulse
Stirrer [rpm]	2000
Purging time [s]	180
Nitrogen gas pressure [bar]	1
Deposition potential [V]	-1
Deposition time [s]	60
Equilibrium time [s]	5
Start potential [V]	-1
End potential [V]	-1.3
Pulse time [s]	0.04
Voltage step [V]	0.005951
Voltage step time [s]	0.4
Sweep rate [V s ⁻¹]	0.0149
Peak position [V]	-1.2 ± 0.08

Table 6.1: Parameters for the voltammetric analysis

A non-digested sample aliquot adjusted to pH 5.2 with glacial acetic acid was used for the determination of Cr(reactive). The voltammetric method was started immediately after addition of the DTPA-buffer-mixture, catalyst and deaeration.

A 2-fold standard addition was carried out for each species of Cr using an appropriate amount of 1.92 µmol/kg Cr⁺⁶ standard.

While Cr(total), Cr(VI) and Cr(reactive) were measured directly, further species can be calculated. Cr(III) was calculated by subtraction of Cr(VI) from Cr(total) and Cr(III_reactive) was determined by subtracting Cr(VI) from Cr(reactive).

Reagent blanks were measured daily for Cr(total) using DI water. The Cr(total) reagent blank detected during the analysis of stations A1, A2, A3, P2 and P3 was 1.54 ± 0.08 nmol/L, n = 5 and similar to the blank value reported by Sander and Koschinsky (2000, 1.07 ± 0.05 nmol/L, n = 5) whereas the Cr(total) reagent blank during the analysis of P3 samples was 2.12 ± 0.08 nmol/L, n = 4. We used the corresponding reagent blanks to correct all results since the voltammetric determination is the same for all species Cr(total), Cr(VI) and Cr(reactive).

6.2.4 LOD and LOQ of the applied method

The limit of detection (LOD) was calculated three times the standard deviation of the Cr(total) reagent blank and was 0.23 nmol/L. The limit of quantification (LOQ) was nine times the standard deviation of the reagent blank of Cr(total), 0.69 nmol/L.

6.2.5 Accuracy of the voltammetric method

We applied spike recovery experiments to natural seawater to determine the accuracy of the voltammetric method. Appropriate amounts of either Cr⁺⁶ or Cr⁺³ were added

to 0.2 μm filtered North seawater leading to a final spike concentration of 3.85 $\mu\text{mol/kg}$ which is in the natural concentration range of Cr(total) in seawater. During UV-digestion of the spiked samples additionally added Cr^{+3} was oxidized to Cr^{+6} leading to similar concentrations of Cr(total) compared to the samples spiked with Cr^{+6} and good spike recovery rates were calculated for both spikes, $96 \pm 7\%$ and $92 \pm 8\%$, respectively (Table 6.2).

Matrix	Measured species (MP)	Conc. of MP [nmol/L]	Cr(III)_ spike [nmol/L]	Cr(VI)_ spike [nmol/L]	Conc. of MP after spike addition [nmol/L]	Recovery [%]
North Seawater	Cr(total)	4.79 ± 0.72	3.85	-	8.47 ± 0.29	96 ± 7
North Seawater	Cr(total)	4.79 ± 0.72	-	3.85	8.31 ± 0.30	92 ± 8
0.6 nmol/L NaCl	Cr(total)	5.12 ± 0.98	1.92	-	7.08	102

Table 6.2: Recovery experiments

Within a second approach a 0.6 mol/L NaCl solution, simulating seawater matrix with respect to salinity, was spiked with Cr^{+3} and the determination of Cr(total) after UV-digestion resulted in 102 % recovery (Table 6.2).

6.2.6 Ancillary data

Temperature, salinity and dissolved oxygen

During the Pacific cruise GP13 conductivity, temperature, depth, and dissolved oxygen were recorded during upcast of a conventional rosette sampler (Seabird 911-plus) which has been deployed at the same stations as for the trace metal-clean sampling. Dissolved oxygen was measured on board to calibrate the results for dissolved oxygen from the CTD sensor following NIWA (National Institute of Water and Atmospheric Research) Ocean CTD facility (NOCF) protocols.

A conventional CTD (Seabird 911-plus) was deployed during M81/1 at the same locations as the trace metal-clean CTD and temperature, salinity and dissolved oxygen were recorded. Dissolved oxygen was also measured on board applying Winkler-titration and the results were used to calibrate the data for dissolved oxygen of the CTD-sensor. Since temperature, salinity and dissolved oxygen are not expected to be affected by the two different sampling techniques (trace metal-clean CTD and conventional CTD) we used only the calibrated data of the conventional CTD in this study.

Nutrients

During GP13 seawater samples for nutrient analysis were collected with the trace metal-clean rosette equipped with 12 Teflon coated bottles and sensors for conductivity, temperature, and depth. Subsampling was performed in a trace metal free laboratory container and the aliquots were collected in 60 ml acid cleaned high density polyethylene (PEHD)-bottles. Nitrate, phosphate and silicate were measured on board during GP13 (Malcolm Woodward and Amadine Sabadel) using a micro-molar autoanalyser; a PML 4 channel segmented flow and colorimetric instrument (Bran and Luebbe AAIII).

Aliquots of seawater samples collected with the conventional CTD during M81/1 were stored frozen until land-based analysis of dissolved nitrate, phosphate and silicate (Frank Malien, Helmholtz Centre for Ocean Research Kiel GEOMAR, Germany). A self-made autoanalyzer using the segmented flow analysis technique (SFA) was applied. According to Grasshoff et al. (1999) dissolved nitrate was reduced to nitrite and the specific absorbance of an azo dye was measured. A spectrophotometric method was applied to detect the absorbance of a reduced phospho-molybdenum complex at 880 nm wavelength (Giedigkeit & Marquardt, 2005). A blue colored silicomolybdic acid was measured at 660 nm wavelength to determine the concentration of dissolved Si in seawater (Grasshoff et al., 1999). For a more detailed description please refer to Poehle & Koschinsky (2017).

Dissolved Al in the Atlantic

During M81/1, filtered subsamples (0.2 μm pore size filters, Sartobran P-MidiCaps) taken under trace metal-clean conditions were used for the on board analysis of dissolved Al applying a fluorometric method after Hydes & Liss (1976) and a 4-point standard addition procedure (Xiaoliang Tang and Michael Ostendorf). More details on the analytical procedure are provided elsewhere (Poehle & Koschinsky, 2017).

The data for surface concentration of dissolved Al (40.0 nmol/L) at station S2 (2.15°N, 20.15°W) agrees with published data collected at approx. 3°N, 21°W during the third Intergovernmental Oceanographic Commission Contaminant Baseline Survey (IOC) (Vink & Measures, 2001).

6.2.7 Hydrography

Pacific Ocean

Water masses in the Pacific were identified based on salinity and temperature data (Figure 6.3).

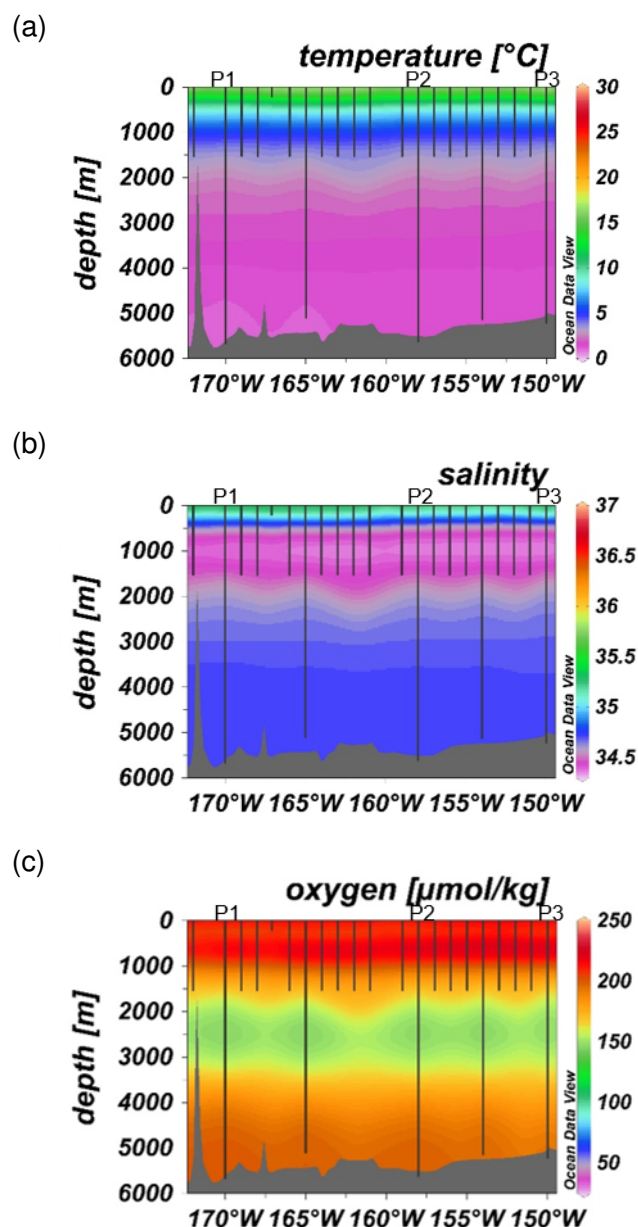


Figure 6.3: Distribution of temperature (a), salinity (b), and oxygen (c) along the cruise track of GP13. Stations P1, P2, and P3 are indicated above the section plots.

Subantarctic Mode Water (SAMW) is formed near the Subantarctic Front (SAF) by convective overturning (Karstensen & Tomczak, 1997) and occupied the depth range between 400 and 800 m during GP13. Underlying Antarctic Intermediate Water (AAIW) is suggested to be formed from subduction of Antarctic Surface Waters below the SAF and is characterized by low salinity and high oxygen concentrations (Deacon, 1937). Recent studies revealed several other regions of the formation of AAIW along the SAF (Hasson et al., 2011; Herraiz-Borreguero & Rintoul, 2010). AAIW was observed between 800 and 1400 m water depth along the GP13 cruise track. Northward flowing Pacific Deep Water (PDW) was tracked between 1400 to 3000 m water depth while underlying

Circumpolar Deep Water (CPDW) deepens to 4000 m. CPDW is a mixture of waters formed in the Antarctic region and Warm Deep Waters (WDW) flowing from the North Atlantic, Pacific and Indian Oceans (Anderson, 1999). Most of the AABW production occurs in the Weddell Sea (Carmack & Foster, 1975) and was observed below CPDW extending towards the bottom during the GP13 cruise. The described stratification applies to all GP13 stations presented in this study.

Atlantic Ocean

The North Equatorial Counter Current (NECC) dominated surface waters at 10°N (station A1) and further south in the East Atlantic. Northward flowing Antarctic Intermediate Water (AAIW), which is characterized by low salinity and high oxygen concentrations was encountered between 500 and 1200 m water depth until 20°N in the East Atlantic and traced only by its low salinity (Figure 6.4b). Mixing with the pronounced oxygen minimum zone (OMZ) off the West African coast (Figure 6.4c) caused by high bioproductivity altered the oxygen characteristics of AAIW in the East Atlantic. In contrast the high oxygen concentration and low salinity of AAIW was obvious in the West Atlantic (Figure 6.4b and c). The core of underlying North Atlantic Deep Water (NADW) was identified at 1700 m water depth in the East Atlantic (station A1) while its core was at 1800 m in the Brazil Basin (stations A2 and A3). Throughout the investigated Atlantic section NADW covers the depth range between 1200 - 3800 m. The upper boundary of the Antarctic Bottom Water (AABW) was detected at 3800 m water depth at a potential temperature near 1.74°C in the West Atlantic (stations A2 and A3). It is cooler, fresher and contains less oxygen compared to overlying NADW (Figure 6.4a, b and c). A small fraction of the AABW enters the East Atlantic through the Romanche Fracture Zone at the Mid-Atlantic Ridge (MAR) and mixing with NADW alters its characteristics while flowing northward. Its upper boundary was detected at 3925 m (S2; 2.15°N, 20.15°W) and deepens towards lower latitudes (station A1).

To conclude, the water mass properties were stronger developed in the West Atlantic while the characteristics are altered in the East Atlantic due to mixing with adjacent waters.

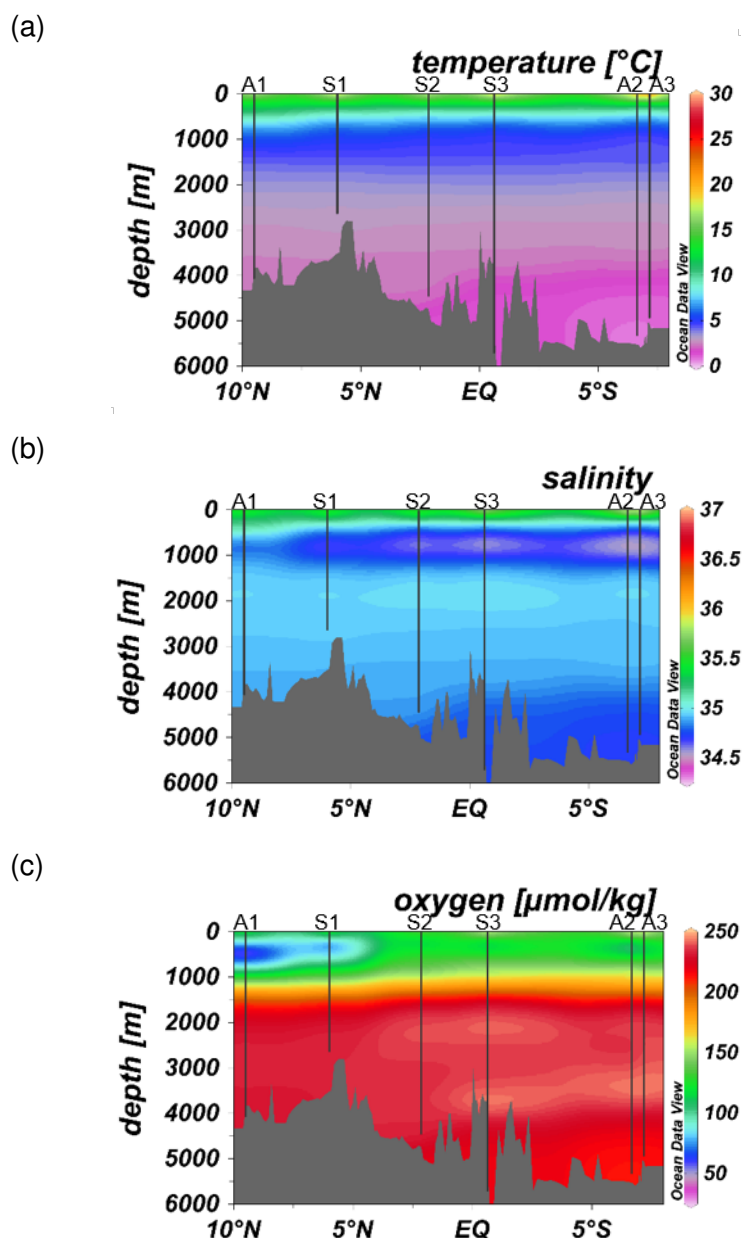


Figure 6.4: Distribution of temperature (a), salinity (b), and oxygen (c) at stations A1, A2, and A3 in the Atlantic Ocean. Supplementary stations are indicated as S1, S2, and S3 and were collected during M81/1.

6.3 Results

The accuracy of the nutrient analysis might have been influenced by the storage under frozen conditions. However, their general distribution with depth should not have been affected (Figure 6.5) allowing correlation with data obtained in this study.

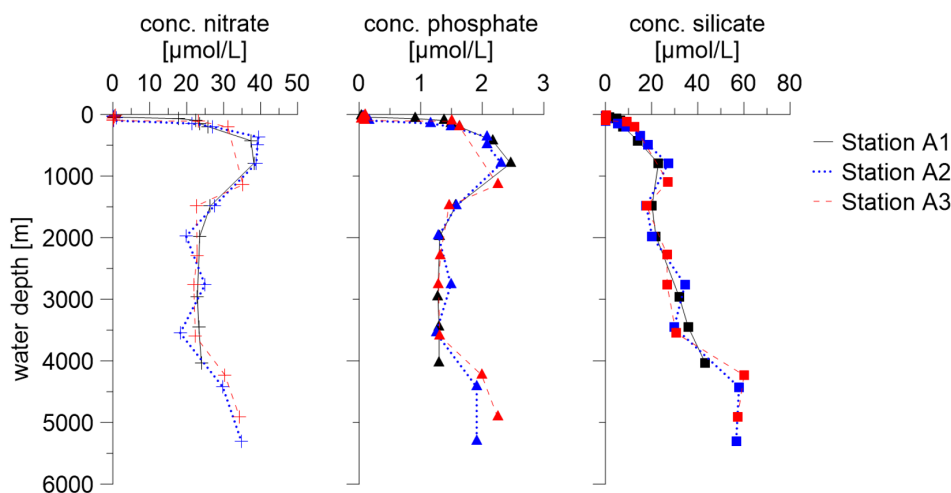


Figure 6.5: Distribution of nutrients in the Atlantic: nitrate (left), phosphate (middle), and silicate (right) with water depth at stations A1, A2, and A3 sampled during research cruise M81/1.

Although we applied a commonly used and sensitive method to determine Cr(total) and its redox species, the detected concentrations of Cr(VI) and Cr(reactive) were below the LOQ of 0.69 nmol/L for some samples. Nevertheless, we intend to show the general trend for the depth distribution and therefore included data exceeding the LOD noting that the absolute concentration may deviate from the true value. Data presented in this study are provided in the appendix (C1.Supplementary Data Table 1) with the respective information whether the concentration was below the LOQ.

6.3.1 Pacific Ocean profiles

Dissolved Cr(total) in the Pacific seawater samples at three stations along a transect at 32.5°S ranged between 2 - 7 nmol/L and a slightly elevated concentration was observed between 1500 and 2500 m water depth at all three stations (Figure 6.6).

Along this transect the concentration of dissolved Cr(VI) ranged between 1 - 5 nmol/L and its depth profiles resembled the distribution of dissolved Cr(total). Below 1500 m water depth, dissolved Cr(VI) was the dominant species of dissolved Cr(total) while dissolved Cr(III) was as abundant as dissolved Cr(VI) in some surface and subsurface samples.

Dissolved Cr(III) concentrations ranged between 0.86 nmol/L and 3.59 nmol/L with an average value of 1.73 ± 0.54 nmol/L for all samples of this Pacific transect. Cr(reactive) ranged between 1.14 - 5.39 nmol/L and consisted almost completely of dissolved Cr(VI) since the concentration of Cr(III_reactive) was very low (0.34 ± 0.25 nmol/L) and often below the LOD. Dissolved Cr(III) was dominated up to 98 % by Cr(III_unreactive) throughout the water column at all three sampled Pacific stations.

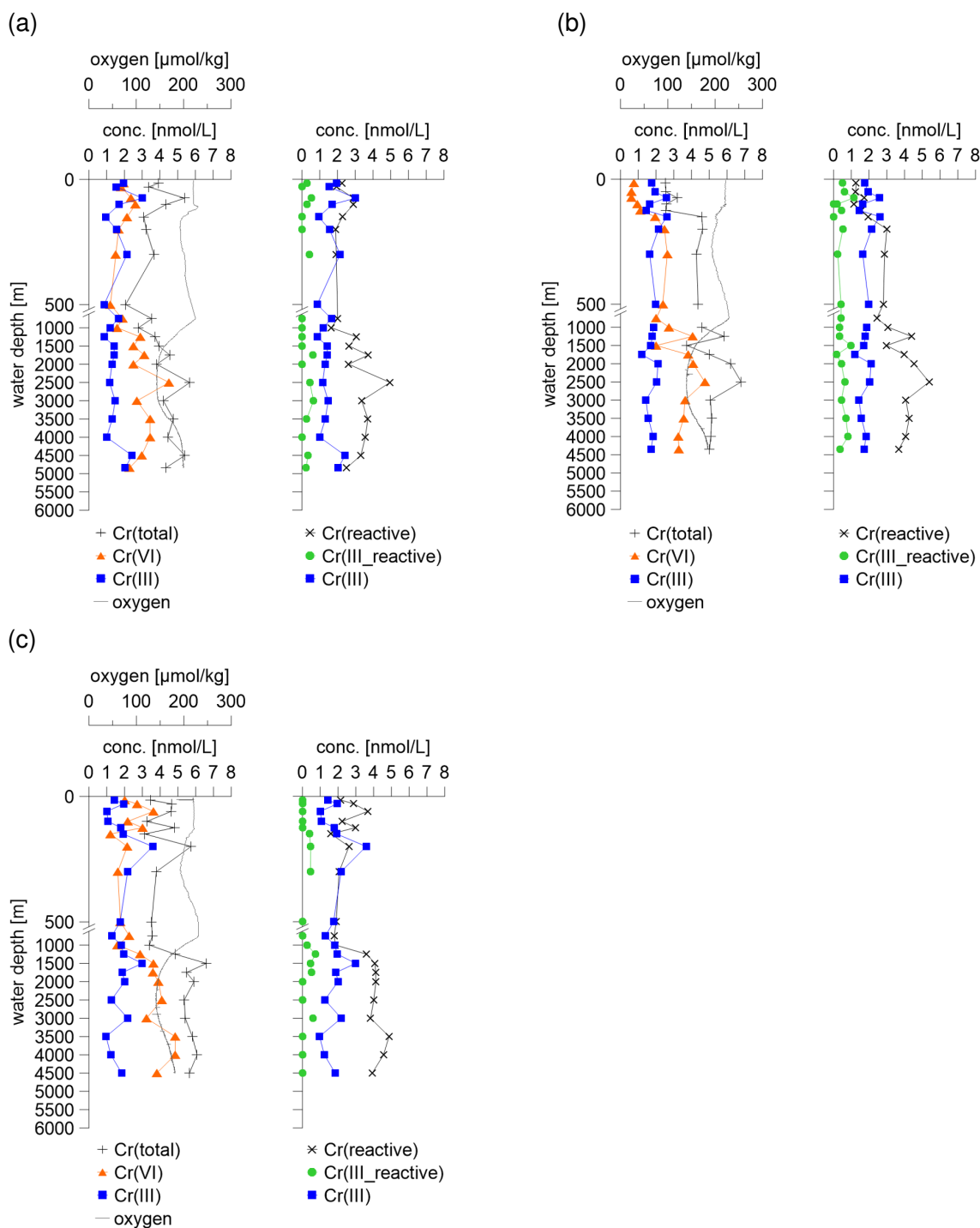


Figure 6.6: Water depth profiles of dissolved Cr(total), Cr(VI), Cr(III), Cr(reactive), and Cr(III_reactive) and dissolved oxygen at stations P1 (a), P2 (b), and P3 (c) sampled during GP13 in the Pacific Ocean along a transect at 32.5°S. Results which were below the LOD are shown as zero values on the depth axis.

6.3.2 Atlantic Ocean profiles

At station A1 (9.50°N, 20.33°W) Cr(total) ranged between 1.40 and 3.75 nmol/L with low concentrations in subsurface and deeper waters (800 - 2000 m). At both open ocean stations located in the West Atlantic the distribution of Cr(total) showed a wider concentration range (A2: 1 - 12 nmol/L, A3: 1 - 5 nmol/L, Figure 6.7).

Cr(III) was the dominant species in the upper 500 m of the water column at all three sampled stations ($83 \pm 20\%$). At depth (2000 - 5500 m) of station A2 Cr(III) and Cr(VI) were present in similar concentrations (approx. 1.2 nmol/L) while Cr(III) dominated the water column at station A3 between 2000 and 4000 m (3.76 ± 1.05 nmol/L).

At station A1 Cr(III_reactive) was observed in significant concentrations in surface and subsurface waters (approx. 0.7 nmol/L). The Cr(III_reactive) concentrations at stations A2 and A3 were very low (0.54 ± 0.62 nmol/L and 0.63 ± 0.27 nmol/L, respectively) and often below the LOD throughout the sampled water column. Cr(reactive) was dominated by Cr(VI) up to 99% at all three stations (Figure 6.7).

To conclude, Cr(total) showed different concentration ranges and water depth profiles at the three Atlantic station and a general trend from surface to deep waters was not observed. Both Cr redox species, Cr(III) and Cr(VI), contributed to different extents to Cr(total) in the three investigated areas in the Atlantic Ocean. In most of the seawater samples Cr(III) was present as Cr(III_unreactive).

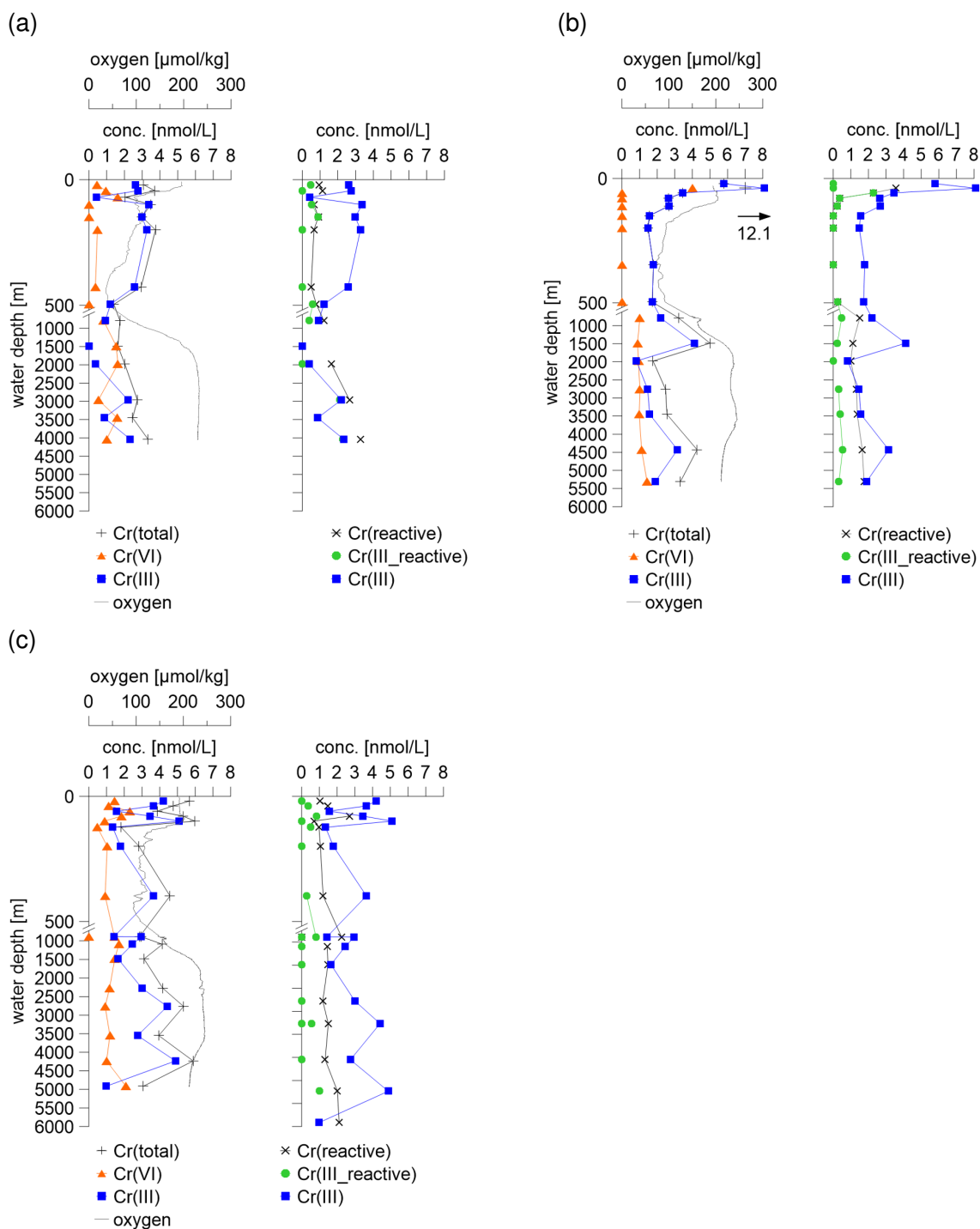


Figure 6.7: Water depth profiles of Cr(total), Cr(VI), Cr(III), Cr(reactive), and Cr(III_reactive) and dissolved oxygen at stations A1 (a), A2 (b), and A3 (c) sampled during M81/1 in the (sub)tropical Atlantic. Results which were below the LOD are shown as zero values on the depth axis. At station A2 the Cr(total) conc. at 39.4 m water depth was 12.1 nmol/L and is indicated with an arrow.

6.4 Discussion

6.4.1 Comparison with published studies for the Pacific and Atlantic Ocean

The distribution of dissolved Cr(total) and its redox species in the Pacific Ocean has been investigated in several studies (Table 6.3). Dissolved Cr(total) concentrations presented in this study, 2.07 - 6.80 nmol/L, agree with published data for the South Pacific (Golimowski et al., 1985; Jeandel & Minster, 1987). Data on Cr(VI) are also in a similar concentration range compared to data for the South Pacific Ocean (Sander et al., 2003a).

Ocean area	Dissolved Cr(total) [nmol/L]	Dissolved Cr(VI) [nmol/L]	Reference
NW Atlantic Ocean	3.2 - 5.2		Campbell & Yeats, 1981
North Atlantic Ocean	2.0 - 4.6		Jeandel & Minster, 1987
North Atlantic Ocean	2.5 - 4.5		Mugo & Orians, 1993
North and South Atlantic Ocean	3.1 - 7.3		Sirinawin et al., 2000
SW Atlantic	5.81 - 6.50		Bonnand et al., 2013
Caribbean Sea		1.5 - 2.5	Sander et al., 2003a
(Sub)tropical Atlantic	1.40 - 12.1	0.13 - 4.21	This work ^a
NE Pacific Ocean		1.6 - 3.5	Cranston & Murray, 1978
NE Pacific Ocean	1.7 - 4.0		Cranston, 1983
East Pacific Ocean		1.2 - 6.0	Murray et al., 1983
East Pacific Rise	1.9 - 15.8		Jeandel & Minster, 1984
South Pacific Ocean	2.4		Golimowski et al., 1985
North and South Pacific Ocean	2.3 - 6.5		Jeandel & Minster, 1987
North Pacific	3.63 - 4.38		Scheiderich et al., 2015
NW Pacific Ocean	2.9 - 4.6	2.1 - 4.2	Isshiki et al., 1989
South Pacific Ocean	6.3 - 19.4	0.7 - 6.8	Sander et al., 2003a
North Pacific Ocean	2.3 - 4.3	2.2 - 4.1	Mugo & Orians, 1993
South Pacific Ocean	6 - 20 (up to 45 ^a)	0 - 6	Sander & Koschinsky, 2000
South Pacific Ocean	2.07 - 6.80	0.80 - 5.62	This work

^a Results refer to unfiltered seawater samples.

Table 6.3: Concentrations of Cr(total) and Cr(VI) in different oceanic regions

Only a few studies have been published on the distribution of Cr and its redox speciation in the Atlantic Ocean and the sampled locations scatter widely in this ocean basin (Table 6.3). Our data for the (sub)tropical Atlantic represent Cr(total) of unfiltered seawater which combines dissolved Cr(total) and acid-leachable Cr of particulate matter. Cr(III) is the particle-reactive redox species and might sorb e.g. onto mineral surfaces or organic matter in the marine environment. Desorption during UV-digestion of the unfiltered sea-

water sample could lead to higher Cr(total) concentrations compared to a filtered aliquot. The voltammetric determination of Cr(VI) includes a 30 min waiting time in which desorption of Cr(VI) from particulate matter might also occur. Data of unfiltered samples (including particulate and colloidal Cr) partly hampers direct comparison with data for filtered samples. The amount of suspended particulate matter (SPM) in surface waters is very low (in the range of $\mu\text{g/L}$) and the Cr content of SPM has been estimated to be at most $1.44 \mu\text{mol/g}$ (Connelly et al., 2006). Therefore, the contribution of particulate Cr to the whole Cr budget in the oceans is negligible. Comparison of Cr(total) in unfiltered and filtered ($0.2 \mu\text{m}$) seawater samples showed that Cr(total) including particulate Cr ranges only slightly higher (up to 10 %) than dissolved Cr(total) (Sander et al., 2003a) which allows to use these data to contrast the Cr species distribution in both oceans.

The concentration range of Cr(total) presented in this study, approx. $1.5 - 6 \text{ nmol/L}$, agrees in general with the concentrations of dissolved Cr(total) observed in the North Atlantic, $2.5 - 4.5 \text{ nmol/kg}$ (Mugo & Orians, 1993), and for the North and South Atlantic, $3.1 - 7.3 \text{ nmol/kg}$ (Sirinawin et al., 2000), except one subsurface sample at station A2 showing 12.1 nmol/L .

Data for Cr(VI) in the Atlantic have only been published for the Caribbean Sea, $1.5 - 2.5 \text{ nmol/L}$ (Sander et al., 2003a), which are slightly higher compared to data in this study. Hydrographical and/or seasonal features might be a viable explanation.

6.4.2 Influence of water masses on the distribution of Cr and its redox species

We observed a slight increase in dissolved Cr(total) concentrations at stations P1 and P2 in the depth range of the PDW. This pattern was, however, not observed at station P3. The analysis of three dissolved Cr(total) depth profiles with respect to its potential for a water mass proxy is, however, not sufficient and more data would be needed for a clear picture.

In the Atlantic Ocean the concentration of Cr(total) in waters below 500 m depth at station A1 was close to a conservative distribution revealing no water-mass dependent concentrations. Mixing of adjacent water masses in the East Atlantic might have altered potential signals. In contrast, both stations located in the West Atlantic, A2 and A3, showed an increase in Cr(total) in the depth range of the NADW (1500 m and 1200 m) and of the AABW (4500 m) and might represent water-mass dependent concentrations.

To conclude, correlations between (dissolved) Cr(total) and water masses in the South Pacific and (sub)tropical Atlantic might exist but more systematic investigation are necessary to prove this idea.

6.4.3 Atmospheric deposition as a parameter influencing Cr and its redox species in seawater

Dissolved Al has been widely applied as a tracer for atmospheric deposition (Dammshäuser et al., 2011; Measures & Vink, 2000; Measures et al., 2008). During the Pacific cruise dissolved Al was not measured but it has been reported that deposition in the area of New Zealand, $0.1 \text{ g}/(\text{m}^2\text{y}^1)$, is significantly lower than for the (sub)tropical Atlantic Ocean, approx. $10 \text{ g}/(\text{m}^2\text{y}^1)$ (Measures & Vink, 2000). Chester (2009) reported that the South Pacific is less affected by dust input compared to the area off West Africa, where the Saharan dust plume carries mineral particles to surface waters.

Hence, sorption onto mineral particles would be less pronounced in the Pacific compared to the Atlantic. However, the dissolved Cr(total) concentrations at the Pacific sites are similar (Table 6.3) to the Cr(total) concentrations in the Atlantic which include also particulate Cr. This might indicate that dust not only provides mineral sorption sites but might also be a source releasing Cr to seawater through dissolution. Both effects might occur, and even level out each other, leading to the similar concentration range of dissolved Cr(total) in the Pacific and Cr(total) in the Atlantic.

A clear dust event was not observed during or shortly before our Atlantic sampling campaign but elevated concentrations of dissolved Al (up to 40 nmol/L) were detected in surface water layers between 12°N and 1°S (Figure 6.8). The observed high Al concentrations might be remnants of former dust events since dissolved Al has a high residence time of up to 3.8 years in Atlantic surface waters (Dammshäuser et al., 2013). Deposited mineral particles provide trace metals including Fe to surface waters, which is known to be a micronutrient for marine bioproductivity (Falkowski et al., 1998; Morel & Price, 2003). The area of dust deposition correlates spatially with the pronounced OMZ and coincides with the highly bioproductive region off West Africa.

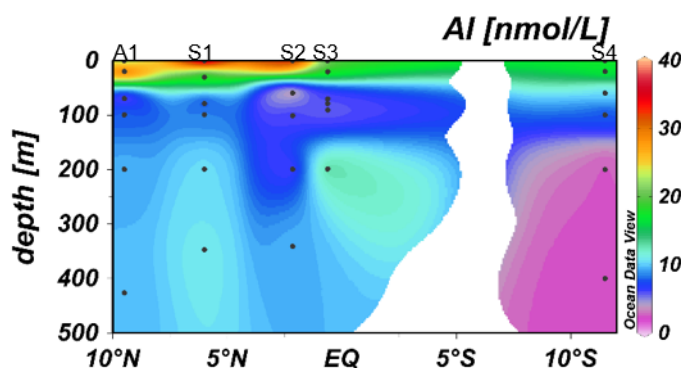


Figure 6.8: Distribution of dissolved Al in surface waters in the Atlantic measured during M81/1 from 10°N to 12°S . This transect includes station A1 and supplementary data from stations S1-S4 while seawater sampled at stations A2 and A3 were not measured for dissolved Al.

Connelly et al. (2006) reported the correlation of Cr(III) presence with high biological

activity. Therefore we would expect a large fraction of Cr(III) in surface waters at station A1. However, the concentration was lower compared to surface waters at station A2 and A3 and sorption onto mineral particles might have scavenged the particle-reactive Cr species, Cr(III). Uptake of Cr(III) into organic matter should also not be neglected at all Atlantic stations. Studies on the photoreduction of Cr(VI) to Cr(III) in the presence of transition metals e.g. Fe, Cu, Mn, marine phytoplankton (Li et al., 2009) and dissolved organic matter (Gaberell et al., 2003) revealed a significant contribution to the Cr(III) fraction in the sunlit water layer. This might also occur to different extents in all investigated surface waters in this study.

The OMZ was also less pronounced at stations A2 and A3 (Figure 6.4c) and dissolved Al was low with approx. 17 nmol/L (Figure 6.8). This could indicate a lower scavenging rate of Cr(III) leading to higher Cr(total) concentrations in surface waters compared to Cr(total) concentrations at station A1.

The concentration of Cr(VI) was in a similar range at all three Atlantic stations, representing a rather constant background.

To conclude, we detect the net effect of several biological and physical processes influencing the concentration of (dissolved) Cr(total) and its redox species but cannot unambiguously distinguish them.

6.4.4 Abundance of trivalent Cr in oxic waters and the OMZ

The depth profile of dissolved O₂ was similar at all three Pacific stations (Figure 6.3c) representing the similar physicochemical environment in this oligotrophic region.

In the oxic surface waters Cr(III) was abundant in significant concentrations (Figure 6.6a-left, b-left and c-left) while inorganic thermodynamic calculations predict Cr(VI) to be the more stable form.

Photoreduction of Cr(VI) to Cr(III) has been reported to be induced either by dissolved organic matter (Sanders & Riedel, 1987), phytoplankton (Li et al., 2009) or inorganic substances e.g. transition metals (Abu-Saba et al., 2000; Buerge & Hug, 1997; Kieber & Helz, 1992) in surface waters. To a certain extent, Cr(III) might result from these photochemical processes and subsequent complexation of the particle-reactive Cr(III) with organic ligands might stabilize Cr(III) in oxic surface waters as described by Hirata et al. (2000).

Two oxygen minima have been observed in all three Pacific profiles; one between 200 - 1000 m (approx. 200 $\mu\text{mol/kg O}_2$) and another between 1000 - 3500 m (approx. 150 $\mu\text{mol/kg O}_2$) (Figure 6.6a-left, b-left and c-left). In the OMZs Cr(III) was abundant at 1.92 ± 0.70 nmol/L which is very similar to the concentration observed for Cr(VI) in the OMZ (1.91 ± 0.44 nmol/L). The formation of stable Cr(III) complexes with organic substances might be a reasonable explanation (Hirata et al., 2000). Small colloids ($< 0.2 \mu\text{m}$) e.g. nanoparticulate Cr(III)OH*, may have contributed to the Cr(III) fraction. A study

on Cr(III) emanated from hydrothermally active sites hypothesized stabilization of Cr(III) through complexation by organic ligands contributing to the dissolved fraction of Cr(III) (Sander & Koschinsky, 2000).

In deep oxic waters Cr(III) was also observed in significant concentrations. Direct release of Cr(III) from sinking organic matter (Achterberg & Van Den Berg, 1997) and organic complexation as discussed for oxic surface waters might be reasonable mechanisms.

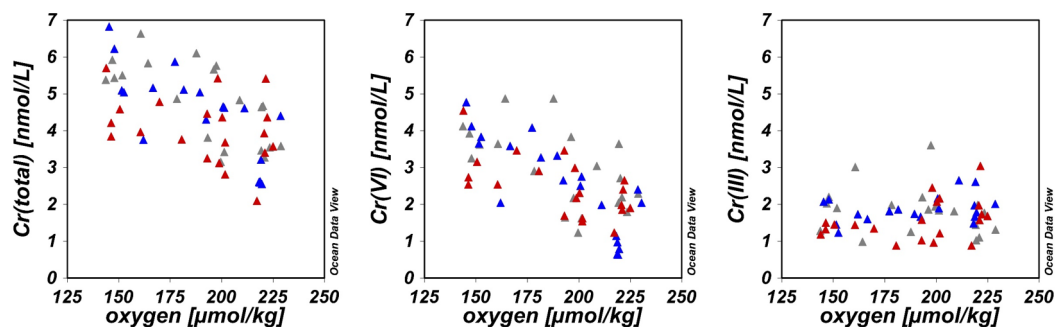


Figure 6.9: Scatter plots of Cr(total) (a), Cr(VI) (b), and Cr(reactive) (c) vs. dissolved oxygen for stations P1 (▲), P2 (▲), and P3 (▲) sampled during GP13.

Throughout the water column Cr(III) displayed a constant background (Figure 6.9c). The slow oxidation of Cr(III) to Cr(VI) and the fast reduction of Cr(VI) to Cr(III) (Schroeder & Lee, 1975) might lead to an accumulation of Cr(III). Since we observed neither a significant increase, nor decrease of Cr(III) concentrations at the Pacific stations, stabilization through organic complexation but also sorption onto particulate surfaces might lead to the observed constant concentration of Cr(III) independent from the oxygen concentration.

In the Atlantic Ocean, Cr(III) was found to be the dominant Cr redox species in oxic shallow and deep waters (approx. 200 $\mu\text{mol/kg}$ dissolved O_2) (Figure 6.7a-left, b-left and c-left) and we assume similar mechanisms as discussed for the Pacific stations (photoreduction of Cr(VI) and stabilization by organic complexation) to be responsible. Station A1 in the East Atlantic is characterized by a pronounced OMZ (50 $\mu\text{mol/kg}$ dissolved O_2) between 300 and 750 m water depth and Cr(III) was the dominant species of Cr(total) with up to 97 % in this water layer. Although the concentration of dissolved O_2 in the OMZs at stations A2 and A3 in the West Atlantic, 200 and 500 m water depth, was higher (approx. 100 $\mu\text{mol/kg}$), Cr(III) was still the dominant species. Since like for the Pacific samples most Cr(III) is Cr(III_unreactive) stabilization of Cr(III) through complexation with organic ligands may again be a reasonable explanation. The oxygen concentrations in the range of 50 - 250 $\mu\text{mol/kg}$ do not exert a significant control on the Cr redox speciation (Figure 6.10).

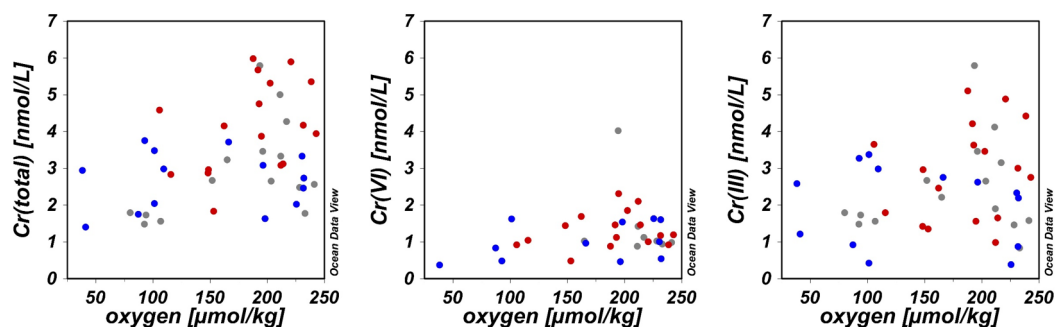


Figure 6.10: Scatter plots of Cr(total) (a), Cr(VI) (b), and Cr(reactive) (c) vs. dissolved oxygen for stations A1 (●), A2 (●), and A3 (●) sampled during M81/1. One data point for A2 (194.5 $\mu\text{mol/kg}$ oxygen, 39.4 m water depth) is excluded serving a better comparison of Pacific and Atlantic scatter plots.

The observed different trends of Cr vs. oxygen at the Pacific and Atlantic sites reflect regional effects e.g. sources and sinks for Cr and the oxygen conditions do not play a major role on the Cr speciation.

6.4.5 Influence of nutrient cycles on the depth distribution of Cr

No correlation between the distribution of (dissolved) Cr(total) and nutrients (nitrate, phosphate, and silicate) was observed at both the Pacific and Atlantic sites (Figures 6.11 and 6.12), which agrees with a previous study on Cr (Sirinawin et al., 2000).

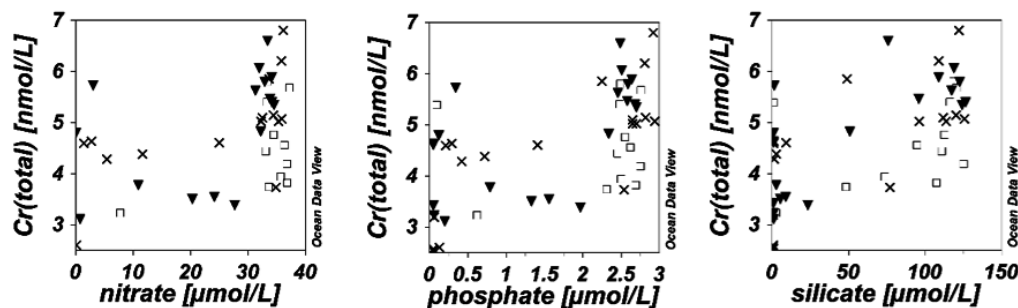


Figure 6.11: Scatter plots of dissolved Cr(total) vs. dissolved nitrate (a), phosphate (b), and silicate (c) for stations P1 (□), P2 (x), and P3 (▼) sampled during GP13.

Connelly et al. (2006) reported only a minimal interaction of Cr with biological uptake and recycling processes based on insignificant ($p < 0.05$) correlation between Cr and nutrients. Apparently, the biogeochemical cycle of Cr is not significantly influenced by the cycling of biological matter.

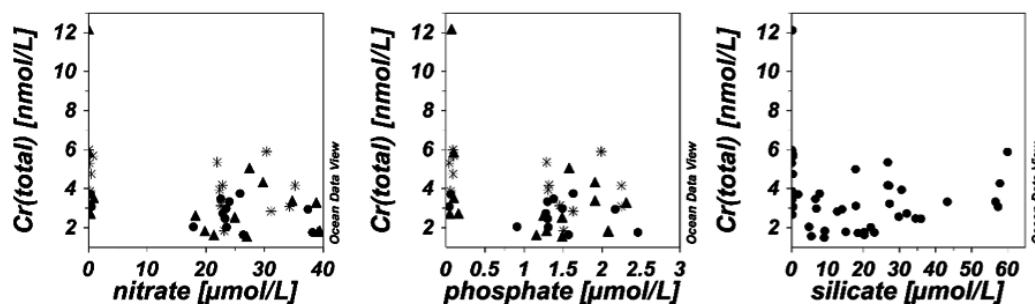


Figure 6.12: Scatter plots of Cr(total) vs. dissolved nitrate (a), phosphate (b), and silicate (c) for stations A1 (●), A2 (▼), and A3 (*) sampled during M81/1.

6.5 Conclusion

This study provides results on (dissolved) Cr(total) and its two main redox species Cr(VI) and Cr(III) in filtered Pacific and unfiltered Atlantic seawater samples which can serve future studies on Cr isotopes since redox reactions affect the fractionation of Cr isotopes.

Our data on dissolved Cr(total) for the South Pacific agree with published data for the North and South Pacific and regional features e.g. input through hydrothermalism was not observed.

Chromium(VI) was the predominant species in the oxic water column of all three Pacific sites reflecting the depth profile of Cr(total). Significant Cr(III) concentrations in oxic surface waters might be due to photoreduction processes and subsequent stabilization by organic ligands. Cr(III) consisted almost quantitatively of Cr(III_unreactive) which corroborates our assumption of organic complexation, since organic complexes are usually less reactive with respect to redox reactions, sorption etc. Throughout the water column Cr(III) was present at approx. 1.8 nmol/L independent of the oxygen concentrations. Different kinetics of Cr(III) oxidation and Cr(VI) reduction reactions might result in an accumulation of Cr(III) which might be balanced by scavenging processes leading to the observed constant background concentration of Cr(III) in the Pacific.

Cr(total) results of unfiltered Atlantic seawater may include a fraction of particulate and colloidal Cr. Our data agree with previous studies on dissolved Cr(total) in the Atlantic. A consistent trend in the fractionation of Cr(total) into Cr(VI) and Cr(III) was not observed for the three Atlantic stations indicating that regional features play an important role affecting the Cr distribution.

Dust deposition off West Africa (station A1) was detected by elevated Al concentrations which might also play a role after long-range transport for the West Atlantic (stations A2 and A3). Cr(total) concentrations were lower at station A1 compared to stations A2 and A3 indicating a more pronounced sorption onto deposited mineral particles off West Africa compared to the West Atlantic sites. Also lower concentrations of Cr(III) have been observed at station A1 compared to stations A2 and A3 located in the West

Atlantic confirming potential sorption processes since Cr(III) is particle-reactive. Significant concentrations of Cr(III) in oxic shallow and deep waters might be due to similar mechanism as discussed for the Pacific sites (photoreduction and organic complexation). Cr(III_unreactive) was the dominant part of Cr(III) as shown for the Pacific sites which seems to be global feature. Our data imply that the redox conditions in the Atlantic water column do not affect the Cr speciation to a significant degree.

At both investigated areas, South Pacific and (sub)tropical Atlantic, no correlation with nutrients or water masses was observed. However, a more systematic approach including more sampling sites as well as a direct comparison of filtered und unfiltered aliquots would be preferable to assess a more detailed picture on the different parameters influencing the distribution of Cr and its redox species in marine waters. However, from our data we can already conclude that redox transitions for Cr do not occur in the oxic water column in oxygen concentration ranges of about 50 - 250 $\mu\text{mol/kg}$, with the implication that also not redox-initiated fractionation of Cr isotopes should take place under these conditions.

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7 Conclusion and Outlook

7.1 Brief summary and conclusion of this PhD-thesis

Within this PhD-thesis dissolved (trace) metals (Zr, V, Nb, Cr, Mo, W) have been studied in seawater considering different aspects. The developed online-preconcentration method and analysis of Ti, Zr, Nb, V, Mo and W as well as its application to Atlantic seawater samples is presented. Some of these metals are well studied in the Pacific (Zr, Nb, Mo, W) whereas data for the Atlantic Ocean are scarce (Mo, W) or were not yet published (Nb). This thesis thoroughly examines the distribution of the above mentioned six metals along an Atlantic transect with respect to regional features. Moreover, Cr and its main redox species have been investigated in Pacific and Atlantic seawater collected in different oxygen regimes.

The progress in analytical techniques for trace metal analysis is a fast process, which allows the release of large data sets in short time periods. This study provides an online-preconcentration method with subsequent ICP-MS determination of six metals (Ti, Zr, Nb, V, Mo and W) in only one hour (chapter 3). The applied SeaFAST-device works as a closed system and performs preconcentration and matrix separation simultaneously, providing an important advantage compared to off-line preconcentration methods. Furthermore, time-consuming and cost-intensive sample treatment in the laboratory is avoided which decreases the risk of contamination significantly. This fact is of particular relevance for the analysis of Ti in seawater: since wall paint often contains Ti species this metal is ubiquitously abundant in a laboratory environment and may significantly affect the determination of Ti in seawater, in which its concentration is only in the range of pmol/L. An acidified NaCl matrix matching the average seawater salinity was used for calibration standards. Indium served as an internal standard to monitor correct filling of the sample loop and elution of the preconcentrated sample from the preconcentration column. The low standard deviation of the presented method enabled the detection of dissolved Ti, Zr, Nb, W in North Sea water (in the range of pmol/kg, except for Ti which is present in the range of nmol/kg in North Sea water) and of small variations in concentration of Mo and V which are present in seawater in the range of nmol/kg. For the determination of the six metals in seawater only 50 ml sample volume are needed which is low compared to the large volumes of up to 1 L required for many published methods. Hence, the application of the herein presented method allows the collection of more individual samples since sample logistics are less extensive. Distinct water layers e.g. surface water layers,

OMZ or near-bottom waters, can be investigated in more detail enabling the small-scale assessment of factors controlling the trace metal distribution.

This work thoroughly investigated the distribution of dissolved Zr and Nb in the Tropical Atlantic along a transect from the Canary Islands to the Caribbean in 194 seawater samples from 16 stations and revealed regional features controlling the distribution patterns (chapter 4). Particles originating from the volcanic rocks of the Canary Islands provided Nb to surface waters, whereas deposited mineral particles from the Saharan desert scavenged Zr and Nb. These local sources and sinks might influence the global marine distribution of both metals since their concentrations in seawater are very low (pmol/kg).

The concentration of Zr and Nb increased in deep waters which was more pronounced for Zr compared to Nb. A linear relationship between Zr and Si occurred for most stations indicating a coupling between Zr and the Si cycle through e.g. sorption or incorporation processes. In deep waters released Zr might be complexed by organic ligands e.g. siderophores, which have been shown to mobilize Fe(III) as well as Zr and Nb from particulate matter. Sequential filtration of deep seawater samples revealed that Zr might be stabilized by metal-ligand complexes smaller than 0.015 μm . Depth profiles reported in this work agree with published water depth profiles for Zr in the Pacific Ocean. This highlights that stabilization with organic ligands is a globally occurring feature controlling the distribution of Zr in the world ocean. Findings of this work might be of relevance for studies on Zr and Nb in other oceanic basins.

Zirconium and Nb are used in various electronic devices and the demand of both metals increased constantly in the current high technological era. In the ocean, they contribute to the formation of valuable ore deposits, e.g. ferromanganese nodules and crusts, on the seafloor. In search for new resources, the interest in exploitation of these metals rises globally. Investigation of the surrounding deep-sea ecosystem is one aim within the Joint Programming Initiative of Healthy and Productive Seas and Oceans (JPI Oceans) and first studies have recently been published (Purser et al., 2016; Vanreusel et al., 2016). Sediment removal, sediment plume dispersion and re-deposition accompanying deep-sea mining activities will also affect the distribution of trace metals e.g. Zr and Nb in deep water layers, which implies the necessity to understand their behaviour in non-disturbed environments.

Dissolved Mo and W have often been reported to show conservative distributions with depth. Data in this study elucidated scavenging processes on dust particles derived from e.g. the Saharan desert for Mo and W leading to deviations from the conservative patterns (chapter 5). The concentrations of Mo and W in this Atlantic study are lower compared to data published for the Pacific Ocean. Since dust input is more pronounced in the Atlantic compared to the Pacific deposited particles might be a sink for both metals in dust affected oceanic regions. The opposite pattern was observed for V, as Saha-

ran dust provided V to surface waters. Comparison of data obtained in this work with Pacific data revealed higher V concentrations in the Atlantic, which agrees with the previous assumption of dust being a crucial parameter for the distribution of V, Mo, and W in surface seawater. Moreover, this work revealed that Amazon freshwater provides V, Mo, and W to the Atlantic, through e.g. higher riverine concentration (W) or desorption and/or release from particulate matter (V, Mo). The Amazon has the highest freshwater discharge worldwide and its impact on the global distribution of these metals should not be neglected.

The variations in concentration with depth were significant for the analytical method but rather small compared to the average concentrations of V, Mo and W in Atlantic seawater and will probably only have a small impact on the global budget of the three metals in oceanic waters. This study, however, might be relevant for the interpretation of local features of these elements in other oceanic basins or specific regions.

This work strengthened our knowledge on the distribution of Cr and its two main redox species, Cr(VI) and Cr(III), in seawater (chapter 6). In Pacific waters Cr(VI) dominated Cr(total) and displayed a similar depth profile while Cr(III) showed a conservative distribution independent from the oxygen condition of the marine environment. Photoreduction and subsequent complexation by organic ligands might stabilize Cr(III) in surface waters. Based on different reaction rates, slow oxidation of Cr(III) and fast reduction of Cr(VI), Cr(III) might accumulate in seawater. In the Atlantic Ocean three oceanographically different settings have been investigated and a consistent trend in the Cr speciation was not observed revealing the importance of regional factors. Off West Africa, an area influenced by dust deposition, lower Cr(total) concentrations were observed compared to stations located in the open ocean and in the West Atlantic. The particle-reactive Cr(III) also reflected this trend confirming that deposited mineral particles served as sorption sites. Cr(III) was abundant in oxic shallow and deep waters and similar mechanisms as discussed for the Pacific samples are assumed to be reasonable explanations. In Pacific and Atlantic waters Cr(III_unreactive) dominated Cr(III) almost quantitatively, which reveals that organic complexation is a globally occurring feature.

The distribution of the Cr redox species and other redox-sensitive metals, e.g. Mo, will be influenced by changes of the ocean temperature and the concentration of dissolved oxygen in seawater pointing out that global warming is an important factor. January 2017 was the globally third-warmest January within the past 137 years of modern temperature recording, which is only one parameter to assess climate change. According to the International Panel on Climate Change (IPCC 2014) human activities have caused warming of the planet Earth within the past 50 years to a probability of 95 %. This affects also surface temperatures of the oceans leading to a lower solubility of oxygen in seawater with increasing water temperature. Schmidtko et al. (2017) reported that the concent of dissolved oxygen in the global ocean decreased by more than 2 % in the past 50 years. The

loss of dissolved oxygen is most pronounced in the North and equatorial Pacific contributing with up to 39.9% to the total oxygen decrease. The expanding of oxygen minimum zones have been observed in the eastern tropical Atlantic and equatorial Pacific in water depth of 300 to 700 m (Stramma et al., 2008). Global warming is one significant parameter controlling oxygen concentration in seawater but natural processes on a basin-scale may also contribute. The observed variations in oxygen concentration, however, and the expanding of sub- and anoxic regions in the global ocean have a significant impact on the distribution of redox-sensitive metals and their redox speciation. The behaviour of redox species in marine waters needs to be investigated thoroughly in order to serve studies on Cr isotopes, which have recently been identified as a promising proxy to trace climate change.

7.2 Outlook

Within this study the applied preconcentration resin may retain also other metals than those investigated. Of particular interest would be the analysis of Hf and Ta, since they form chemical twin pairs with Zr and Nb, Zr/Hf and Nb/Ta, respectively. Both pairs have been used as proxies for past redox conditions of seawater. The analysis of Ta and Hf in seawater is challenging, since their concentrations are very low (sub-pmol/kg). During this thesis project first attempts on their preconcentration and analysis applying the SeaFAST system showed that the preconcentration resin retained both metals but not yet quantitatively under the tested conditions presented herein. The pH of the column, the elution acid and the size of the sample loop are only some parameters which can be optimized aiming at the preconcentration and analysis of dissolved Hf and Ta in seawater. The determination of the chemical twin pair Zr/Hf in seawater applying the SeaFAST would facilitate future studies on trace metal sources to the oceans and on water mass circulation.

The online-preconcentration method and ICP-MS analysis has been developed for Ti among other trace metals but a contamination problem regarding Ti occurred prior to the application to the seawater samples collected during research cruise M81/1. The contamination source could be eliminated, and the method could be applied to the M81/1 samples, which have been preserved by acidification and are therefore still available for Ti analysis. Comparison of the Ti distribution patterns with depth profiles obtained for Zr and Nb might reveal whether similar mechanisms control their geochemical behaviour since all three metals belong to the same physico-chemical group of the HFSE.

A highly resolved data set on the dissolved phase of metals in seawater has been provided in this study. In order to assess sources and sinks for the dissolved phase, research focusing on atmospheric input or sedimentation related processes e.g. sedimentation rate, fraction of trace metals in sediments, resuspension of sediment, would be of high

interest. For this purpose, the methods developed within this work could also be applied to other matrices, e.g. river water or pore water, provided that the colloidal fraction is negligible, as colloids and/or nanoparticles may block the preconcentration column. Especially samples from the Amazon and its estuary would be interesting to investigate; as this could help to understand the impact of riverine discharge onto the dissolved concentrations of the elements of interest in the (sub)tropical Atlantic. Moreover, the analysis of filtered (applying different pore sizes for fractionation e.g. $0.2\ \mu\text{m}$ and $0.015\ \mu\text{m}$) and unfiltered samples from marine and riverine waters would improve our knowledge onto the fractionation into the truly dissolved, colloidal and particulate phase. This could help to assess the role of each fraction for the transport in the water column (contribution of organic ligands for stabilization) or for the formation of ore deposits.

Redox-sensitive metals such as V, Cr and Mo need to be investigated in more detail since redox reactions affect the isotopic composition of these metals. Recently, Cr has been of high interest since Cr isotope measurements in marine carbonates have been used to trace weathering of the continental crust (Frei et al., 2011) and for reconstruction of past redox conditions in the ocean and on land (Frei et al., 2009). Moreover, Cr isotopes have been applied as a tracer for atmospheric oxygenation (Crowe et al., 2013). Environmental redox conditions e.g. seawater anoxia can be traced by Mo isotopes (Pearce et al., 2009). Chemical mechanisms for Mo sequestration into sediments is reflected by the Mo isotopic signature determined in sediments (Poulson et al., 2006). A summary of various applications of Mo isotopes in the (bio)geochemical sector is provided in Kendall et al. (2017). Hence, the evaluation of isotopic data will benefit from the profound knowledge on the redox species distribution. Filtered (e.g. $0.015\ \mu\text{m}$, $0.2\ \mu\text{m}$) and unfiltered aliquots would be an option to investigate the role of organic complexation and to assess the fractionation into the truly dissolved, colloidal and particulate phases, such as partly carried out in this study for Zr and Nb. Combined with other important parameters such as rain rate and aerosol analysis, a better picture of the redox speciation might be achieved serving future studies on the isotopic distribution of redox-sensitive metals.

Besides the Amazon, the Congo river provides large amounts of freshwater to the Atlantic and its role for the distribution of the elements of interest in this study in the South Atlantic is not fully investigated yet. Recently, the research cruise M121 (RV Meteor, Nov. - Dec. 2015) covered an area off Namibia and Angola within the GEOTRACES program. Different geological and oceanographical factors have been considered for the planning of the sampling sites e.g. upwelling areas, input of dust originating from the desert Namib, and riverine discharge of the river Congo. The analysis of samples collected during this cruise regarding the distribution of (trace) metals will help to assess the impact of the above mentioned regional parameters. Additionally, water column profiles from the upwelling system offshore Namibia with sub- and anoxic waters will reveal the impact of low-oxygen conditions on the concentration and behaviour of trace elements

that are redox-sensitive by themselves or are controlled e.g. by the release or binding on/from Mn or Fe oxide particles or colloids. Since similar regional impacts (Saharan dust deposition, Amazon freshwater discharge) have been investigated in this PhD-work, comparison with data obtained herein will enable to evaluate whether these regional factors have a significant impact on the concentration and distribution patterns of Zr, Nb, V, Mo, and W in the Atlantic.

8 Related scientific work

8.1 Stay abroad

8.1.1 Swedish Museum of Natural History - Stockholm, Sweden

From October until November 2011, I stayed for 6 weeks in the working group of Prof. Dr. Per Andersson in the Laboratory for Isotope Geology (LIG), Swedish Museum of Natural History, Stockholm. His research focuses on isotope analyses such as silicon in seawater and rare earth elements (REE) in the Arctic Ocean.

The natural concentration of REE in seawater is low and preconcentration needed prior to the analytical determination. A solid phase extraction method to preconcentrate neodymium (Nd) and samarium (Sm), which belong to the group of REE, and the subsequent isotope dilution - thermal ionization mass spectrometry (ID - TIMS) is routinely used (Persson et al., 2011) in the laboratory of the working group. Using the experience of this working group I intended to apply and adjust this preconcentration method to Zr and Hf as proxys for the HFSE, which are of high interest in this PhD-work. The preconcentration procedure included (1) loading the metals onto the resin, (2) wash and remove the matrix, and (3) elution of Zr and Hf. Several fractions have been collected at different steps of this procedure and were analyzed in our home laboratory using ICP - MS. The results showed that both metals were not eluted quantitatively which is required if ID - techniques are not available. The pH conditions during the loading process and the use of different elution acids are only some of many parameters which need to be investigated aiming at a quantitative recovery.

Working in a clean laboratory environment, cleaning labware dedicated for trace metal analysis, and the application of new analytical techniques have been important goals from which I benefited a lot to develop the online-preconcentration method presented herein. This research stay was partly funded by COST Action ES0801 'The ocean chemistry of bioactive trace metals and paleoclimate proxies' supporting such Short Term Scientific Missions (STSM) embedded into the international GEOTRACES project.

8.1.2 Universidade Federal de Santa Maria - Santa Maria, Brazil

September 2012

Within the DAAD (German Academic Exchange Service) funded program PRO-BRAL, which supports the research exchange between German and Brazilian scientist,

I stayed for three weeks in Brazil. My stay at the Department of Chemistry at the Universidade Federal de Santa Maria (UFSM) in the working group of Prof. Dr. Leandro Machado de Carvalho lasted one week. Electrochemical methods are routinely used in the LACHEM laboratory at the UFSM to determine organic compounds in plant tissues, to trace pharmaceutical residues, but also to analyze trace metals in different sample matrices, e.g. plant tissue and seawater. Since parts of my PhD-study focus on the distribution of Cr redox species in seawater this stay was a perfect opportunity to gain profound knowledge on voltammetric determinations. A voltammetric device of the same type we use in the laboratory at Jacobs University was used to analyze seawater samples. Preparation of chemical solutions, sample storage and treatment as well as evaluation of the generated data have also been discussed.

In collaboration with our Brazilian partners at the UFSM, we organized a sampling campaign and collected river water from tributaries of the Amazon (River Tocantins, River Para) and samples from the Amazon estuary. The samples were dedicated for the analysis of trace metals, e.g. HFSE and REE, within the framework of B.Sc. theses at Jacobs University Bremen. Results obtained from these samples will help to assess the influence of river water discharge on the distribution of trace metals in seawater.

During my stay I also participated in the Geoanalysis conference (oral presentation) in Buzios, Brazil.

October 2013

In October 2013, I had again the opportunity to stay for one week in the working group of Prof. Dr. Leandro Machado de Carvalho, Department of Chemistry at the Universidade Federal de Santa Maria, Santa Maria, within the DAAD funded program PROBRAL. We practiced the determination of dissolved Ti, Zr, V, and Mo in seawater samples using the same voltammetric device as during my previous stay. It is still debated whether not only truly dissolved but also colloiddally bound metals can be detected by voltammetry. Comparison of the results obtained by the voltammetric analysis with the results obtained from the herein presented online-preconcentration method (Poehle et al., 2015) might enable insights in the fractionation of trace metals between the colloidal and dissolved phase. The aim had been to establish the voltammetric method in our laboratory at Jacobs University. An application of the voltammetric method to river water and seawater has been published recently (Schneider et al., 2016).

Again, we organized a sampling campaign and collected river water from the main tributaries of the Amazon (Rio Negro and Rio Solimões) in the second week of my research stay. These samples have been analyzed for HFSE and REE within the framework of B.Sc theses at Jacobs University.

8.2 Conferences and workshops

8.2.1 Conferences

Poehle, S., Koschinsky A. (2015): Non-conservative distribution of dissolved W and Mo in the Atlantic Ocean. Association for the Sciences of Limnology and Oceanography (ASLO), Granada, Spain. **Talk.**

Koschinsky, A., **Poehle, S.** (2015): Distribution of dissolved Zr and Nb in the oceanic water column under consideration of the colloidal phase. Association for the Sciences of Limnology and Oceanography (ASLO), Granada, Spain. **Talk.**

Poehle, S., Koschinsky, A., Schmidt, K. (2014): Distribution of Zr, Nb, V, Mo and W in the water column of the Atlantic. Ocean Sciences Meeting (OSM), Honolulu, USA. **Talk.**

Poehle, S., Koschinsky, A., Moos, S., and Sander, S. (2013): Chromium speciation in the oceanic water column. ASLO, New Orleans, USA. **Talk.**

Poehle, S., Koschinsky, A., and Schmidt, K. (2012): Determination of Zr, Hf, Nb and Ta in seawater by the use of an online-preconcentrations system connected to inductively coupled mass - spectrometry (ICP - MS). Geoanalysis, Brazil. **Talk.**

Moos, S.B., **Poehle, S.**, Koschinsky, A. (2011): Redox speciation of chromium in the water column of the Tropical Atlantic Ocean. 43rd International Liège Colloquium on Ocean Dynamics. Liège, Belgium. **Talk.**

8.2.2 Workshops

'Voltammetry and GEOTRACES' - COST Action workshop held in Šibenik, Croatia

This workshop was held in Šibenik, Croatia, from October 6th - 9th, 2012. Applications of voltammetric analyses in the past, present, and future research were of interest, and new sensors have been presented. The development of standard operating procedures for data treatment and speciation calculation have been discussed.

I presented first results about the Cr redox species in the (sub)tropical Atlantic orally entitled 'Chromium speciation in the oceanic water column' (co-supervised B.Sc. work, Simone Beatrice Moos). Important input for further analysis and data evaluation was gained during this workshop.

8.3 Co-supervised B.Sc. project

Simone Beatrice Moos (2011): Redox speciation of chromium in the water column of the Tropical Atlantic Ocean. Jacobs University Bremen.

8.4 Co-Authorship of research publications

Schneider, A. B., Koschinsky, A., Kiprotich J., **Poehle, S.**, Nascimento P. C. (2016): An experimental study on the mixing behavior of the transition metals Ti, Zr, V and Mo in the Elbe, Rhine and Weser estuaries, Estuarine, Coastal and Shelf Science, 170, 34-44.

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Michael showed me new and different perspectives related to my project which were very interesting but to fruitfully follow and implement them in detail in my work I would have needed much more time, and unfortunately time is always a critical factor during a PhD-thesis.

Most of the samples I worked with were collected during a research cruise of which Martin Frank was the chief scientist. Although at this time, I was working for the Institute for Baltic Sea Research, Warnemünde, and represented a one-women-working group I easily felt home on board, which was also due to Martins warm and welcoming attitude. He also enabled a first introduction to the SeaFAST-system at the GEOMAR.

During my stay in the lab of Per S. Anderson I learned so many details and little things which have to be kept in mind while working with trace metal-clean sampled seawater and which helped me a lot for the work done in this thesis.

My co-author Sylvia Sander was a great help in improving my scientific writing skills which pushed the manuscript on chromium forward.

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Appendix

A Chapter 4 Depth profiles of Zr and Nb: Role of organic complexation

A1. Supplementary Data Table 1: Sampling sites of cruise M81/1, sampled water depths, and all measured concentrations of dissolved Zr and Nb.

Station	Latitude (°)	Longitude (°)	Depth (m)	Zr (pmol/kg)	Nb (pmol/kg)
2	29.00	-15.34	19.1	98.8	2.82
			39.8	79.7	3.30
			67.4	98.3	3.26
			96.8	74.9	2.99
			147.7	88.0	2.71
			179.6	93.4	2.68
			347.1	113	2.87
			496.2	112	2.70
			693.2	140	2.95
			999.6	143	2.65
			1976.9	181	3.37
			3448.0	206	3.50
4	28.07	-16.06	19.1	74.2	3.98
			39.7	109	3.82
			69.6	103	3.88
			96.3	84.8	3.85
			148.5	74.4	4.66
			195.0	72.4	3.33
			295.4	79.3	2.86
			395.9	99.3	3.19
			493.5	106	3.14
			693.5	168	3.62
			889.2	158	2.90
5	27.20	-17.00	1483.6	284	8.49
			18.7	118	3.24

APPENDIX

Station	Latitude (°)	Longitude (°)	Depth (m)	Zr (pmol/kg)	Nb (pmol/kg)
6	25.30	-17.52	39.1	122	3.80
			68.4	127	3.22
			100.2	115	3.11
			144.4	154	2.79
			197.4	90.1	2.98
			347.7	156	2.86
			496.1	129	4.17
			694.1	156	2.45
			891.2	173	2.74
			1483.3	195	3.40
			2468.5	219	2.73
			28.2	114	3.94
			36.9	93.0	3.28
			69.9	140	4.12
			98.5	79.3	3.98
			148.5	79.1	3.42
			199.5	89.6	3.20
			347.3	107	3.21
			495.2	119	2.89
			692.3	243	3.49
7	24.00	-23.00	891.5	144	3.56
			1485.0	166	3.59
			2470.3	175	3.70
			39	88.8	2.82
			68.9	62.2	3.03
			100.3	137	2.76
			198.5	99.6	2.76
			350.6	135	3.21
			494.8	98.3	2.73
			745.8	164	3.15
			1485.4	173	2.94
			2471.0	218	3.61
9	19.42	-20.42	3448.5	240	3.25
			4423.8	211	2.70
			37.8	224	2.93
			69.1	99.7	2.43
			100.1	324	2.58
			148.6	130	2.31

Station	Latitude (°)	Longitude (°)	Depth (m)	Zr (pmol/kg)	Nb (pmol/kg)
10	12.98	-20.98	199.2	103	2.19
			348.6	88.7	2.45
			497.5	107	2.55
			744.6	208	2.14
			992.1	124	2.25
			1486.6	325	3.23
			1978.4	275	2.72
			2471.5	160	2.85
			39.9	43.7	1.93
			70.0	57.0	1.04
			99.5	50.9	0.90
			199.9	60.3	1.45
			297.6	78.2	1.36
			447.4	93.3	1.94
			892.0	130	2.11
			1091.1	174	1.80
			1487.3	143	3.56
			2472.5	155	2.11
			3451.6	152	1.82
			4426.6	160	1.50
12	9.50	-20.50	44.0	71.3	2.77
			69.9	82.2	2.40
			99.6	62.2	2.81
			148.1	61.1	2.43
			199.6	66.7	2.30
			426.5	91.9	2.78
			496.1	100	3.28
			793.4	133	3.50
			1485.7	360	3.31
			2470.9	156	3.27
			3452.2	194	2.69
			4037.2	153	2.78
13	6.00	-20.00	60.1	47.6	1.74
			79.4	79.4	2.16
			99.4	51.3	1.65
			149.9	58.6	2.16
			199.4	67.7	2.11
			346.9	83.8	2.35

APPENDIX

Station	Latitude (°)	Longitude (°)	Depth (m)	Zr (pmol/kg)	Nb (pmol/kg)
14	2.15	-20.15	497.7	95.2	2.30
			744.9	232	2.65
			992.0	124	2.19
			1485.5	145	2.63
			1980.3	148	2.36
			2619.1	169	2.41
			39.4	35.5	2.74
			59.6	26.2	2.90
			101.1	50.8	2.73
			148.8	29.5	2.49
			199.8	49.2	1.93
			341.3	60.9	2.27
			496.4	74.6	2.42
			795.3	117	2.30
			1091.2	141	2.81
			1488.1	129	2.83
15 + 16	-0.62	-20.62	2963.2	151	2.98
			4429.6	139	2.80
			40.2	29.4	2.46
			70.5	35.2	2.49
			90.9	37.4	2.10
			147.6	77.2	2.35
			198.9	51.5	2.57
			328.0	84.8	2.84
			506.0	100	2.57
			695.8	103	2.56
			1089.0	141	2.63
			1487.1	150	3.34
			2177.8	179	3.09
			4428.2	215	3.08
			5692.2	196	3.30
			39.4	8.59	2.09
18	-6.65	-25.65	58.0	53.9	2.42
			110.4	59.2	1.80
			149.9	91.6	1.88
			198.7	41.1	2.09
			147.7	61.2	2.55
			496.5	90.5	2.38

Station	Latitude (°)	Longitude (°)	Depth (m)	Zr (pmol/kg)	Nb (pmol/kg)
19	-11.50	-28.50	793.9	112	2.58
			1485.3	117	2.90
			1978.6	205	2.84
			3452.0	359	2.58
			5303.7	187	3.06
			40.2	42.9	3.09
			58.8	45.3	3.71
			98.5	34.9	3.12
			150.3	49.8	3.09
			199.4	54.6	2.51
			297.3	54.0	2.48
			396.6	72.4	2.81
			793.4	114	2.62
			1090.8	148	2.75
			1487.0	180	3.31
			2766.6	168	3.46
			4814.7	240	3.40
			38.4	44.0	3.05
			59.3		2.90
20	-7.17	-31.17	99.1	23.4	2.62
			123.8	6.6	2.45
			199.2	43.1	2.68
			398.0	49.9	2.42
			886.7	77.3	2.51
			889.4	81.4	2.72
			1092.0	112	2.83
			1486.3	102	3.07
			2766.8	135	2.95
			4915.4	207	4.14
			20.7	36.5	2.24
			40.7	44.7	2.43
			60.5	48.1	2.25
21	0.60	-39.91	79.4	25.8	2.21
			100.5		9.61
			149.7	58.5	3.29
			199.1	43.8	1.71
			398.6	73.9	1.95
			497.1	86.9	2.02

APPENDIX

Station	Latitude (°)	Longitude (°)	Depth (m)	Zr (pmol/kg)	Nb (pmol/kg)
22	7.77	-48.77	695.0	94.6	2.07
			991.6	120	3.91
			1486.7	148	2.75
			18.0	68.1	2.69
			38.1	77.0	2.23
			69.9	230	2.42
			98.8	58.4	2.70
			148.9	280	4.61
			199.2	99.7	3.30
			299.0	127	2.71
			496.3	114	3.27
			742.2	163	2.97
			1191.0	140	2.90
			1683.4	155	3.14
			2750.5	198	3.13
			3453.6	161	2.97

See Figures 4.6, 4.7, 4.9, 4.11, 4.12, 4.13, 4.15.

A2. Supplementary Data Table 2: Sampling sites of the normal CTD deployed at the same locations as the trace metal-clean CTD; water depth and dissolved nitrate, phosphate and silicate derived from samples collected with the normal CTD¹

Station	Latitude (°)	Longitude (°)	Depth (m)	Nitrate ($\mu\text{mol/L}$)	Phosphate ($\mu\text{mol/L}$)	Silicate ($\mu\text{mol/L}$)
2	29.00	-15.34	148.6	1.7	0.1	1.1
			198.2	2.7	0.2	1.2
			347.7	7.3	0.4	3.0
			496.9	15.2	0.7	6.0
			743.9	22.3	1.3	11.7
			892.5	23.8	1.4	13.7
			1976.8	21.5	1.4	22.6
			3447.1	17.7	1.3	29.7
4	28.07	-16.06	19.0	0.15	0.02	0.19
			38.8	0.07	0.02	0.16
			68.7	0.02	0	0.08
			98.3	0	0	0
			146.9	1.77	0.07	0.52
			197.5	3.67	0.18	1.11
			296.6	8.35	0.38	2.68
			395.2	8.93	0.59	3.32
			494.6	15.90	0.89	6.08
			755.2	12.58	1.08	7.02
5	27.20	-17.00	891.3	24.03	1.40	15.18
			19.5	0.33	0.04	0
			39.5	0.25	0.04	0
			69.0	0.45	0.04	0.08
			99.2	2.39	0.11	0.60
			148.1	4.26	0.24	1.29
			197.6	6.58	0.37	1.99
			348.8	12.07	0.67	4.12
			495.3	17.89	1.02	7.20
			735.2	24.61	1.60	13.19
			890.5	28.97	1.84	17.77
			1487.1	23.50	1.52	19.76

¹Storage of the seawater samples till the analysis of nutrients have influenced the total concentrations of nitrate, phosphate and silicate shifting them to values compared to previously published data for the Tropical Atlantic (http://www.egeotraces.org/sections/GA03_e_NITRAT.html). The general distribution with depth have not been affected.

APPENDIX

Station	Latitude (°)	Longitude (°)	Depth (m)	Nitrate ($\mu\text{mol/L}$)	Phosphate ($\mu\text{mol/L}$)	Silicate ($\mu\text{mol/L}$)
6	25.30	-17.52	2470.8	22.46	1.50	28.75
			19.8	0.21	0.08	0
			40.7	0.08	0.03	0.01
			58.5	0	0.01	0.14
			100.4	0.09	0.02	0.15
			148.7	3.71	0.25	1.01
			198.5	6.48	0.47	1.75
			348.9	6.65	0.45	1.95
			493.6	12.22	0.86	4.45
			743.5	31.92	1.94	16.35
			889.1	27.61	1.76	15.59
			1485.4	21.43	1.41	16.43
			2469.2	18.28	1.33	20.17
7	24.00	-23.00	39.2	0	0	0.17
			68.4	0.88	0.05	0.14
			100.1	1.96	0.12	0.36
			196.3	4.94	0.23	1.13
			347.5	13.86	0.68	4.26
			496.2	13.21	0.86	4.94
			632.4	24.92	1.12	11.73
			1486.3	12.86	1.00	10.50
			2467.5	15.82	1.16	18.43
9	19.42	-20.42	4424.8	21.53	1.49	38.03
			40.9	0.11	0.11	0.10
			69.4	0.28	0.11	0.14
			99.3	11.38	0.69	2.72
			146.0	16.24	0.93	4.32
			196.5	24.31	1.39	6.79
			328.4	24.71	1.54	7.72
			494.6	22.84	1.55	8.87
			745.0	25.73	1.91	13.60
			993.3	34.15	2.19	21.50
			1485.4	20.27	1.51	15.62
			1977.2	17.18	1.29	17.09
10	12.98	-20.98	2468.6	23.12	1.53	27.87
			39.6	0.09	0.11	1.13
			55.3	15.06	0.91	3.87
			99.6	23.71	1.45	6.38

Station	Latitude (°)	Longitude (°)	Depth (m)	Nitrate ($\mu\text{mol/L}$)	Phosphate ($\mu\text{mol/L}$)	Silicate ($\mu\text{mol/L}$)
12	9.50	-20.50	198.0	27.64	1.70	8.77
			298.3	31.65	1.90	10.26
			436.6	38.14	2.27	13.95
			695.0	36.22	2.14	19.50
			990.3	34.79	2.14	21.62
			1386.7	27.81	1.60	20.99
			2469.3	22.61	1.31	28.34
			3447.2	18.41	1.07	28.93
			4426.4	24.36	1.29	44.55
			44.2	0.31	0.06	1.81
			69.4	17.88	0.91	4.82
			99.7	22.53	1.38	6.62
			146.8	23.47	1.49	6.85
			199.3	25.82	1.63	7.75
			427.9	37.39	2.17	14.05
			794.6	38.20	2.46	22.98
			1487.5	26.38	1.57	20.19
			2470.5	21.63	1.22	28.18
			3450.4	23.28	1.30	35.90
13	6.00	-20.00	4037.0	23.98	1.30	43.29
			59.3	11.55	0.54	3.34
			98.0	20.82	1.22	5.33
			147.3	21.58	1.26	6.69
			200.0	26.87	1.60	8.26
			346.8	36.45	2.10	13.58
			495.8	39.37	2.33	17.70
			744.7	40.17	2.14	23.82
			1089.5	35.02	2.13	24.75
			1486.1	26.24	1.62	19.61
14	2.15	-20.15	1978.5	23.39	1.47	22.16
			2272.4	23.41	1.48	24.44
			39.2	0	0.02	0
			60.1	6.28	0.41	1.83
			99.6	18.71	1.18	4.95
			148.1	19.47	1.22	5.85
			197.0	22.99	1.44	6.99
			342.0	32.27	1.98	13.51
			497.3	35.04	2.14	16.67

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Station	Latitude (°)	Longitude (°)	Depth (m)	Nitrate (μmol/L)	Phosphate (μmol/L)	Silicate (μmol/L)
15 + 16	-0.62	-20.62	792.3	38.53	2.43	26.80
			1091.4	31.36	1.98	25.46
			1484.8	25.11	1.52	18.45
			2690.9	23.16	1.45	33.12
			4425.8	24.43	1.51	44.28
			39.5	0	0.07	0
			69.0	0.64	0.17	0.45
			88.6	7.93	0.63	2.15
			148.1	15.00	0.95	4.96
			198.9	19.90	1.30	5.71
			327.5	25.48	1.60	8.91
			694.2	36.06	2.40	25.08
			1090.2	32.58	2.13	25.30
			2175.6	20.71	1.20	20.00
			4425.9	20.38	1.34	34.53
18	-6.65	-25.65	5692.2	19.30	1.58	23.63
			40.6	0	0.07	0.21
			60.4	0.88	0.10	0.20
			100.9	0.32	0.16	0.16
			148.1	21.37	1.16	5.50
			199.7	27.02	1.49	9.01
			368.2	39.43	2.08	15.05
			496.9	39.14	2.08	18.44
			794.5	38.86	2.31	27.26
			1486.2	27.44	1.58	17.74
			1978.2	19.84	1.29	20.23
			3548.4	18.23	1.25	29.80
			5301.4	43.77	1.91	56.67
			40.7	0.57	0.06	0.08
			59.0	0.50	0.07	0.13
19	-11.50	-28.50	99.8	0.43	0.10	0.05
			139.5	1.19	0.23	0.45
			396.1	12.25	0.88	3.34
			398.7	30.45	1.83	14.83
			769.3	34.03	2.32	28.22
			1485.9	28.38	1.66	19.38
			2567.5	25.13	1.36	26.97
			4814.8	35.12	2.12	66.32

Station	Latitude (°)	Longitude (°)	Depth (m)	Nitrate ($\mu\text{mol/L}$)	Phosphate ($\mu\text{mol/L}$)	Silicate ($\mu\text{mol/L}$)
20	-7.17	-31.17	39.1	0.46	0.09	0.33
			59.6	0.26	0.06	0.10
			99.9	0.05	0.09	0.07
			100.2	0.29	0.15	0.37
			112.8	23.15	1.51	9.20
			297.1	35.77	1.81	16.56
			1141.6	35.23	2.25	27.08
			1485.3	22.61	1.46	17.84
			2763.5	21.92	1.29	26.73
			4911.8	34.31	2.25	57.36
22	7.77	-48.77	19.5	0.99	0.04	0.44
			40.4	0.64	0.01	0.41
			99.3	10.74	0.51	2.91
			148.3	20.97	1.26	7.17
			198.0	25.67	1.34	10.18
			396.9	32.44	1.68	14.43
			744.6	35.25	2.29	23.85
			1190.3	32.15	1.66	23.07
			1683.7	22.63	1.11	14.07
			2568.7	18.92	1.05	21.54

See Figures 4.3, 4.9, 4.11, 4.15.

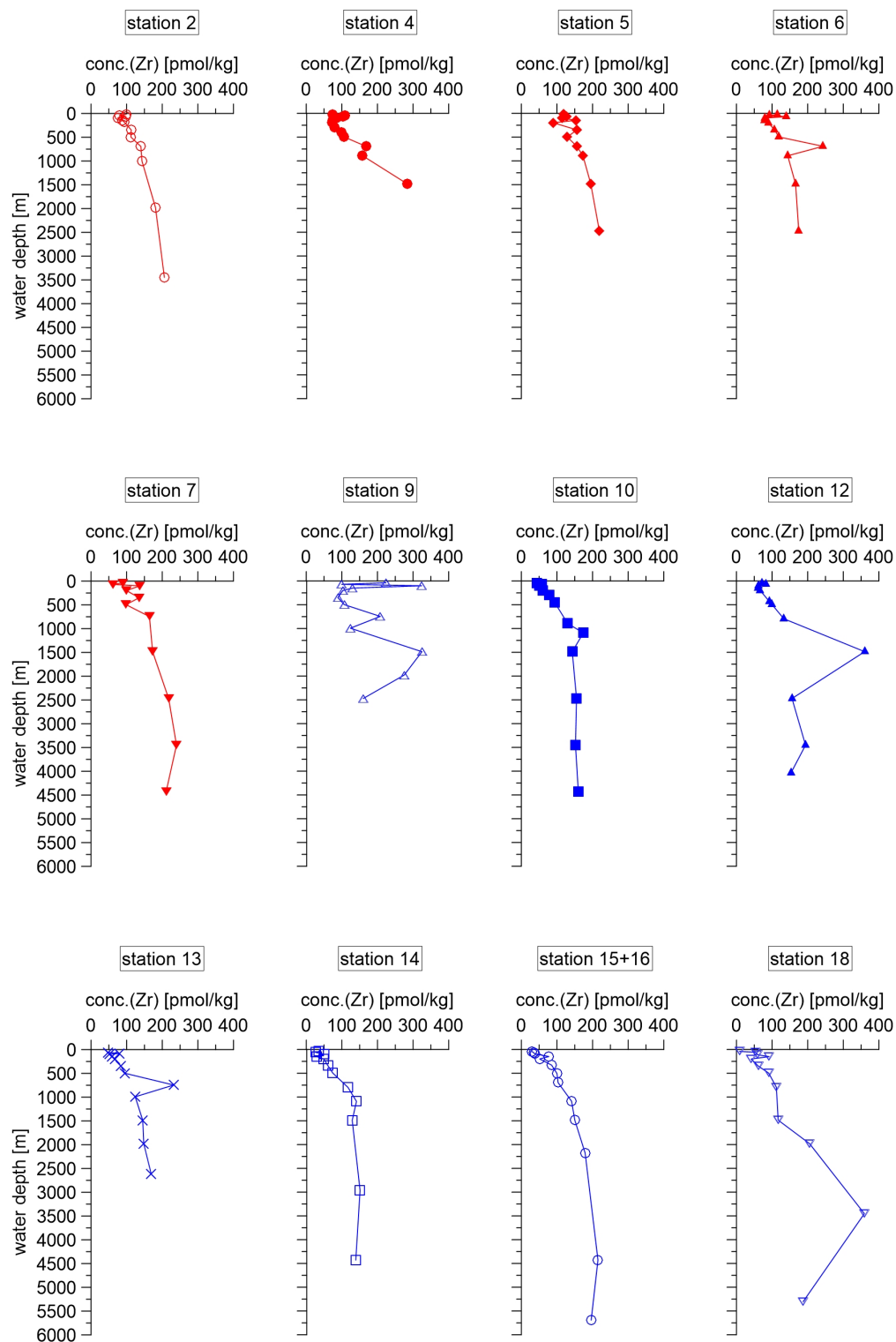
A3. Supplementary Data Table 3: Concentrations of dissolved Al in selected samples of the depth profiles

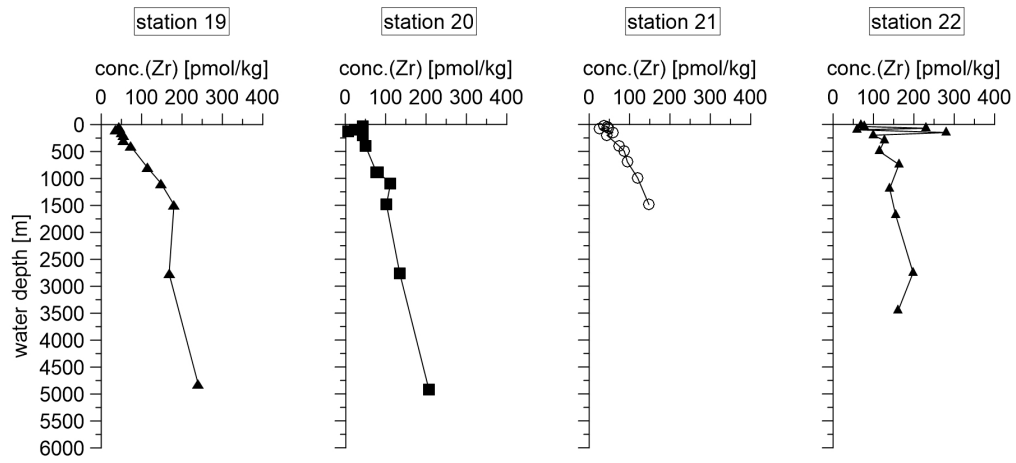
Station	Latitude (°)	Longitude (°)	Depth (m)	Al (nmol/L)
2	29.00	-15.34	4.9	13.2
			19.1	11.3
			39.8	13.8
			67.4	12.3
			96.8	12.1
			147.7	15.6
			179.6	15.3
			347.1	16.8
			496.2	22.2
			693.2	18.6
			999.6	20.2
			1482.2	24.7
			1976.9	22.8
			3448.0	26.5
6	25.30	-17.52	28.2	18.3
			36.9	15.0
			69.9	13.8
			98.5	13.2
			148.5	11.2
			199.5	11.7
7	24.00	-23.00	39.0	10.3
			100.3	26.7
			198.5	17.8
			990.0	18.6
			2471.0	16.8
9	19.42	-20.42	0	1.4
			20.0	4.2
			69.1	2.5
			100.1	3.6
			199.2	11.0
			328.3	8.7
10	12.98	-20.98	18.7	22.0
			70.0	5.0
			99.5	6.2

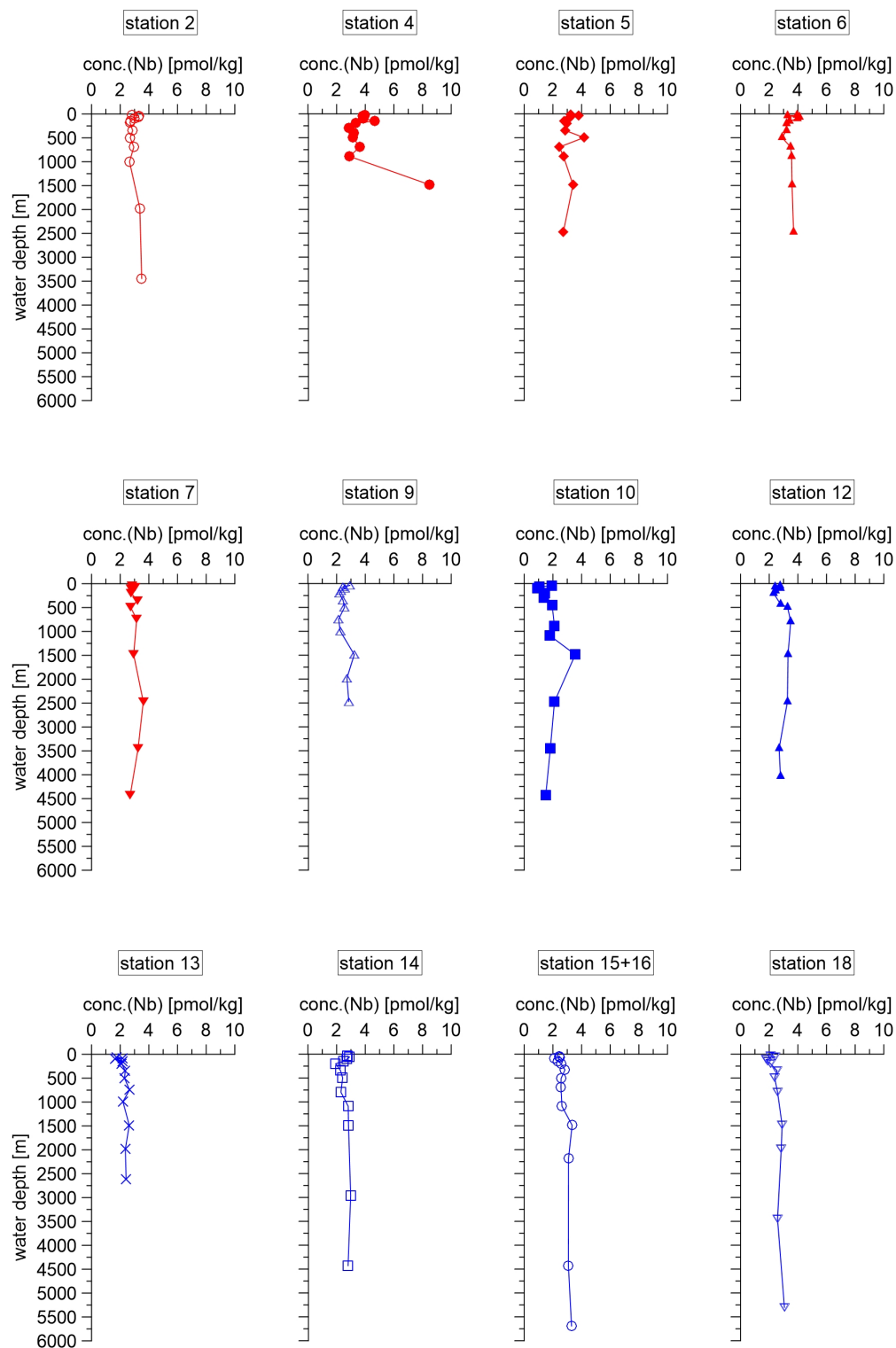
Station	Latitude (°)	Longitude (°)	Depth (m)	Al (nmol/L)
12	9.50	-20.50	199.9	10.8
			297.6	12.7
			4426.6	15.5
			0	22.1
			20.2	30.3
			69.9	4.7
			99.6	8.2
			199.6	9.3
			426.5	9.7
13	6.00	-20.00	0	36.4
			30.3	17.3
			79.4	7.0
			99.4	8.8
			199.4	10.4
			346.9	10.7
14	2.15	-20.15	0	40.0
			59.6	1.9
			101.1	6.3
			199.8	5.0
			341.3	9.4
			4429.6	15.7
15 + 16	-0.62	-20.62	0	15.9
			20.4	16.9
			70.5	6.3
			78.8	5.6
			90.9	5.2
			198.9	14.2

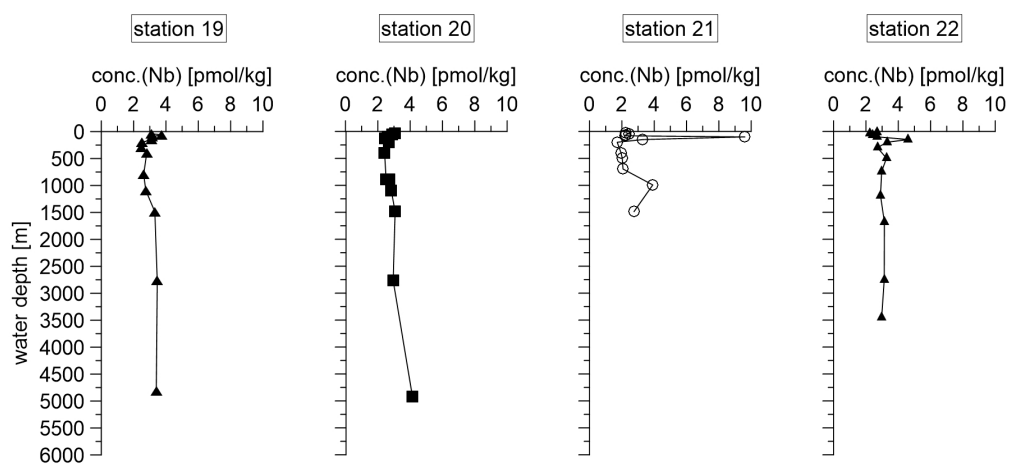
See Figure 4.10.

A4. Depth profiles of dissolved Zr measured in all seawater samples collected during research cruise M81/1, 16 stations.





A5. Depth profiles of dissolved Nb measured in all seawater samples collected during research cruise M81/1, 16 stations.



B Chapter 5 Distribution of dissolved V, Mo and W in the Atlantic

B1. Supplementary Data Table 1: Sampling sites of cruise M81-1, sampled water depths, and all measured concentrations of dissolved V, Mo and W

Station	Latitude (°)	Longitude (°)	Depth (m)	V (nmol/kg)	Mo (nmol/kg)	W (pmol/kg)
2	29.00	-15.34	19.1	43.1	93.8	51.0
			39.8	41.9	91.0	48.8
			67.4	41.3	90.7	47.7
			96.8	37.5	90.3	48.6
			147.7	41.4	89.1	45.1
			179.6	40.0	86.8	43.9
			347.1	41.0	93.3	46.3
			496.2	40.4	92.0	44.7
			693.2	38.6	89.6	45.5
			999.6	39.7	92.6	45.3
			1976.9	33.5	94.2	43.8
			3448.0	39.1	96.0	41.2
4	28.07	-16.06	19.1	50.4	99.1	48.6
			39.7	44.0	105.1	49.7
			69.6	42.1	105.1	50.0
			96.3	51.2	106.2	48.1
			148.5	53.2	105.2	52.0
			195.0	52.7	104.8	49.5
			295.4	53.6	105.4	49.8
			395.9	45.1	106.1	48.5
			493.5	53.4	105.7	49.0
			693.5	51.5	102.0	50.1
5	27.20	-17.00	18.7	45.0	97.0	51.9
			39.1	46.3	99.3	52.5
			68.4	45.0	91.8	50.9
			100.2	46.9	97.8	49.9
			144.4	35.3	94.7	51.3
			197.4	47.3	95.1	48.3
			347.7	45.0	95.6	50.8
			496.1	46.4	94.5	52.2

Station	Latitude (°)	Longitude (°)	Depth (m)	V (nmol/kg)	Mo (nmol/kg)	W (pmol/kg)
6	25.30	-17.52	694.1	45.5	92.1	50.6
			891.2	45.9	95.1	49.7
			1483.3	36.7	93.3	49.3
			2468.5	44.6	90.8	46.1
			28.2	47.6	93.2	50.1
			36.9	48.2	91.9	49.6
			69.9	37.7	94.2	53.6
			98.5	48.4	92.1	50.0
			148.5	47.3	91.9	50.6
			199.5	42.4	92.1	49.0
			347.3	40.5	88.6	48.6
			495.2	39.6	91.8	51.5
			692.3	49.4	90.0	50.6
			891.5	49.8	88.3	50.5
			1485.0	46.9	88.6	48.8
7	24.00	-23.00	2470.3	48.2	88.7	49.6
			39	42.5	105.5	44.8
			68.9	55.9	86.9	45.9
			100.3	58.0	100.0	48.3
			198.5	60.7	102.8	43.0
			350.6	41.2	100.7	45.4
			494.8	57.3	96.5	45.4
			745.8	42.0	105.7	43.7
			1485.4	43.4	107.8	45.3
			2471.0	47.6	103.3	42.4
9	19.42	-20.42	3448.5	44.5	106.8	43.8
			4423.8	56.4	103.8	42.2
			37.8	49.3	92.5	37.9
			69.1	47.5	91.5	40.1
			100.1	48.4	87.6	39.1
			148.6	49.1	89.9	40.1
			199.2	46.0	87.9	39.0
			348.6	46.5	89.2	41.2
			497.5	45.9	92.3	41.1
			744.6	48.9	89.4	37.7
			992.1	47.1	90.2	39.6
			1486.6	38.4	92.4	38.3
			1978.4	49.9	91.8	40.3

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Station	Latitude (°)	Longitude (°)	Depth (m)	V (nmol/kg)	Mo (nmol/kg)	W (pmol/kg)
10	12.98	-20.98	2471.5	50.5	92.2	40.1
			39.9	39.8	90.4	39.3
			70.0	45.5	89.2	30.9
			99.5	42.7	91.0	30.1
			199.9	44.0	88.1	30.4
			297.6	44.1	90.7	30.0
			447.4	41.3	90.0	30.3
			892.0	40.3	88.7	27.2
			1091.1	40.3	89.6	30.7
			1487.3	41.5	90.5	28.8
			2472.5	40.3	85.6	28.8
			3451.6	42.3	92.8	28.0
			4426.6	41.8	87.4	25.8
12	9.50	-20.50	44.0	54.9	96.9	50.0
			69.9	54.9	94.2	49.2
			99.6	52.6	96.4	46.6
			148.1	54.9	95.4	45.1
			199.6	55.3	93.9	46.1
			426.5	51.7	94.8	41.6
			496.1	55.3	95.2	41.9
			793.4	50.7	91.0	39.3
			1485.7	50.9	92.5	40.4
			2470.9	49.3	89.6	40.7
			3452.2	51.4	85.4	41.2
			4037.2	49.8	87.9	37.9
13	6.00	-20.00	60.1	44.9	94.0	42.4
			79.4	39.0	95.2	42.4
			99.4	44.5	96.0	41.7
			149.9	46.6	100.3	45.1
			199.4	45.2	96.3	44.0
			346.9	47.7	98.1	42.7
			497.7	46.0	94.9	40.3
			744.9	40.9	95.6	37.6
			992.0	48.1	99.9	41.5
			1485.5	45.7	98.4	40.2
			1980.3	48.3	102.1	40.5
			2619.1	48.4	103.8	44.1
14	2.15	-20.15	39.4	59.4	89.9	41.8

Station	Latitude (°)	Longitude (°)	Depth (m)	V (nmol/kg)	Mo (nmol/kg)	W (pmol/kg)
15 + 16	-0.62	-20.62	59.6	47.2	90.9	39.6
			101.1	47.9	88.0	40.2
			148.8	53.2	94.0	38.4
			199.8	49.3	95.7	39.9
			341.3	54.1	100.5	37.0
			496.4	49.0	96.6	39.5
			795.3	60.3	96.4	38.6
			1091.2	47.2	98.6	39.2
			1488.1	61.9	94.0	40.6
			2963.2	47.0	95.5	37.7
			4429.6	54.0	97.6	37.7
			40.2	41.1	102.5	45.3
			70.5	43.1	103.1	48.0
			90.9	42.2	99.4	46.8
			147.6	44.9	101.2	44.7
			198.9	44.5	99.0	44.7
			328.0	43.7	99.6	46.3
			506.0	43.4	97.1	44.0
			695.8	45.0	99.1	44.0
			1089.0	43.6	99.6	43.2
18	-6.65	-25.65	1487.1	44.3	101.4	44.5
			2177.8	39.2	98.1	43.1
			4428.2	43.3	96.9	41.3
			5692.2	43.1	103.8	43.1
			39.4	48.6	96.8	43.0
			58.0	50.5	99.0	37.1
			110.4	46.3	95.6	38.8
			149.9	51.5	94.2	38.9
			198.7	49.8	95.9	36.9
			147.7	47.5	95.5	35.5
			496.5	45.9	92.3	37.0
			793.9	46.7	94.4	36.5
19	-11.50	-28.50	1485.3	45.5	89.5	37.3
			1978.6	43.4	84.7	38.1
			3452.0	53.0	91.0	36.8
			5303.7	51.6	88.6	36.0
			40.2	59.6	97.5	48.2
			58.8	46.0	97.9	46.2

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Station	Latitude (°)	Longitude (°)	Depth (m)	V (nmol/kg)	Mo (nmol/kg)	W (pmol/kg)
20	-7.17	-31.17	98.5	51.9	97.5	47.3
			150.3	41.4	100.8	44.4
			199.4	42.9	99.2	43.1
			297.3	49.6	102.0	40.1
			396.6	52.0	100.5	42.4
			793.4	46.9	102.6	43.2
			1090.8	58.5	102.8	39.3
			1487.0	40.8	103.1	44.9
			2766.6	46.4	102.9	36.4
			4814.7	44.9	102.6	35.7
			38.4	51.2	100.9	43.7
			59.3	51.3	103.2	44.9
			99.1	52.1	101.7	40.3
			123.8	51.4	101.2	41.7
			199.2	50.9	99.1	40.8
			398.0	49.4	97.3	36.7
			886.7	49.2	96.6	36.3
			889.4	48.9	96.4	36.7
			1092.0	49.3	96.3	34.0
			1486.3	47.5	97.1	35.6
21	0.60	-39.91	2766.8	46.8	96.2	33.7
			4915.4	48.3	95.6	34.0
			20.7	38.6	81.8	42.9
			40.7	38.2	83.6	37.4
			60.5	39.6	96.0	39.5
			79.4	40.0	92.3	45.7
			100.5	42.4	97.3	46.0
			149.7	41.5	94.9	41.3
			199.1	41.6	93.5	42.2
			398.6	42.3	91.2	43.5
22	7.77	-48.77	497.1	42.3	95.5	45.6
			695.0	42.9	93.7	44.5
			991.6	43.5	100.4	46.1
			1486.7	44.1	100.2	43.0
			18.0	39.0	94.3	45.3
			38.1	49.8	98.0	50.5
			69.9	46.1	100.9	52.9
			98.8	49.6	102.6	51.9

Station	Latitude (°)	Longitude (°)	Depth (m)	V (nmol/kg)	Mo (nmol/kg)	W (pmol/kg)
			148.9	38.1	100.9	50.7
			199.2	39.0	101.9	
			299.0	38.5	97.1	51.2
			496.3	39.5	101.5	53.8
			742.2	38.8	97.6	49.9
			1191.0	40.7	100.2	57.8
			1683.4	52.2	96.4	53.7
			2750.5	36.9	88.0	52.0
			3453.6	52.6	97.7	57.1

See Figures 5.6, 5.7, 5.13, 5.14.

B2. Supplementary Data Table 2: Sampling sites of the trace metal - clean CTD deployed at the same locations as the conventional CTD; water depth and relative changes of nitrate, phosphate and silicate concentrations (values represent concentration at specific depth divided by concentration in the surface sample) derived from samples collected with the normal CTD²

Station	Latitude (°)	Longitude (°)	Depth (m)	Rel. nitrate	Rel. phosphate	Rel. silicate
2	29.00	-15.34	19.0	1.00	1.00	1.00
			38.8	0.47	1.00	0.84
			68.7	0.13	0.00	0.42
			98.3	0.00	0.00	0.00
			146.9	11.80	3.50	2.74
			197.5	24.47	9.00	5.84
			296.6	55.67	19.00	14.11
			395.2	59.53	29.90	17.47
			494.6	106.00	44.50	32.00
			755.2	83.87	54.00	36.95
			891.3	160.20	70.00	79.89
5	27.20	-17.00	19.5	1.00	1.00	
			39.5	0.76	0.50	
			69.0	1.36	1.00	1.00
			99.2	7.24	2.75	7.50
			148.1	12.91	6.00	16.13
			197.6	19.94	9.25	24.88
			348.8	36.58	16.75	51.50
			495.3	54.21	25.50	90.00
			735.2	74.58	40.00	164.88
			890.5	87.79	46.00	222.13
			1487.1	71.21	38.00	247.00
6	25.30	-17.52	2470.8	68.06	37.50	359.38
			19.8	1.00	1.00	
			40.7	0.38	0.38	1.00
			58.5	0.00	0.13	14.00
			100.4	0.43	0.25	15.00

²Storage of the seawater samples till the analysis of nutrients have influenced the total concentrations of nitrate, phosphate and silicate shifting them to values compared to previously published data for the Tropical Atlantic (http://www.egeotracers.org/sections/GA03_e_NITRAT.html). The general distribution with depth have not been affected and we will therefore use the relative changes of nutrients with depths in this study.

Station	Latitude (°)	Longitude (°)	Depth (m)	Rel. nitrate	Rel. phosphate	Rel. silicate
7	24.00	-23.00	148.7	17.67	3.13	101.00
			198.5	30.86	5.88	175.00
			348.9	31.67	5.63	195.00
			493.6	58.19	10.75	445.00
			743.5	152.00	24.25	1635.00
			889.1	131.48	22.00	1559.00
			1485.4	102.05	17.63	1643.00
			2469.2	87.05	16.63	2017.00
			39.2			1.00
			68.4	1.00	1.00	0.82
			100.1	2.23	2.40	2.12
			196.3	5.61	4.60	6.65
			347.5	15.55	13.60	25.06
			496.2	15.01	17.20	29.06
			632.4	28.32	22.40	69.00
			1486.3	14.61	20.00	61.76
			2467.5	17.98	23.20	108.41
			4424.8	24.47	29.80	223.71
9	19.42	-20.42	40.9	1.00	1.00	1.00
			69.4	2.55	1.00	1.40
			99.3	103.45	6.27	27.20
			146.0	147.64	8.45	43.20
			196.5	221.00	12.64	67.90
			328.4	224.64	14.00	77.20
			494.6	207.64	14.09	88.70
			745.0	233.91	17.36	136.00
			993.3	310.45	19.91	215.00
			1485.4	184.27	13.73	156.20
			1977.2	156.18	11.73	170.90
10	12.98	-20.98	2468.6	210.18	13.91	278.70
			39.6	1.00	1.00	1.00
			55.3	167.33	8.27	3.42
			99.6	263.44	13.18	5.65
			198.0	307.11	15.45	7.76
			298.3	351.67	17.27	9.08
			436.6	423.78	20.64	12.35
			695.0	402.44	19.45	17.26
			990.3	386.56	19.45	19.13

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Station	Latitude (°)	Longitude (°)	Depth (m)	Rel. nitrate	Rel. phosphate	Rel. silicate
12	9.50	-20.50	1386.7	309.00	14.55	18.58
			2469.3	251.22	11.91	25.08
			3447.2	204.56	9.73	25.60
			4426.4	270.67	11.73	39.42
			44.2	1.00	1.00	1.00
			69.4	55.88	15.17	2.66
			99.7	70.41	23.00	3.66
			146.8	73.34	24.83	3.78
			199.3	80.69	27.17	4.28
			427.9	116.84	36.17	7.76
			794.6	119.38	41.00	12.70
			1487.5	82.44	26.17	11.15
			2470.5	67.59	20.33	15.57
			3450.4	72.75	21.67	19.83
			4037.0	74.94	21.67	23.92
13	6.00	-20.00	59.3	1.00	1.00	1.00
			98.0	1.80	2.26	1.60
			147.3	1.87	2.33	2.00
			200.0	2.33	2.96	2.47
			346.8	3.16	3.89	4.07
			495.8	3.41	4.31	5.30
			744.7	3.48	3.96	7.13
			1089.5	3.03	3.94	7.41
			1486.1	2.27	3.00	5.87
			1978.5	2.03	2.72	6.63
14	2.15	-20.15	2272.4	2.03	2.74	7.32
			39.2		1.00	
			60.1	1.00	20.50	1.00
			99.6	2.98	59.00	2.70
			148.1	3.10	61.00	3.20
			197.0	3.66	72.00	3.82
			342.0	5.14	99.00	7.38
			497.3	5.58	107.00	9.11
			792.3	6.14	121.00	14.64
			1091.4	4.99	99.00	13.91
			1484.8	4.00	76.00	10.08
			2690.9	3.69	72.50	18.10
			4425.8	3.89	75.50	24.20

Station	Latitude (°)	Longitude (°)	Depth (m)	Rel. nitrate	Rel. phosphate	Rel. silicate
15 + 16	-0.62	-20.62	39.5		1.00	
			69.0	1.00	2.43	1.00
			88.6	12.39	9.00	4.78
			148.1	23.44	13.57	11.02
			198.9	31.09	18.57	12.69
			327.5	39.81	22.86	19.80
			694.2	56.34	34.29	55.73
			1090.2	50.91	30.43	56.22
			2175.6	32.36	17.14	44.44
			4425.9	31.84	19.14	76.73
18	-6.65	-25.65	5692.2	30.16	22.57	52.51
			40.6		1.00	1.00
			60.4	1.00	1.43	0.95
			100.9	0.36	2.29	0.76
			148.1	24.28	16.57	26.19
			199.7	30.70	21.29	42.90
			368.2	44.81	29.71	71.67
			496.9	44.48	29.71	87.81
			794.5	44.16	33.00	129.81
			1486.2	31.18	22.57	84.48
19	-11.50	-28.50	1978.2	22.55	18.43	96.33
			3548.4	20.72	17.86	141.90
			5301.4	39.51	27.29	269.86
			40.7	1.00	1.00	1.00
			59.0	0.88	1.17	1.63
			99.8	0.75	1.67	0.63
			139.5	2.09	3.83	5.63
			396.1	21.49	14.67	41.75
			398.7	53.42	30.50	185.38
			769.3	59.70	38.67	352.75
20	-7.17	-31.17	1485.9	49.79	27.67	242.25
			2567.5	44.09	22.67	337.13
			4814.8	61.61	35.33	829.00
			39.1	1.00	1.00	1.00
			59.6	0.57	0.67	0.30
			99.9	0.11	1.00	0.21
			100.2	0.63	1.67	1.12
			112.8	50.33	16.78	27.88

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Station	Latitude (°)	Longitude (°)	Depth (m)	Rel. nitrate	Rel. phosphate	Rel. silicate
22	7.77	-48.77	297.1	77.76	20.11	50.18
			1141.6	76.59	25.00	82.06
			1485.3	49.15	16.22	54.06
			2763.5	47.65	14.33	81.00
			4911.8	74.59	25.00	173.82
			19.5	1.00	1.00	1.00
			40.4	0.65	0.25	0.93
			99.3	10.85	12.75	6.61
			148.3	21.18	31.50	16.30
			198.0	25.93	33.50	23.14
			396.9	32.77	42.00	32.80
			744.6	35.61	57.25	54.20
			1190.3	32.47	41.50	52.43
			1683.7	22.86	27.75	31.98
			2568.7	19.11	26.25	48.95

See Figures 5.10, 5.11, 5.12.

B3. Supplementary Data Table 3: Concentrations of dissolved Al in selected samples of the depth profiles

Please refer to Appendix A3. Supplementary Data Table 3. Data of dissolved Al are used to plot Fig. 5.9 of manuscript 'Sources, biogeochemical cycling and depth distribution of dissolved V, Mo and W in the Atlantic Ocean'.

Appendix C Chapter 6 Chromium redox species in Pacific and Atlantic seawater

C1. Supplementary Data Table 1: Concentrations of Cr(total), Cr(VI), Cr(reactive), Cr(III) and Cr(III_reactive) for stations investigated in the Pacific (P1, P2, P3) and in the Atlantic Ocean (A1, A2, A3)³. Corresponding to the sampled depths, oxygen, salinity and temperature data are provided.

³Concentrations indicated with (a) were below the limit of quantification (LOQ) of the applied method but exceeded the limit of detection (LOD). These values are provided to show a general trend in distribution noting that the absolute concentration may deviate from the true value.

Station	Latitude [°]	Longitude [°]	Depth [m]	Oxygen [μmol/kg]	Salinity	Temperature [°C]	Cr(total) [nmol/L]	Cr(VI) [nmol/L]	Cr(reactive) [nmol/L]	Cr(III) [nmol/L]	Cr(III_reactive) [nmol/L]
P1	-32.5	-170.0	15	220.76	35.52	19.34	3.91	1.96	2.25	1.95	0.29 ^(a)
			30	221.11	35.52	19.34	3.38	1.83	1.95	1.55	0.13 ^(a)
			75	221.51	35.53	19.04	5.39	2.38	2.90	3.02	0.53 ^(a)
			100	222.20	35.53	18.81	4.34	2.63	2.90	1.71	0.28 ^(a)
			150	198.83	35.38	15.73	3.10	2.15	2.28	0.94	0.13 ^(a)
			200	193.07	35.27	14.35	3.23	1.67	1.89	1.56	0.22 ^(a)
			300	201.75	35.03	12.20	3.66	1.52	1.93	2.134	0.41 ^(a)
			500	217.23	34.51	8.19	2.07	1.21		0.86	
			750	225.03	34.37	6.67	3.55	1.88	2.01	1.66	0.13 ^(a)
			1000	201.75	34.33	5.21	2.79	1.60	1.65	1.19	0.06 ^(a)
			1250	180.65	34.38	3.82	3.74	2.88	3.08	0.86	0.19 ^(a)
			1500	160.59	34.52	2.88	3.94	2.52	2.65	1.42	0.13 ^(a)
			1750	150.58	34.59	2.52	4.56	3.13	3.73	1.43	0.61 ^(a)
			2000	146.36	34.62	2.32	3.82	2.52	2.63	1.30	0.11 ^(a)
			2500	143.95	34.65	2.05	5.68	4.52	4.96	1.16	0.44 ^(a)
			3000	146.38	34.67	1.84	4.19	2.71	3.37	1.48	0.65 ^(a)
P2	-32.5	-158.0	3500	169.82	34.70	1.64	4.76	3.44	3.71	1.32	0.27 ^(a)
			4000	193.00	34.72	1.33	4.44	3.44	3.57	1.00	0.13 ^(a)
			4500	198.15	34.71	1.07	5.40	2.97	3.32	2.43	0.35 ^(a)
			4838	200.38	34.71	1.04	4.34	2.29	2.52	2.05	0.23 ^(a)
			15	219.63	35.47	19.27	2.53	0.77	1.27	1.76	0.50 ^(a)
			30	221.11	35.52	19.34	3.38	1.83	1.95	1.55	0.13 ^(a)
			75	218.63	35.44	19.14	3.19	0.61 ^(a)	1.74	2.59	1.13

Station	Latitude [°]	Longitude [°]	Depth [m]	Oxygen [μmol/kg]	Salinity	Temperature [°C]	Cr(total) [nmol/L]	Cr(VI) [nmol/L]	Cr(reactive) [nmol/L]	Cr(III) [nmol/L]	Cr(III_reactive) [nmol/L]
P2	-32.5	-158.0	100	219.16	35.44	19.19	2.60	0.95	1.14	1.64	0.19(a)
			125	218.76	35.43	19.09	2.58	1.12	1.57	1.46	0.45(a)
			150	218.23	35.43	18.94	4.59	1.96	1.94	2.63	
			200	211.12	35.36	17.00	4.63	2.48	3.01	2.14	0.53(a)
			300	200.76	35.29	15.75	4.28	2.63	2.88	1.64	0.24(a)
			500	192.48	34.99	12.94	4.38	2.38	2.81	1.99	0.42(a)
			750	228.73	34.44	7.75		2.02	2.44		0.42(a)
			1000	230.50	34.33	6.33	4.60	2.73	3.08	1.87	0.35(a)
			1250	201.36	34.31	4.82	5.85	4.06	4.40	1.79	0.35(a)
			1500	177.31	34.39	3.53	3.73	2.02	2.99	1.71	0.97
			1750	162.02	34.50	2.87	5.02	3.81	3.99	1.21	0.18(a)
			2000	152.56	34.59	2.47	6.20	4.10	4.54	2.11	0.44(a)
			2500	147.92	34.63	2.20	6.80	4.75	5.39	2.05	0.63(a)
			3000	145.33	34.66	1.90	5.07	3.63	4.08	1.43	0.44(a)
			3500	151.50	34.67	1.72	5.14	3.65	4.26	1.58	0.70
P3	-32.5	-150.0	4000	166.65	34.69	1.53	5.09	3.25	4.07	1.84	0.82
			4352	181.63	34.70	1.35	5.02	3.30	3.67	1.72	0.83
			15	219.30	35.45	19.05	3.44	2.02	2.15	1.42	0.13(a)
			30	220.21	35.45	19.05	4.65	2.69	2.88	1.96	0.19(a)
			60	219.48	35.45	19.06	4.62	3.62	3.67	1.00	0.06(a)
			100	220.96	35.45	19.00	3.25	2.17	2.22	1.08	0.05(a)
			125	208.80	35.44	17.41	4.81	3.02	2.98	1.79	
			150	199.67	35.41	16.70	3.13	1.21	1.61	1.92	0.39(a)

Station	Latitude [°]	Longitude [°]	Depth [m]	Oxygen [μmol/kg]	Salinity	Temperature [°C]	Cr(total) [nmol/L]	Cr(VI) [nmol/L]	Cr(reactive) [nmol/L]	Cr(III) [nmol/L]	Cr(III_reactive) [nmol/L]
P3	-32.5	-150.0	200	197.46	35.23	15.17	5.74	2.15	2.62	3.58	0.46 ^(a)
			300	193.32	34.96	12.42	3.79	1.62	2.06	2.17	0.45 ^(a)
			500	223.44	34.47	7.99	3.52	1.77	1.89	1.75	0.13 ^(a)
			750	228.88	34.35	6.44	3.56	2.27	1.79	1.29	
			1000	201.35	34.32	4.95	3.40	1.60	1.86	1.81	0.26 ^(a)
			1250	178.35	34.39	3.56	4.84	2.88	3.61	1.96	0.73
			1500	160.74	34.51	2.85	6.61	3.62	4.08	2.99	0.46 ^(a)
			1750	151.81	34.59	2.53	5.48	3.60	4.12	1.88	0.52 ^(a)
			2000	146.93	34.63	2.26	5.90	3.90	4.13	2.00	0.22 ^(a)
			2500	143.76	34.65	1.95	5.36	4.10	4.01	1.26	
			3000	147.90	34.67	1.78	5.41	3.23	3.83	2.18	0.60 ^(a)
			3500	164.26	34.69	1.62	5.81	4.85	4.87	0.96	0.02 ^(a)
			4000	187.75	34.71	1.38	6.08	4.85	4.56	1.23	
			4500	196.27	34.71	1.16	5.64	3.81	3.92	1.84	0.12 ^(a)
			20.2	196.33	35.32	26.58	3.08	0.46 ^(a)	0.94	2.62	0.48 ^(a)
A1	9.50	-20.33	44.0	166.18	35.90	20.47	3.71	0.96	1.13	2.75	
			69.9	101.29	35.61	15.93	2.04	1.62		0.42 ^(a)	
			99.6	101.26	35.48	14.43	3.48		0.65 ^(a)	3.37	0.54 ^(a)
			148.1	109.42	35.36	13.45	2.98		0.90	2.98	0.90
			199.6	92.79	35.26	12.67	3.75	0.48 ^(a)	0.65 ^(a)	3.27	
			426.5	38.25	35.16	10.59	2.94	0.37 ^(a)	0.50 ^(a)	2.58	
			496.1	41.03	35.13	9.84	1.40		0.79	1.21	0.60 ^(a)
			793.4	87.24	34.77	6.31	1.75	0.83	1.21	0.92	0.38 ^(a)

Station	Latitude [°]	Longitude [°]	Depth [m]	Oxygen [μmol/kg]	Salinity	Temperature [°C]	Cr(total) [nmol/L]	Cr(VI) [nmol/L]	Cr(reactive) [nmol/L]	Cr(III) [nmol/L]	Cr(III_reactive) [nmol/L]
A1	9.50	-20.33	1485.7	198.13	34.95	4.19	1.63	1.54			
			1979.8	225.60	34.96	3.45	2.02	1.63	1.63	0.38(a)	
			2961.2	231.97	34.92	2.67	2.73	0.54(a)	2.65	2.19	2.12
			3452.2	231.70	34.91	2.51	2.46	1.60		0.87	
			4037.2	230.47	34.89	2.33	3.33	1.00	3.27	2.33	2.27
A2	6.70	-25.70	21.1	193.52	36.33	27.92	5.79				
			39.4	194.50	36.33	27.76	12.12	4.02	3.56	8.10	
			58.0	196.08	36.34	27.52	3.46		2.29	3.46	2.29
			79.5	203.49	36.64	25.28	2.65		0.37(a)	2.65	0.37(a)
			110.4	151.85	36.27	19.85	2.67		0.23(a)	2.67	0.23(a)
			149.9	106.76	35.42	13.73	1.56			1.56	
			198.7	92.48	35.08	11.18	1.48			1.48	
			347.7	80.06	34.79	8.80	1.79			1.79	
			496.5	93.97	34.63	7.11	1.73		0.25(a)	1.73	0.25(a)
			793.9	164.89	34.44	4.40	3.23	1.02	1.50	2.21	0.48(a)
A3	7.20	-31.2	1485.3	211.20	34.94	4.22	5.00	0.88	1.12	4.12	0.23(a)
			1978.6	233.03	34.96	3.51	1.77	0.94	1.00	0.83	
			2764.2	228.28	34.91	2.72	2.48	1.02	1.33	1.46	0.31(a)
			3452.0	241.19	34.91	2.51	2.56	0.98	1.37	1.58	0.38(a)
			4427.8	216.89	34.76	1.05	4.27	1.12	1.65	3.15	0.54(a)
			5303.7	211.85	34.71	0.73	3.33	1.42	1.75	1.90	0.33(a)
			19.1	191.82	36.31	28.40	5.67	1.46	1.04	4.21	
			38.4	192.90	36.31	28.34	4.75	1.12	1.48	3.63	0.37(a)

Station	Latitude [°]	Longitude [°]	Depth [m]	Oxygen [μmol/kg]	Salinity	Temperature [°C]	Cr(total) [nmol/L]	Cr(VI) [nmol/L]	Cr(reactive) [nmol/L]	Cr(III) [nmol/L]	Cr(III_reactive) [nmol/L]
A3	7.20	-31.2	59.3	194.87	36.37	28.07	3.87	2.31		1.56	
			79.2	202.57	36.64	26.61	5.31	1.85	2.69	3.46	0.85
			99.1	187.68	36.67	23.54	5.98	0.88	0.69	5.10	
			123.8	153.11	36.25	19.89	1.83	0.48	0.98	1.35	0.50 ^(a)
			199.0	115.63	35.08	11.37	2.83	1.04	1.06	1.79	
			398.0	105.68	34.73	8.38	4.58	0.92	1.21	3.65	0.29 ^(a)
			886.7	148.20	34.48	4.64	2.87	1.44	2.25	1.42	0.81
			889.4	148.55	34.48	4.63	2.96			2.96	
			1092.9	162.24	34.62	4.14	4.15	1.69	1.44	2.46	
			1486.3	213.85	34.95	4.27	3.12	1.46	1.48	1.65	
			2276.4	231.50	34.93	3.07	4.17	1.17	1.19	3.00	
			3550.8	242.87	34.91	2.46	3.94	1.19	1.33	2.75	
			4233.8	229.75	34.78	1.26	5.89	1.00	2.02	4.88	1.02
			4915.4	211.98	34.72	0.76	3.08	2.10	2.12	0.98	

