# Influence of ocean warming and acidification on trace metal biogeochemistry

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ABSTRACT: Rising atmospheric $CO_2$ concentrations will have profound effects on atmospheric and hydrographic processes, which will ultimately modify the supple and chemistry of trace metals in the ocean. In addition to an increase in sea surface temperatures, higher $CO_2$ results in a decrease in seawater pH, known as ocean acidification, with implications for inorganic trace metal chemistry. Furthermore, direct or indirect effects of ocean acidification and ocean warming on marine biota will affect trace metal biogeochemistry via alteration of biological trace metal uptake rates and metal binding to organic ligands. We still lack a holistic understanding of the impacts of decreasing seawater pH and rising temperatures on different trace metals and marine biota, which complicates projections into the future. Here, we outline how ocean acidification and ocean warming will influence the inputs and cycling of Fe and other biologically relevant trace metals globally and regionally in high and low latitudes of the future ocean; we discuss uncertainties and highlight essential future research fields.

KEY WORDS: Ocean acidification · Ocean warming · Trace metals

## INTRODUCTION

Rising atmospheric $CO_2$ concentrations affect the marine environment directly via the uptake of $CO_2$ that acidifies the oceans (Caldeira & Wickett 2003, Doney et al. 2009b) and indirectly via global temperature increase that also results in sea-surface warming. Ocean warming is particularly evident in the Arctic (Wassmann et al. 2011) and in some Antarctic regions (Schofield et al. 2010). Modeling simulations reveal further effects of a changing climate, such as increasing stratification that results in reduced upwelling and wind-driven mixing (Doney 2006), changing wind patterns (Tokinaga et al. 2012), expansion of the areal extent of oxygen minimum zones (Gruber 2011), and changes in the thermohaline circulation (Rahmstorf & Ganopolski 1999, Boyd & Doney 2003).

Although there is a wealth of published information on the importance of trace metals and their inputs and cycling in marine systems (Morel & Price 2003, Boyd & Ellwood 2010), the impacts of rising atmospheric $CO_2$ on trace metal biogeochemistry are presently difficult to foresee. The role of trace metals for oceanic carbon sequestration, and thus their climate relevance, has received much attention since the seminal work of Martin (1990) and was recently highlighted again by Smetacek et al. (2012). However, investigations into the influence of rising atmospheric $CO_2$ on marine processes and trace metal biogeochemistry still appear as isolated disciplines. This is puzzling, as pH and temperature are 2 master variables in all chemical and biological processes and therefore intimately link the disciplines of trace metal biogeochemistry, ocean acidification, and sea surface warming.

Dissolved metals in seawater are usually present at low concentrations due to their low solubility (as in the case of Fe) and/or because of adsorption onto particles. Seawater pH and temperature will affect both

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solubility and adsorption of metals, and thus likely change the dissolved concentrations of metals in the future ocean. The inorganic solubility of Fe is greater in colder waters (Liu & Millero 2002) but also largely depends on the organic content of seawater. Furthermore, increasing temperatures will increase the rates of all chemical reactions, which should increase ferric oxide and hydroxide precipitation as well as oxide aging with negative effects for dissolved Fe concentrations. A clear dependency of metal solubility upon temperature has not been established for many elements, and therefore quantifications of the effect of rising sea surface temperature (SST) on metal solubility in the future ocean are difficult. On the other hand, the expected decrease in seawater pH from pre-industrial 8.25 to 7.85 within this century, and of up to 0.7 units by the year 2300 (Caldeira & Wickett 2003, Jacobson 2005), will significantly affect the inorganic solubility of several trace metals, particularly those forming strong complexes with hydroxide and carbonate ions (Millero et al. 2009). The case of Fe is the most multifaceted and is discussed here briefly. When seawater pH falls below 8, changes in the inorganic speciation result in an increase in the thermodynamic solubility of Fe(III) hydroxide. Based on measurements of Kuma et al. (1996) and Millero (2001), the overall Fe(III) solubility may increase by approximately 460 pmol $kg^{-1}$ as a result of the expected drop in seawater pH from currently 8.10 to 7.85 by the year 2100. In parallel, Fe(II) is much more soluble than Fe(III) but is unstable at current seawater pH due to rapid oxidation. Ocean acidification will slow Fe(II) oxidation rates significantly and thus increase the residence time of Fe(II) (Kuma et al. 1996, Millero 2001, Breitbarth et al. 2010b).

Compared to the well-studied Fe redox reactions in seawater, only a few studies have addressed Cu redox reactions in the field (Moffett & Zika 1987, 1988). As for Fe, a shift in Cu speciation can be expected (Millero et al. 2009). Cu forms strong carbonate complexes, and the decrease in $CO_3^{2-}$ ions due to ocean acidification will result in an increase in the free Cu(II) ion concentration (Millero et al. 2009). In parallel, Cu(II) reduction will increase, while Cu(I) complexation by chloride and reoxidation kinetics by $H_2O_2$ remain largely unchanged (Millero et al. 1991). It is unclear today whether these changes in the Cu redox cycle will be of biological relevance. In contrast, Cd and Zn are not subjected to a dynamic redox cycle in the surface ocean, and their solubility in seawater is much higher than for Fe(III). The effect of ocean acidification on the inorganic Cd and Zn solubility may thus be negligible.

However, the influence of changing ocean acidity and temperature on trace metal biogeochemistry is more complex than a direct pH/temperature relationship with solubility. Metal solubility is controlled by the interrelationship of inorganic solubility, organic complexation, redox chemistry, and the phytoplankton–trace metal feedback mechanisms (Fig. 1). The majority of the total concentration of bio-active metals such as Fe, Co, Cd, Cu, Ni, Zn, and Pb are not in their inorganic form, but bound to organic complexes. The ligand-bound fraction of metals can be up to 100% for Co (Saito & Moffett 2001, Saito et al. 2005), >99% for Fe and Cu (Sunda & Hanson 1987, Coale & Bruland 1988, Sunda & Huntsman 1991, Rue & Bruland 1995), from 50 to 90 and >98% for Zn (Bruland 1989, Baars & Croot 2011), and >70% for Cd (Bruland 1992). Possible effects of rising oceanic $CO_2$ concentrations on organic trace metal ligands will therefore play a major role in overall trace metal bioavailability in the future ocean, but only very few studies have addressed this topic so far. Assessments of ocean acidification effects on marine trace metal chemistry are still largely based on theoretical considerations of inorganic and organic metal speciation and therefore tell us little about potential effects on metal uptake, requirements, toxicity thresholds, and possible biological feedback mechanisms (Millero et al. 2009, Breitbarth et al. 2010a).

In the last decade, an enormous amount of published work on the influence of ocean acidification on marine biota has been assembled (Gattuso & Hansson 2011). However, publications concerning the interactions of multiple factors such as seawater pH, temperature, and trace metals are scarce but point towards the significance and complexity thereof (Boyd et al. 2010). For example, it has been demon-
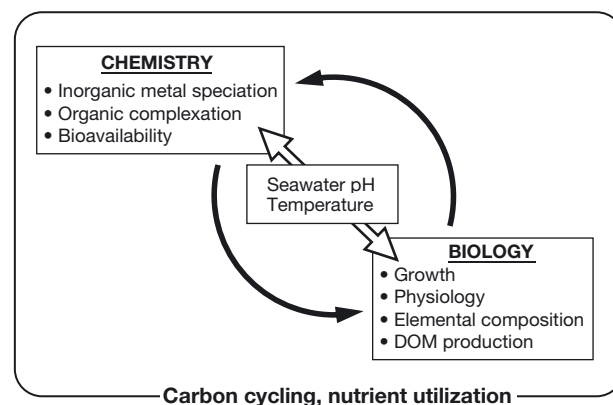


Fig. 1. Predicted relationship between the effects of ocean acidification and warming on trace metal chemistry and phytoplankton biology in seawater

strated that $N_2$ and $CO_2$ fixation rates as well as growth of the marine unicellular diazotrophic cyanobacterium *Crocosphaera* only increased with increasing $pCO_2$ if Fe concentrations were not limiting (Fu et al. 2008).

Temperature and Fe have synergistic effects on phytoplankton growth rates in the Ross Sea (Rose et al. 2009). Moreover, King et al. (2011) state that complex feedback mechanisms between vitamin $B_{12}$ and $pCO_2$ interactions affect the uptake and metal net use efficiency of Fe, Co, Zn, and Cd by *Atthyea* sp., a subarctic diatom. Under $B_{12}$-replete conditions and high $pCO_2$, this diatom grew faster, had lower Fe, Zn, and Cd quotas, and used the metals more efficiently compared to low $pCO_2$ conditions. Under $B_{12}$ limitation, however, diatom growth rate was much lower and did not change with changing $pCO_2$. Also, the net use efficiency of Fe, Zn, Co, and Cd decreased with increasing $pCO_2$ under $B_{12}$ limitation (King et al. 2011). At a higher trophic level, work by Lacoue-Labarthe et al. (2009, 2011, 2012) suggests potential ecotoxicological impacts of trace metals with seawater warming and decreasing seawater pH due to altered permeability of egg shells and the embryonic metabolism in the cephalopod species *Loligo vulgaris* and *Sepia officinalis*. All of these examples demonstrate the need to consider multiple factors when trying to assess the implications of ocean acidification and warming on the marine ecosystem.

The importance of a multivariate approach especially when investigating essential trace elements is founded in Liebig's law of the minimum (Salisbury & Ross 1992). For example, changes in Fe bioavailability may not result in increased phytoplankton growth if another nutrient is ultimately limiting. Likewise, ocean acidification effects on phytoplankton growth and nutrient uptake may be masked if nutrient limitation, which in the open ocean is often governed by Fe, is elevated due to contamination artifacts associated with the experimental set-up. Acknowledging this, some groups now have developed 'trace-metal clean' experimental protocols for ocean acidification work (Hoffmann et al. in press).

It seems that decreasing seawater pH and warming will both influence trace metal–phytoplankton interactions in various ways; however, robust predictions of these interactions are not yet possible. In order to assess the effects of ocean acidification and SST warming on trace metal biogeochemistry in the future ocean, we need to look at how trace metals are supplied, cycled, and lost from the upper ocean. Table 1 summarizes how global change may affect metal input in the future ocean on a global scale, as well as in high- and low-latitude regions. In the following sections, we will discuss the primary factors that control the interplay of temperature, ocean acidification, and trace metals in the ocean and how they might affect marine phytoplankton both globally and regionally.

Table 1. Overview of potential global change effects on trace metal chemistry. TM: trace metal; DOM: dissolved organic matter

| Parameter | Global | | | | High latitudes | | | Low latitudes | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | SST ↑ | pH ↓ | Precipitation ↕ | Wind ↕ | Sea ice cover ↓ | Land ice Glaciers ↓ | Permafrost ↓ | Desertification ↑ | Riverine input ↓ | Coastal upwelling ↑ |
| Metal input | | | ↕ Dry/wet deposition | ↕ Aerosol input; vertical mixing | Geographic shift of seasonal deposits from ice | ↑ Erosion, riverine TM input (coastal) | ↑ Direct and riverine TM input (coastal) | ↕ TM input via dust (open ocean) | ↓ Riverine TM input (coastal) | ↑ |
| Inorganic chemistry | ↓ Fe solubility; ? solubility of other metals; ↑ metal oxidation | ↑ Fe solubility; ↓ Fe, Cu inorganic complexation; ↑ metal reduction | ? Possible cloud chemistry effects on metal solubility | | Effects on photo-reductive metals | | | | | |
| Organic complexation | ? | ? | | | ? | ↑ Erosion, riverine DOM input (coastal) | ↑ Direct and riverine DOM input (coastal) | | ↓ Riverine DOM input (coastal) | |

Legend: ↑ increase, ↓ decrease, ↕ regionally dependent, ? unknown effect

## GLOBAL EFFECTS OF CLIMATE CHANGE AND OCEAN ACIDIFICATION ON MARINE TRACE METAL SUPPLY AND CYCLING

### Metal sources

Climate change is likely to influence global trace metal biogeochemistry by affecting both metal sources and cycling in the future ocean. For surface waters, the main global trace metal inputs are aerosol particles from desert dust (Jickells et al. 2005), anthropogenic sources (Sedwick et al. 2007, Sholkovitz et al. 2009), and volcanic eruptions (Olgun et al. 2011). In coastal regions, riverine inputs and upwelling of trace metal-rich deep water play an additional important role (Boyd 2009). Sediments are a major source of trace metals in shelf waters (e.g. Laës et al. 2007, Ussher et al. 2007), and the 'island wake' effect is of local importance in remote ocean systems (Blain et al. 2007). It has been suggested recently that trace metals from deep-sea hydrothermal vents can potentially reach surface waters via ocean circulation allied to an excess of organic compounds that bind to and stabilize the metals in hydrothermal fluids (Sander & Koschinsky 2011).

Climate change will potentially influence global dust and riverine trace metal inputs into the ocean, but accurate predictions are not yet possible (Boyd & Ellwood 2010). Global dust models predict scenarios that vary from a 60 % decrease to a 3.8 % increase in dust emissions during the 21st century (Mahowald & Luo 2003, Tegen et al. 2004, Woodward et al. 2005, Stier et al. 2006), making robust projections about future changes in dust as a trace metal source a major challenge. Model predictions suggest an increase in precipitation for the monsoon regimes, over the tropical Pacific, as well as at high latitudes, while a decrease in precipitation is predicted in the subtropics (Meehl et al. 2007). Therefore, riverine trace metal inputs are likely to change significantly on a global scale with large regional differences depending on a range of factors, such as complex interactions of their terrestrial sources, redox processes, and colloid chemistry in estuaries.

The supply of trace metals, in particular from aerosols, will further be influenced by the projected changes in $CO_2$ and other anthropogenically-influenced gases. Increasing atmospheric concentrations of carbon dioxide, sulfur dioxide, and nitrogen oxides decrease the pH of cloud water and result in acid rain (Badr & Probert 1993, Bogan et al. 2009, Vahedpour & Zolfaghari 2011). The direct contribution of sulfur and nitrogen gases to ocean acidification will be neg-

ligible (Hunter et al. 2011), but the effect on atmospheric trace metal inputs could be significant. As in seawater, a lower pH of cloud water results in increased solubility of trace metals from aerosol particles such as desert dust or volcanic ash with potentially significant effects for the net flux of trace metals from these sources to the future ocean (Desboeufs et al. 2001). Mahowald et al. (2009) estimated that the higher acidity in the atmosphere caused by human activities may double the bioavailable Fe in the ocean via increased solubility from desert dust.

On a global scale, model predictions suggest a future increase in precipitation as well as water vapor and evaporation, while regional variations are pronounced (Meehl et al. 2007). Together, altered patterns in wind and precipitation, as well as riverine transport, will ultimately modify the supply of trace metals to the open ocean. The effects of these physico-chemical changes on marine productivity and biogeochemical cycling may be profound (Boyd & Doney 2003, Feely et al. 2004, Jickells et al. 2005, Orr et al. 2005).

### Inorganic metal speciation

As mentioned above, the inorganic speciation of metals will be altered by ocean warming and ocean acidification. One example thereof is the observed increase in Fe(II) concentrations and Fe(II) half-life times under lower pH in a coastal mesocosm experiment (Breitbarth et al. 2010b). In addition, changes in surface ocean stratification will likely have effects on particle residence times in the euphotic zone. When stratification increases, there is less mixing with deeper waters, which means that particles in the surface mixed layer may reside for longer in this stratum (Doney 2006). This would increase the mean light intensity to which particles in the surface mixed layer are exposed, with possible implications for photochemical metal redox dynamics. For example, increased light and temperature increase Mn oxide dissolution rates (Sunda & Huntsman 1994). Furthermore, the photoreduction of Fe(III) complexes increases under higher light intensities, resulting in higher Fe(II) concentrations (Kuma et al. 1995). In addition, the photosynthetic apparatus of marine phytoplankton is downregulated under higher light intensities, resulting in lower Fe requirements (Sunda & Huntsman 1997, Maldonado et al. 1999, Feng et al. 2010). However, stronger stratification will also lead to increased warming of the surface waters, which may decrease Fe(II) concentrations due to higher

reoxidation rates, as observed in the Gulf of Aquaba (Shaked 2008). Lower Fe requirements for marine phytoplankton, as a result of elevated light intensities, are thus mainly to be expected in colder oceanic regions (Sunda & Huntsman 2011). Likewise, ocean acidification will affect the redox speciation of Cu, yielding a larger Cu(I) fraction (Millero et al. 2009). The potential biological implications thereof are unknown today.

In general, even slight changes in the bioavailability of Fe and Cu may have profound effects for marine ecosystems, as these metals are known to interact with each other. Cu is needed by some marine phytoplankton for sufficient Fe acquisition (Peers et al. 2005, Wells et al. 2005, Maldonado et al. 2006, Annett et al. 2008), and Cu requirements of natural phytoplankton communities increase under Fe limitation (Semeniuk et al. 2009). On the other hand, Cu is a potentially toxic metal whose toxicity to marine phytoplankton is strongly regulated by organic ligand complexation.

## Organic metal speciation

Organic trace metal complexation in seawater is controlled by the functional groups within dissolved organic matter, including phytoplankton exudates, siderophores produced by heterotrophic bacteria, and bioremineralization products (Boyd & Ellwood 2010, Breitbarth et al. 2010a). To date, research on trace metal bioavailability has focused on measurements of ligand concentrations and ligand binding strength in natural waters, and metal uptake in controlled laboratory experiments using metal chelators. Studies addressing ocean acidification effects on organic ligand binding are rare. In a first study, Shi et al. (2010) investigated the effect of pH on Fe uptake from 3 Fe-ligand complexes with different functional groups. They found reduced Fe uptake by marine phytoplankton under lower pH in EDTA- and DFOB-buffered media but no pH effect on Fe uptake from the siderophore Fe-Azotochelin. This was expected, as the catechol groups of Azotochelin are protonated in seawater and thus the free Fe concentration should not be affected by changes in seawater pH (Shi et al. 2010). In the case of EDTA, cellular Fe acquisition decreases with decreasing seawater pH as the dissociation of Fe-EDTA (and any chelator with acidic binding groups that are not protonated in seawater) becomes less favored at low pH due to reduced competition with OH$^-$ for Fe chelation, and thus the Fe' concentration decreases (Stumm & Mor-

gan 1996). However, as acknowledged by Shi et al. (2010), Fe' uptake from Fe-EDTA is a simplistic scenario in which Fe' is the only bioavailable form of Fe. Such an approach has limited applications to the open ocean, as natural organic ligands possess a variety of metal binding sites (Barbeau et al. 2003) with different H$^+$ stoichiometries (Sillén & Martell 1971, Breitbarth et al. 2010a). The observed decrease in Fe uptake from Fe-DFOB under lower pH was not caused by a pH effect on the dissociation of the Fe-DFOB complex, as this is not affected by seawater pH (Shi et al. 2010). Rather, this was most likely due to pH effects on the enzymatic cell surface reduction of the Fe-DFOB complex (Shi et al. 2010). In addition, a substantial body of work points towards the multiplicity of Fe uptake mechanisms in marine phytoplankton, which include models of ligand-bound Fe (FeL) uptake, cell surface reduction of the FeL complex, and direct uptake of Fe(II) (Hutchins et al. 1999, Maldonado & Price 1999, Shaked et al. 2005, Salmon et al. 2006, Morel et al. 2008). Therefore, the diverse range of chemical and biological processes in marine trace metal biogeochemistry, and how they each will be altered by ocean acidification, is likely to be multifaceted and complex.

Short-term (1 to 2 h) Fe uptake experiments with the coastal diatom *Thalassiosira weissflogii* in natural seawater did not show significant differences between different pH/$p$CO$_2$ treatments within the same water mass (Shi et al. 2010). However, a body of literature is evolving on physiological effects of ocean acidification on marine phytoplankton (Engel et al. 2004, Doney et al. 2009a, Hutchins et al. 2009, Boyd et al. 2010). Therefore, experiments over periods long enough for phytoplankton to grow could result in significant impacts on organic Fe complexation. Results from a coastal mesocosm CO$_2$ enrichment experiment show 2 to 3 nM higher dissolved Fe concentrations under lower pH compared to the mid- and high pH treatments (Breitbarth et al. 2010b). This large difference cannot be solely explained by an increased inorganic Fe solubility under lower pH (Millero et al. 2009), and thus pH effects on the organic Fe complexation are one likely explanation next to pH effects on colloid formation, Fe chelation, and Fe hydroxide precipitation (Breitbarth et al. 2010b).

While the effect of ocean acidification on heterotrophic bacterial growth seems to be small (Liu et al. 2010, Weinbauer et al. 2011), bacterial enzymatic activity and polysaccharide degradation increases under lower seawater pH in coastal waters (Grossart et al. 2006, Piontek et al. 2010). Increasing tempera-

tures have been shown to increase bacterial growth, production, and respiration (Vaqué et al. 2009, Kritzberg et al. 2010). The direct effects thereof upon trace metal bioavailability have not been assessed at present, but it is possible that these mechanisms will also affect the siderophore production by hetero-trophic bacteria with consequent implications for Fe bioavailability in the future ocean. Moreover, changes in organic complexation, either via shifts in ligand: $H^+/OH^-$ stoichiometry or as an effect of ligand con-centration changes, should also affect Fe retention rates in surface waters (Sunda 2010).

The Fe(III)-binding groups of marine siderophores can be hydroxamate, catecholate, or α-hydroxy carbo-xylate moieties (Barbeau et al. 2003). While hydroxa-mate and catecholate groups are photochemically resistant when bound to Fe(III), α-hydroxy carboxy-late groups undergo light-induced ligand oxidation and reduction of Fe(III) to Fe(II) (Barbeau et al. 2001, 2003). Increased mean light intensities in the pre-dicted future shallower surface mixed layers (Doney 2006) would thus enhance the photolysis of some organic Fe(III) complexes and increase reactive Fe(II) in surface seawater. Cu-binding ligands differ from Fe-binding ligands in that they can be directly pro-duced by some marine phytoplankton species when exposed to higher concentrations of Cu (and other toxic metals such as Cd and Zn) (Ahner & Morel 1995, Moffett & Brand 1996, Croot et al. 2000, Ahner et al. 2002, Dupont & Ahner 2005). Thereby, the ligand can be released into the water and bind Cu (or other toxic metals such as Cd and Zn) extracellularly (Moffett & Brand 1996, Croot et al. 2000, Dupont & Ahner 2005), or the metals are taken up into the cell and detoxified by intracellular binding to the ligand (Ahner et al. 2002, Dupont et al. 2004). These thiols are low molecular weight sulfhydryl-containing com-pounds such as glutathione and phytochelatin. Both glutathione and phytochelatin bind Cd, Cu, and Pb via sulfhydroxyl coordination (Rabenstein 1989, Strasdeit et al. 1991). Louis et al. (2009) described a decrease in the interaction between organic ligands and Cu(II) when seawater pH fell below 8. As a re-sult, the inorganic Cu fraction increased with de-creasing pH, similar to what was described earlier for fresh waters (Averyt et al. 2004). It is unknown so far whether Cu ligand production will be affected by ocean acidification and warming and what the effects for Cu toxicity would be. Intracellular Cu binding is unlikely to be directly affected by sur-rounding seawater pH but could possibly be indi-rectly affected via ocean acidification and warming effects on phytoplankton physiology.

A recent study described the effect of pH on the uptake of Zn and Cd in marine phytoplankton (Xu et al. 2012). Here, short-term (3 to 4 h) Zn and Cd uptake in natural phytoplankton assemblages de-creased with decreasing pH in contrast to experi-ments with single metal chelators in the laboratory. The authors concluded that in natural systems, Zn and Cd bioavailability is lower under lower pH, which they explained by the potential interaction of strong and weak ligands in natural waters. These results illustrate that care must be taken when extrapolating results from laboratory experiments using artificial metal chelators to the field.

For future research, the interplay between SST, pH, and dissolved organic matter (DOM) content of seawater and their effects on metal bioavailability needs to be established in order to better understand the effect for metal uptake by marine phytoplankton at a global level. In the context of ocean acidification and ocean warming effects on trace metal biogeo-chemistry, it is important to establish a holistic view of the many facets of trace metal chemistry. Future predictions of the nature of trace metal–phytoplank-ton interactions are difficult, as most studies have so far focused on Fe and neglected possible impacts of other metals. Because of growing evidence that the interplay of a particular metal with other metals, as opposed to the bioavailable concentration of one metal alone, will determine its biological impact (Sunda & Huntsman 1983, 1996, 2000, Peers et al. 2005, Maldonado et al. 2006), we have to move away from the dominant focus on Fe as a sole controlling trace metal in marine biogeochemistry. In addition to the importance of Cu for Fe uptake, the interplay between Cd, Fe, and Zn might have important rami-fications with regard to the effects of ocean acidifica-tion. Zn is needed in the enzyme carbonic anhydrase in marine phytoplankton and can be substituted by Cd and/or Co under Zn limitation (Price & Morel 1990). Low Zn concentrations have been shown to decrease $HCO_3^-$ uptake and thus limit phytoplank-ton growth (Morel et al. 1994, Buitenhuis et al. 2003). Higher $pCO_2$ in a more acidic ocean should lower the Zn requirements of marine phytoplankton and would thus also lower the need for substitution by Cd (Cullen et al. 1999).

The 'kink' in the Cd:$PO_4$ relationship at intermedi-ate $PO_4$ concentrations (~1.3 µmol kg$^{-1}$) and devia-tions thereof are also associated with Fe chemistry (Cullen 2006). Experiments have shown that Cd interferes with the uptake of Fe(II) and that the Cd:C and Cd:P ratios increase under Fe limitation and de-crease with increasing Fe (Cullen et al. 2003, Lane et

al. 2008, 2009). It is not clear, though, how important phylogenetic differences in the Cd uptake are in this context (Quigg et al. 2003), or what the interrelationship of Cd, Fe, and Zn in a warmer, more acidic ocean may be. Since changes in the biogeochemistry of Fe and Zn may likewise affect Cd chemistry in seawater, this also complicates the use of Cd as a tracer for past seawater nutrient concentrations (Cullen 2006). Furthermore, Cd and Zn appear to compete for the same ligands in fresh water (Sander et al. 2007); however, investigations on this topic are lacking for seawater.

In summary, ocean acidification and ocean warming will ultimately alter metal biogeochemistry on multiple levels, from affecting trace metal sources, via primary chemical effects on inorganic trace metal speciation, through to physiological effects on microbial cellular metal acquisition, and finally as a product of potential biological feedback mechanisms of heterotrophic bacteria and phytoplankton ecophysiology and altered community structure.

## INTERPLAY OF TRACE METAL SUPPLY, OCEAN ACIDIFICATION, AND TEMPERATURE AT HIGH LATITUDES

The variability in the projections from recent global dust and precipitation model simulations points to the need for a more regional view to better identify future changes in trace metal supply. In polar regions, the main sources of trace metals to the ocean are aerosol deposition and ice melting, as well as riverine input in the Arctic (Wagener et al. 2008, Shaw et al. 2011, Boyd et al. 2012, Klunder et al. 2012; Table 1). Asian dust fluxes that can reach the North Pacific are expected to decrease markedly in the future (Tsunematsu et al. 2011), but as mentioned earlier, these fluxes are difficult to predict on a basin scale because of regional differences in soil moisture and vegetation (Ravi et al. 2011).

Ocean acidification and warming have already resulted in distinct changes of the polar marine ecosystem. Sea ice cover and the areal extent of land ice glaciers have decreased significantly in recent years both in the Arctic and Antarctic (Anisimov et al. 2007, Perovich & Richter-Menge 2009, Comiso 2012), and this trend is expected to increase in the near future. Further, in the Arctic Ocean, increasing $p$CO$_2$ concentrations and sea ice melting have already resulted in aragonite undersaturation (Yamamoto-Kawai et al. 2009).

The result of rapid ice melting in both regions is an increased input of fresh water, which, together with an increase in SST, will enhance stratification at high latitudes and reduce the exchange with nutrient- and trace metal-rich deeper waters with impacts on deepwater formation and the thermohaline circulation (Marsland et al. 2007, Wassmann & Reigstad 2011). An additional consequence of melting ice in both polar regions is an effect on the light climate of the mixed layer. A reduction in Arctic sea ice cover strongly increases the light penetration into surface waters and thus will influence the photochemical redox-processing of trace metals. In Antarctic waters, where light limitation is mainly caused by deep mixing, the effects will probably not be as pronounced as in the Arctic. However, Boyd et al. (2008) predicted a shoaling of mixed layer depths in the Southern Ocean, which will also increase the mean light intensity in surface waters. In the case of Fe, increased photochemical Fe(III) reduction will lead to a larger pool of Fe(II) supported by a higher residence time due to slower oxidation rates at lower pH and cold temperatures (Kuma et al. 1995, Sunda & Huntsman 2003).

A further consequence of increased melting of drifting Arctic sea ice, which is formed in the shallow coastal zones and contains entrained sediments, may be a major input of Fe, other trace metals, and terrestrial organic matter to offshore waters of the Arctic Ocean. It is suggested that Fe incorporated in sea ice and subsequently released with meltwaters may also contribute to observed intense ice edge blooms (Hölemann et al. 1999, Measures 1999, Fitzwater et al. 2000). Similar processes have been described for the Antarctic (van der Merwe et al. 2011), and it has been suggested that particularly the role of icebergs for metal supply to the open ocean may increase with the decline of Antarctic ice shelves (Lin et al. 2011). However, Lannuzel et al. (2011) suggested that seawater is the main source for metal accumulation in Antarctic sea ice and that seasonal melt mainly affects Fe input into seawater. Hendry et al. (2008) showed increased Cd in coastal Antarctic waters from terrestrial and continental shelf sediments with implications for the local Cd:PO$_4$ ratio. Their results suggest that sea ice cover influences the metal content of Antarctic deep water.

An important factor that will most likely influence the organic trace metal complexation in the Arctic Ocean is permafrost melting. A significant reduction of the permafrost regions around the Arctic Ocean is expected by the end of this century (Delisle 2007, Lawrence et al. 2008). In its 2007 report, the Intergovernmental Panel on Climate Change emphasized that '[t]he most sensitive regions of permafrost degrada-

tion are coasts with ice-bearing permafrost that are exposed to the Arctic Ocean' (Lemke et al. 2007, p. 372). However, no information about potential effects of meltwater runoff on marine ecosystems is given. Permafrost melting will introduce nutrients, organic substances, and trace metals from land into the sea in a manner that is comparable to spring snowmelt (Rember & Trefry 2004). As the Arctic Ocean is N limited as a result of denitrification in the Pacific Ocean (Yamamoto-Kawai et al. 2006), the input of nitrate will likely have a significant effect on Arctic primary productivity. Further, an increased input of organic substances could increase or decrease the bioavailability of trace metals in the Arctic Ocean via changes in their organic complexation. This could further affect the productivity of coastal ecosystems and thus may have serious consequences for the arctic marine biogeochemistry. Arrigo & van Dijken (2011) reported that the total annual net primary production (NPP) in the Arctic increased by 20% between 1998 and 2009, and the authors concluded that this was mainly caused by a reduction in sea ice cover and a subsequent increase in light intensity. The possibility that at least part of this increase in NPP could also be influenced by an increase in metal supply was not discussed, but the authors stated that: '[n]utrient fluxes into Arctic surface waters need to be better understood to determine if these projected increases are sustainable' (Arrigo & van Dijken 2011, p. 1).

Trace metal cycling is further strongly affected by the metal uptake and downward export of biota. Climate-change driven alterations in polar phytoplankton and bacterial species composition as reported by Tortell et al. (2008) and productivity might therefore have significant implications for marine trace metal cycling in the future. Phytoplankton growth is limited by Fe supply (and light) in the Southern Ocean and the subarctic Pacific. When Fe is not limiting, temperature can have a significant additional effect on diatom growth (Rose et al. 2009). Climate-related changes in the bioavailability of Fe (and other trace metals) as discussed above might therefore have strong implications for the phytoplankton community at high latitudes, especially in combination with increasing SST.

## INTERPLAY OF TRACE METAL SUPPLY, OCEAN ACIDIFICATION, AND TEMPERATURE AT LOW LATITUDES

At low latitudes, coastal upwelling, aerosol deposition, and riverine input are the major sources of trace metals to the surface oceans (Landry et al. 1997,

Mackey et al. 2002, Mahowald et al. 2005, Tovar-Sanchez et al. 2006). Riverine trace metal inputs are likely to change significantly as a result of climate change-driven effects on rainfall in these areas. In general, models predict a decrease in rainfall in subtropical regions and an increase in some equatorial regions of east Africa and Asia (Meehl et al. 2007).

Coastal upwelling brings nutrient- and trace metal-rich deep water to the surface ocean at low latitudes. Due to climate change, upwelling events are expected to become less frequent but stronger and longer in duration (Bakun 1990, Iles et al. 2012). Temperature and seawater pH shifts are expected to be less extreme at low latitudes versus high latitudes (Gruber 2011). Therefore, ocean acidification and ocean warming effects on the inorganic metal solubility are likely to be less important at low latitudes. On the other hand, the areal extent of oxygen minimum zones at high and low latitudes has already expanded (Whitney et al. 2007, Stramma et al. 2008). Future modeling predictions indicate that this process will be more pronounced in the low-oxygen regions at low latitudes (Gruber 2011), which will play an important role for nutrient and metal cycling in these regions. Oxygen minimum zones harbor a large amount of Fe in its reduced form Fe(II) that would otherwise rapidly precipitate as Fe(III) and thus get lost from the upper ocean Fe cycle (Fig. 2). Oxygen minimum zones could be a source of Fe(II) for surface waters as discussed for the Baltic Sea (Breitbarth et al. 2009). Paralleled by their role for P and Mn cycling (Turnewitsch & Pohl 2010), the regional importance of oceanic oxygen minimum zones for Fe cycling could therefore increase in the future. Similar to Fe, Cu reduction is higher under low oxygen conditions, and therefore Cu(I) concentrations could be higher here.

The reduced freshwater input into the future oceans in subtropical regions will ultimately also reduce the amount of DOM that is transported to the oceans. Therefore, organic trace metal complexation may decrease here. Whether phytoplankton/bacterial feedback mechanisms could counteract this, e.g. by an increased production of metal-binding ligands, remains speculative, but these mechanisms could play a role if the bioavailable fraction of essential metals becomes limiting.

A reduced input of DOM could also reduce the substrate availability for marine bacteria and subsequently their trace metal ligand production. On the other hand, ocean acidification has been shown to increase the activity of some microbial enzymes, which might result in enhanced polysaccharide pro-
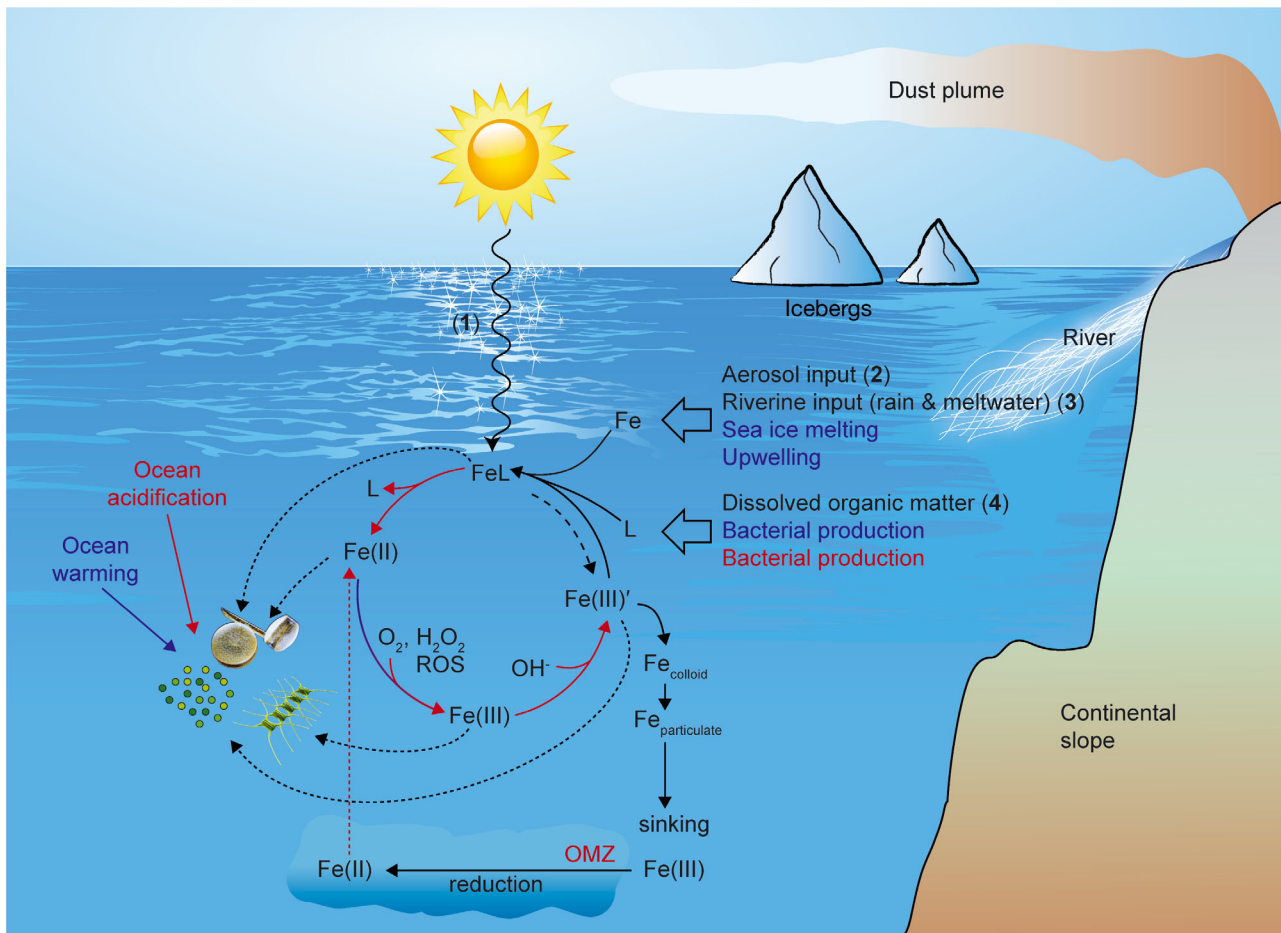
Fig. 2. Direct effects of ocean acidification (red) and ocean warming (blue) on Fe chemistry in seawater. Ocean acidification and ocean warming both influence phytoplankton and bacterial physiology with possible effects for biological Fe uptake and ligand production. Further climate change factors that may influence the marine Fe cycle are (1) changes in stratification and the effects thereof upon light climate, (2) changes in the input of dissolved organic matter, (3) changes in the input of Fe from aerosol particles, and (4) riverine inputs. FeL: ligand-bound iron; L: ligand; Fe(III)′: sum of all inorganic Fe(III) species; OMZ: oxygen minimum zone; ROS: reactive oxygen species. Iron cycle redrawn after Sunda (2001), Croot et al. (2005), and Breitbarth et al. (2009)

cessing in the future surface ocean (Piontek et al. 2010). However, effects of ocean acidification for marine microorganisms are often contradictory (Weinbauer et al. 2011), and implications for future trace metal cycling are thus difficult to predict.

At low latitudes, diazotrophic phytoplankton are a major group within the phytoplankton community (Boyd et al. 2010). Both carbon and nitrogen fixation rates of the dominant nitrogen-fixing cyanobacterium *Trichodesmium* are higher under lower seawater pH (Barcelos e Ramos et al. 2007, Hutchins et al. 2007, 2009, Levitan et al. 2007). Increasing growth rates will further increase the cellular Fe demands of nitrogen fixers, which are already higher compared to other phytoplankton groups (Kustka et al. 2003). This could result in a further increase in Fe limitation of $N_2$ fixation in the future ocean. This is supported

by observations that nitrogen fixation rates do not increase under high $pCO_2$ when Fe concentrations are depleted (Fu et al. 2008, Law et al. 2012).

Overall, increased upwelling, changes in dust deposition, and reduced riverine input will expose marine ecosystems at low latitudes to a multitude of environmental stressors in the future. Today, it is impossible to predict how these will influence the trace metal budget of these waters, but their implications for marine productivity are highly likely.

## CONCLUSIONS

Understanding the potential effects of global change on trace metal biogeochemistry requires an integrated, multidisciplinary approach combining tra-

ditionally segregated fields of geochemistry, physical oceanography, biology, and marine trace metal chemistry. The abiotic effects of ocean acidification and warming cascade into interwoven basic processes of marine biogeochemistry which need to be addressed individually as well as on a system level. These are as follows: (1) seawater pH and temperature effects on inorganic trace metal complexation, redox reactions, precipitation, and oxide aging; (2) seawater pH and temperature effects on organic metal complexation and redox cycling; (3) seawater pH and temperature effects on microbial community composition, growth, organic ligand production, phytoplankton metal uptake, requirements, and toxicity thresholds; (4) changing bioavailability of trace metals to marine primary producers as a result of (1), (2), and (3); and (5) potential biological feedback mechanisms on all of the above (Fig. 1).

We have illustrated how several environmental factors at high versus low latitudes may affect trace metal biogeochemistry in the future and how large the uncertainties of these estimations still are. However, studying these aspects results in significant methodological challenges. While recent advances in multi-element trace metal analytical protocols allow for a much improved sample throughput with excellent accuracy and precision (Milne et al. 2010, Biller & Bruland 2012), detailed metal speciation studies still require manual titrations of the metal of interest versus a competing ligand added to the seawater sample. Some working groups have developed automated protocols (S. Sander pers. comm.), which represent a great advance for sample processing of the essential organic speciation measurements. However, trace metal concentration and speciation methods still have in common the approach that the analytical solution is buffered to a standard measurement pH and measurements are performed at room temperature, making their application for ocean acidification research difficult. Refined protocols are thus needed to determine metal–organic interactions at different seawater pH and temperatures.

During its emerging phase, the ocean acidification research field was hindered by a lack of consensus on methodological issues, which has now been overcome by a community agreement in the form of a 'Guide to best practices for ocean acidification research and data reporting' (Riebesell et al. 2010). It would be unfortunate if the evolution of the interdisciplinary ocean acidification field (or in a broader context, multiple ocean change effects) and trace metal biogeochemistry, have to undergo a similarly redundant process. As an example, while performing constant pH monitoring during a trace-metal-clean phytoplankton incubation experiment, we observed that the acid cleaning treatment of the incubation bottles had lowered the seawater pH by ~0.2 units in the control treatment (Hoffmann et al. in press). A bottle pre-conditioning step with seawater was required, even though the material (LDPE) was rigorously rinsed with purified water after the last acid cleaning step. This effect likely went unnoticed and provided an accidental ocean acidification treatment in many previous trace metal clean seawater incubations. A full characterization of the seawater carbonate system throughout experiments is advised in the aforementioned guide (Riebesell et al. 2010). A community-based agreement for interdisciplinary ocean acidification–trace metal biogeochemical research that adapts this guide is needed to define suitable standards for future studies.

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