IRON AND MANGANESE IN THE OCEAN

Atmospheric Input by Dust and Coastal Ocean Time Series

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ABSTRACT

Trace metals such as iron (Fe) and manganese (Mn) are essential micronutrients in the biogeochemistry of the ocean (Turner and Hunter, 2001), and dry deposition is a substantial source of both Fe and Mn to the surface ocean (Duce and Tindale, 1991; Guieu *et al.*, 1994). Kinetic and thermodynamic values for the release of metals from dust are needed for computer models which incorporate dust as part of their ocean system. Here we investigate the thermodynamic and kinetics parameters involved in the dissolution of metals from dust in seawater. We added dust from the Sahara and the Western United States to seawater in a variety of ways to investigate the dissolution patterns of Fe and Mn.

Results show different apparent thermodynamic constants for manganese (Mn) and iron (Fe). The final Mn concentrations are proportional to the added dust concentration and light intensity, and independent of initial dissolution rate. Fe concentrations in fresh seawater reach a maximum concentration of less than 2 nM. However, depletion of organic ligands lead to the precipitation of Fe oxide from solution, and the addition of siderophores enhanced both the total Fe capacity of the seawater and the rate of Fe dissolution from dust. The first order rate constant for the dissolution of dust differed by dust source and was dependent on oxalate concentration and intensity of natural UV light. We conclude that final Mn concentrations are limited by available Mn on the dust surface, while Fe concentrations are limited by the ligand concentrations in the seawater, which ultimately are determined by the biological community.

Because the coastal ocean plays a significant role in global biogeochemical cycles, (Smith and Hollibaugh, 1993; Tsunogai and Noriki, 1991), we conducted a coastal ocean time series to investigate the basic modes and cycles which characterize the ocean. We found that Mn is highly dependent on seasonal rain events, with surface water concentrations observed as high as 30 nM after rain events. Fe within the coastal ocean is highly variable and can be used as a tool to track water mass movements and mixing patterns.

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Introduction

IRON AND MANGANESE IN THE OCEAN

Iron (Fe) and manganese (Mn) are essential micronutrients required for enzymatic pathways such as: respiration, nitrogen and carbon fixation, and electron transfer in photosynthetic marine biology (Turner and Hunter, 2001). The availability of these trace metals can be critical to the biological productivity of the ocean. Therefore, a complete understanding of the mechanisms which control the trace metal cycles, and their sources & sinks is important to the overall knowledge of biological cycles in the ocean.

Mn is specifically important for photosynthetic and radical scavenging enzymes (Horsburgh et al., 2002; Kernen et al., 2002). Thermodynamically, Mn in fully oxygenated waters at natural pH is Mn(IV) and precipitates out of the water in the form MnO_2. However, dissolved Mn ocean profiles reveal that the surface waters contain high levels of soluble Mn(II). A portion of this soluble Mn is from direct atmospheric deposition (Guieu et al., 1994; Siefert et al., 1998), and while slow oxidation to the +3 or +4 forms allow Mn to stay dissolved on the order of days, Mn should oxidize over time and precipitate from the surface ocean (Stumm and Morgan, 1996). Oxidation does occur, but the build up of oxidized Mn is prevented by organic material (Sunda et al., 1983). Light in the surface ocean can promote an electron transfer between organics, such as humic material, and Mn, resulting in the photoreduction of Mn to the +2 oxidation state. This results in a large concentration of soluble Mn in the surface water, available for biological use.

Fe is the fourth most abundant element in the Earth's crust (Wedepohl, 1995). However in oxic pH 8 seawater the stable oxidation state, Fe (III), is relatively insoluble limiting the concentration to 0.1 nM (Morel and Hering, 1993). Any inorganic iron above this concentration will either form an Fe oxide solid or quickly adsorb onto nearby surfaces

(Rose and Waite, 2002). Despite this limit, dissolved oceanic Fe concentrations range from 0.1 – 2 nM (or higher in the coastal ocean). A major source of Fe to the ocean is dust (Duce and Tindale, 1991). While these aerosols are aloft in the atmosphere, photochemical reactions with a variety of oxidants can convert a significant fraction of the total Fe into soluble Fe(II) (Siefert et al., 1996). Therefore, Fe(II) additions to the surface water from aerosol deposition can elevate the total dissolved Fe concentration (Bruland et al., 1994; Erel et al., 1993; Johansen et al., 2000); however, like Mn(II), these too will quickly oxidize. Therefore, Fe must have a non-inorganic method for maintaining dissolved Fe in the seawater. Organic ligands appear to be responsible for this elevation of Fe concentrations. (Barbeau et al., 2001; Buck et al., 2007; Rue and Bruland, 1995; van den Berg, 1995). It is believed that marine bacteria produce these organic ligands, known as siderophores, under Fe depleted conditions in order to secure ample Fe resources from the ocean water (Davis and Byers, 1971; Haygood et al., 1993). During times of Fe depletion organisms which produce these ligands and have multiple pathways for Fe uptake will not become limited in their growth and cell production.

In high nutrient low chlorophyll (HNLC) waters Fe can be the limiting or co-limiting nutrient (Maldonado et al., 1999; Martin et al., 1989; Mills et al., 2004). Early bottle incubations studies in the Gulf of Alaska confirmed that Fe limitation does control ocean productivity within HNLC regions (Boyd et al., 2007; Martin and Fitzwater, 1988). Later studies found some HNLC regions to be permanently Fe limited over time such as the Southern Ocean (Boyd et al., 2000) and Equatorial Pacific (Martin et al., 1994), and others to be seasonally limited such as the Gulf of Alaska and the Northern California Coast (Johnson et al., 2001). Because Fe limitation can control biological production in large regions of the world's ocean, Fe may be a limiting factor in the flux of inorganic carbon, in the form of carbon dioxide (CO_2), from the atmosphere to the ocean. This flux of carbon can have an influence on the total atmospheric CO_2 and therefore global temperatures possibly effecting glacial to interglacial changes. The process of atmospheric Fe input to the ocean controlling the global carbon budget and temperature is known as the Iron Hypothesis (Martin, 1990). Several mesoscale Fe addition experiments including IronEx I and II (equatorial Pacific) and SOIREE and SOFeX (Southern Ocean), have been conducted to investigate the Iron Hypothesis. Each experiment found increased phytoplankton growth, especially diatoms, followed by an increased grazer population (Boyd et al., 2007). The later experiments found that surface ocean carbon dioxide levels decreased during the course of the fertilization. However no mesoscale experiment to date has found an increase in organic carbon flux to the deep ocean or the permanent burial of carbon (Boyd et al., 2007).

Each of these Fe addition experiments were conducted in conditions far from nature. In Martin's Iron Hypothesis, dust is blown onto a HNLC ocean releasing Fe and promoting biological productivity. However, in the mesoscale experiments $FeCl_3$ is releases in pulses spaced several days apart. In a natural setting there would be dissolution of Fe from the dust, in the form of Fe(II) and Fe(III) occurring over time scales of seconds and days. Fe (III) may be complexed to organic molecules which would promote solubility, and other trace material associated with dust may also be key to a natural large scale Fe addition. In addition, for a global carbon dioxide effect, dust deposition must occur on a more continuous basis rather than the short pulses used in the experiments.

For comparison there are several natural Fe addition experiments which occur in the oceans today. Saharan dust is regularly blown off the coast of Africa and onto the North Atlantic ocean. There are periodic Chinese wind storms which blow Gobi desert dust onto the Pacific ocean, and Santa Ana winds located in Southern California can blow mineral and anthropogenic dust hundred of kilometers out to sea. (Powell et al., 1995) found Fe concentration in excess of 10 nM in the North Atlantic Ocean beneath the Sahara dust plume. These high levels of Fe have been linked to blooms of the nitrogen fixer, trichodesmium, forcing phosphate, rather that nitrate to be the limiting nutrient (Karl et al., 2002). The bio-productivity effects of Chinese dust over North Pacific have been observed by several research cruises. In one experiment, autonomous floats were released in the North Pacific to observe chlorophyll and particulate organic matter. Two coincident dust events from China revealed that chlorophyll increased over a seven day period following the dust event, and particulate organic matter was transport below the thermocline approximately two weeks following each event. These results suggest that the biological response to a natural fertilization event is different from our synthetic Fe additions.

The overall importance of Fe to the ocean and potential importance to the global temperature has be verified by both these mesoscale fertilization experiments, and many laboratory studies. This has lead to the incorporation of Fe into computer models (Aumont et al., 2003; Moore et al., 2006) to more accurately describe overall ocean biogeochemical cycles. However, data comparisons to these models can be difficult due to the lack of complete temporal and spatial coverage of the world's ocean. An alternative to the global ocean model, is a regional ocean model, such as the coastal region, which can be used as a proxy for the global ocean (Smith and Hollibaugh, 1993; Tsunogai and Noriki, 1991). The Santa Ana winds and Southern California Bight region can provide a natural Fe addition experiment along the coast.

In the present work we studied Fe addition by dust within the Southern California Bight in order to clarify several aspects of the Iron Hypothesis. We have organized our work into three sections: developing and refining an accurate Fe measurement technique, a series of dust addition experiments, and participation is a coastal ocean time series.

In order to study Fe in the ocean we need to be able to accurately measure Fe. To that end, we adapted and modified an inductively coupled plasma mass-spectrometer (ICP-MS) technique (Wu and Boyle, 1998). In this method, we concentrate the trace amount of Fe by precipitating it along with magnesium hydroxides; therefore, we can also measure any other element which adsorbs onto these magnesium hydroxide particles. In addition to Fe we measured Mn, due to its importance in ocean productivity. The first chapter will describe the mechanics of this technique, the theoretical reasons for each step, and finally the statistical information on our accuracy and precision for both Fe and Mn measurements in seawater.

Martin's Iron Hypothesis requires Fe to be released by wind blown dust into seawater. Therefore we need to understand the thermodynamics, kinetics, and mechanisms behind Fe dissolution from dust. We have conducted several laboratory experiments to study the mechanism in which trace metals, such as Fe and Mn, enter the ocean through dust input. We ran three dust dissolution experiments which we outline and discuss in chapters 2 and 3. The first experiment sought to study the differences in trace metal input by dust origin and dust concentration. Based on the results from the first experiment, our next dust experiment focused on the seawater organic background matrix, specifically concentrating on known small Fe binding molecules and aerobactin, a natural Fe binding ligand known as a siderophore. Our third experiment focused on the effects of light on dust dissolution for Fe and Mn in the presence of aerobactin.

Finally, we wanted to investigate whether a pulsed dust input into a coastal ocean region could have productivity effects. We chose to study the Santa Ana winds effect on the Southern California Bight. In collaboration with UCLA we participated in a biweekly time series in the Santa Monica Bay to examine the temporal cycles of Fe and Mn in the coastal ocean, described in chapter 4. This type of time series is needed to capture the events that may lead to changes in the biological production, but more importantly it is required to first understand the basic modes and cycles which characterize the ocean. After these background states have been observed and analyzed, the changes in biological production due to events like Santa Ana winds can be placed into their proper context.

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