THE INTERACTION BETWEEN IRON, PHYTOPLANKTON AND THE CO_2 SYSTEM

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LONG TERM GOALS

Our proposed work on the physical chemistry of coastal waters during the last cycle was not supported by ONR. We were given funds to support the wrap up of our past studies on the interaction of iron, phytoplankton and the CO_2 system. This report thus discusses our work over the last year on the iron work. It also discusses some of our measurements that were continued in coastal waters over the last year. This includes the development of flowing systems that can make continuous measurements of iron and nutrients in coastal waters. The basic aim of this work is to obtain an understanding of the chemical interactions between iron, phytoplankton, and the carbon dioxide system in the oceans. We hope to be able to determine how the growth of phytoplankton and its limitations on iron in some regions of the oceans affects the carbonate system. We also hope to determine how the speciation of iron affects its uptake by phytoplankton and examine how the competition of surface sites on phytoplankton with ligands in seawater affect the uptake.

OBJECTIVES

Iron is a biologically essential trace metal that because of its low levels may be limiting to the growth of phytoplankton in the oceans especially in areas of high nutrients and low chlorophyll. In addition iron may also affect the growth of phytoplankton in areas thought to be nitrogen limited and be a selective factor underlying the succession and diversity of phytoplankton species. It is now understood that the speciation of metals especially with organic ligands can play an important role in the availability and toxicity of metals in seawater. The inorganic and organic speciation of iron in seawater is not completely understood. Iron can exist in two oxidation states that have differences. Fe(II) is thought to be unstable in seawater and to be mostly in the free form. Fe(III) forms strong interactions with OH^- and is not very soluble in seawater. The possible existence of iron colloids adds a further complication to the activity of iron in the oceans. In this study we are attempting to understand the chemical interactions between iron, phytoplankton, and the carbon dioxide system in the oceans. We are making laboratory measurements and modeling studies to understand the speciation of iron in seawater and

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field measurements during the IRONEX studies to understand how the addition of iron to ocean waters can affect the carbonate system. This work is supported by the Office of Navel Research Physical Oceanography Program

APPROACH

Our laboratory measurements on the rates of oxidation and reduction of iron in natural waters are being made using the chemiluminese techniques developed by O'Sullivan et al. (in press) and King et al. (1995). We also are examining the speciation of iron in seawater using polarography. We are modeling the speciation using Pitzer equations (Millero et al., 1995). Our field measurements have been made as part of the IRONEX I and II studies in the equatorial Pacific. Measurements were made of the changes in total carbon dioxide, total alkalinity and partial pressure of carbon dioxide in the iron enriched patch. More recent measurements have been made in Miami coastal waters.

WORK COMPLETED

Over the last year we have completed a number of studies on the rates of oxidation and reduction of iron in natural waters and the speciation of iron (see publications). We also have examined the speciation of iron in seawater using the Pitzer model. We have used this model to estimate the solubility of iron in seawater. As part of this work we have developed methods that can be used to make continuous measurements of pH, TA, TCO_2, pCO_2, NO_3, NO_2, PO_4, SiO_2 and Fe (see references). The overall results of the first IRONEX experiment have been published (Martin et al., 1994; Watson et al., 1994). We have also completed a data report which summarizes our CO_2 measurements and two papers (in press) to a special issue of Deep-Sea Research that will contain all the work resulting from the first experiment. Several papers were published this year on the effect of iron on carbon dioxide in the oceans (see references). We participated in the IRONEX II experiment May-June 1995 and made pH, TA, TCO_2 and pCO_2 measurements. Unlike the IRONEX I studies, iron was added more than once to the patch. This resulted in a larger pull-down of nutrients and carbon dioxide. The pCO_2 was decreased by 60 μatm and the TCO_2 by 30 $\mu mol\ kg^{-1}$. The TA showed little or no changes when corrected for salinity. The combined measurements of pCO_2 by our group and the nutrients by Sakamoto and Fredrich (IMBAR) show an excellent co-variation as found in the first experiments. More recently we have used two flowing systems to study coastal waters from Miami and through the Bahama Banks

RESULTS

The Ironex experiments have led to a better understanding of the effect of nutrients and the resultant grazing of zooplankton in natural systems. The issue of whether iron additions can sequester substantial quantities of atmospheric CO_2 will lead to further debates.

IMPACT

These experiments demonstrate that open ocean manipulative experiments are possible and ecological studies in the open ocean are no longer limited to passive observations. This will change significantly the way geochemical and ecological experiments are done in the future.

TRANSITIONS

Over the last year we have initiated studies of coastal waters near Miami in cooperation with Rod Zika's group here at the University of Miami.

RELATED PROJECTS

The carbon dioxide system in the Southern Ocean and the study of ionic interactions of Fe in coastal waters.

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