

Dissolved titanium distributions in the Mid-Atlantic Bight

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Abstract

Although titanium is abundant in Earth's crust, its sources and distribution in the ocean are poorly understood. To elucidate its behavior, distributions of dissolved ($<0.2 \mu\text{m}$) Ti were determined in surface waters and vertical profiles from the Mid-Atlantic Bight (MAB). Concentrations of Ti decreased from 390 pM at the Delaware Bay mouth to <100 pM across the Delaware continental shelf. In vertical profiles, small increases in bottom waters suggest a possible flux of Ti from shelf sediments, consistent with previous reports of pore water enrichments of dissolved Ti in MAB sediments. Concentrations in surface waters of the outer shelf and slope ranged between 30 and 140 pM, with most values below 90 pM. Concentrations in a 1000 m vertical profile in the eastern Gulf Stream ranged between 110 and 280 pM, and showed a variable distribution attributed to the mixing of water masses in the outer MAB. A simple model of Ti sources to the MAB suggests that atmospheric deposition of dissolved Ti is comparable to net riverine contributions and therefore must be considered in applications of Ti as a tracer of oceanographic processes.

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1. Introduction

Titanium is abundant in Earth's crust (0.5% by weight; Taylor and McLennan, 1985), yet its behavior in the ocean is the most poorly known of all the major elements. Dissolved Ti in natural waters is highly hydrolyzed and very reactive with respect to particle scavenging, consistent with its predicted speciation (i.e., 100% as $\text{TiO}(\text{OH})_2$; Turner et al., 1981; Clegg and Sarmiento, 1989). In the ocean, this reactivity is indicated by a very short residence time of 100–200 years (Oriens et al., 1990).

The transport of dissolved Ti from rivers to the ocean is greatly influenced by reactions in estuaries, in which a

large fraction of dissolved Ti is transferred from the dissolved or colloidal phase to the particulate phase by coagulation, precipitation, or adsorption during the initial mixing of freshwater with seawater (Skrabal et al., 1992; Skrabal, 1994, 1995). Variability in the continental source (e.g., watershed size and composition, weathering intensity, river flow), estuarine reactions, and biogeochemical processes all contribute to the large dynamic range of Ti concentrations in natural waters. These concentrations range from 0.1 to >100 nM in riverine, estuarine, and near-coastal waters (Kennedy et al., 1974; Yan et al., 1991; Yokoi and van de Berg, 1991; Skrabal et al., 1992; Skrabal, 1994, 1995), and 0.005 to 0.35 nM in open ocean waters (Oriens et al., 1990; van den Berg et al., 1994). Open ocean profiles show low surface concentrations indicative of intense scavenging, with a progressive increase

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with depth suggestive of benthic fluxes or deep water remineralization (Orians et al., 1990). Marine sediment pore waters are enriched in dissolved Ti relative to overlying waters (Skrabal and Terry, 2002), indicating conditions favorable for a diffusive benthic flux consistent with the oceanographic profiles.

It has been proposed recently that the relative Ti content of marine sediments can be used to examine biogeochemical processes in the ocean, including the estimation of accumulation rates in biogenic sediments (Murray and Leinen, 1996) and the tracing of particle flux and export production (Kryc et al., 2003). The basis of these applications derives from the assumption that, although most Al and Ti are of terrigenous origin, their removal mechanisms and carrier phases in the water column differ significantly. An improved understanding of Ti geochemistry commensurate with what is known about elements such as Al might lead to further applications of Ti as an oceanic tracer.

Only the nine data points from the 2000-m vertical profile of Orians et al. (1990) in the central Sargasso Sea have been available to interpret the behavior of dissolved Ti in the Atlantic Ocean. This study addresses an important gap in our knowledge of the geochemical behavior of Ti by examining distributions in the dynamic transition zone between the coastal and open oceans. Distributions of dissolved Ti have been determined in a surface transect in the Mid-Atlantic Bight (MAB) from the eastern Gulf Stream to the mouth of Delaware Bay and in vertical profiles from the continental shelf of New Jersey and Delaware and the outer Bight. A simple model is presented to compare the relative importance of riverine and atmospheric fluxes of dissolved Ti in the MAB.

2. Study area

The MAB includes several large estuaries (Hudson, Delaware, Chesapeake) that contribute significant amounts of freshwater to the shelf, and a complex hydrography that results from the mixing of shelf, slope, Gulf Stream, and Sargasso Sea waters (Churchill et al., 1993). Configurations of these water masses relative to transect station positions during October 1991 were delineated from sea surface temperatures obtained by satellite imagery (Fig. 1). Water transport on the Delaware shelf is dominated by the Delaware Coastal Current, a persistent, buoyancy-driven flow originating from the efflux of lower salinity bay water into coastal waters of higher salinity. The Coastal Current has an average width of 20 km at a distance of 30 km south of

the bay mouth and flows southerly alongshore while maintaining nearly constant contact with the bottom (Garvine, 1991; Wong and Münchow, 1995). Sharp gradients in temperature and salinity mark the shelf/slope break (Halliwell and Mooers, 1979; Mooers et al., 1979). The dynamic nature of this front engenders various horizontal and vertical turbulent exchange processes, including entrainment and fragmentation of shelf and slope waters in filaments and eddies and transient upwelling on small spatial and temporal scales (Halliwell and Mooers, 1979; Gawarkiewicz, 1991; Churchill et al., 1993). Further seaward, the northeasterly flowing Gulf Stream interacts with cooler, fresher shelf/slope water at its western boundary and with warm, high-salinity Sargasso Sea water at its eastern boundary. Exchange processes between Sargasso Sea and Gulf Stream waters comprise various phenomena, such as filaments and rings, that cause variability in a variety of physical and biological properties in the region (e.g., Bower and Rossby, 1989; Lillibridge et al., 1990; Hitchcock et al., 1994).

3. Methods

3.1. Sample collection and processing

The data discussed in this paper were obtained on three cruises aboard the R/V *Cape Henlopen* in July 1990 and February and October 1991 (Appendix A). Locations of the surface water and profile stations occupied on the cruises are shown in Fig. 1. All samples were obtained using acid-cleaned 10-L Go Flo (General Oceanics) bottles mounted on an epoxy-coated aluminum rosette (Neil Brown) equipped with conductivity, temperature, depth, and oxygen sensors, and standard conducting hydrowire. This same system and filtration apparatus was used to collect apparently uncontaminated samples for Fe in the MAB (Wu and Luther, 1994, 1996).

Samples were filtered by pressurizing the Go-Flo bottles using high-purity, filtered N₂. Acid-washed PVC tubing was attached to the Go Flo drain outlet and connected to the filtration apparatus which was contained within a Class-100 laminar-flow clean bench. On the July 1990 and February 1991 cruises, samples were filtered through well-flushed 0.2 μm Gelman filter capsules (polysulfone filter medium) into 500 or 100 high-density polyethylene (HDPE) bottles.

Samples from these cruises were immediately frozen in dry ice and stored frozen until thawing and acidification with quartz-distilled HNO₃ (Fisher Optima; 1 mL per liter of sample, final HNO₃ concentration of

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