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The marine geochemistry of trace metals



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Abstract

The marine geochemical cycles of iron, copper, nickel, and cadmium were studied in order to provide a basis for oceanographic models for trace metals. Copper, nickel, and cadmium can be determined in a 100 ml seawater sample using cobalt pyrrolidine dithiocarbamate chelate coprecipitation and graphite atomizer atomic absorption spectrometry. Concentration ranges likely to be encountered and estimated (1 μ) analytical precisions are copper, 1 to 6 nanomole/kg (± 0.1); nickel, 3 to 12 nanomole/kg (± 0.3); and cadmium, 0.0 to 1.1 nanomole/kg (± 0.1). The technique may be applied to freshwater samples with slight modification. A survey of several east coast U. S. estuaries established that an iron removal process occurs commonly when rivers mix with seawater. Laboratory mixing experiments using water from the Merrimack River (Mass.) and the Mullica River (New Jersey) demonstrated that rapid iron precipitation occurs as negatively-charged iron-organic colloids react with seawater cations and coagulate. This phenomenon was modeled using a synthetic, organic-stabilized colloidal suspension of goethite. The generality of the mechanism suggests that the world-average net river input of iron to the oceans is less than 1 μ mole/kg of river water, an order of magnitude below previous estimates. Profiles of cadmium were obtained for 3 GEOSECS stations in the Pacific Ocean. Cadmium shows a consistent linear correlation with phosphate which demonstrates that cadmium is regenerated in a shallow cycle within the water column. The water column correlation is consistent with data on cadmium in marine organisms. Cadmium is enriched in upwelling regions which explains reports of cadmium enrichment in plankton from the Baja California upwelling region. Copper and nickel measurements have been made for three profiles from the Pacific Ocean. Observed copper concentrations range from 1 to 6 nanomole/kg; nickel varies from 3 to 12 nanomole/kg. Copper and nickel are removed from surface waters by uptake into organisms. As noted previously, nickel is regenerated partially in a shallow cycle (like P) and also in a deep cycle (like Ba). Copper is regenerated from biological debris at the bottom but is also scavenged from the mid and deep water column by an undetermined mechanism. The scavenging residence time is 1400 years. An estimate for the continental input of Ni, 7 nanomole/kg of river water, and Cu, 18 nanomole/kg of river water, was derived from measurements in the Amazon estuary. The oceanic residence times for nickel and copper are about 10,000 years. Evidence available on the uptake laws for trace metals by plankton suggests that a consistent relationship between the uptake law and the depth of regeneration may apply.

Description

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at

the Massachusetts Institute of Technology and the Woods Hole Oceanographic Institution
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