

**THE MARINE BIOGEOCHEMISTRY OF ZINC ISOTOPES**

By

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## Abstract

Zinc (Zn) stable isotopes can record information about important oceanographic processes. This thesis presents data on Zn isotopes in anthropogenic materials, hydrothermal fluids and minerals, cultured marine phytoplankton, natural plankton, and seawater. By measuring Zn isotopes in a diverse array of marine samples, we hope to understand how Zn isotopes are fractionated in the oceans and how Zn isotopes may be used as tracers of marine biogeochemical processes. Common forms of anthropogenic Zn had  $\delta^{66}\text{Zn}$  from +0.08 ‰ to +0.32 ‰, a range similar to Zn ores and terrigenous materials. Larger variations were discovered in hydrothermal fluids and minerals, with hydrothermal fluids ranging in  $\delta^{66}\text{Zn}$  from 0.02 ‰ to +0.93 ‰, and chimney minerals ranging from -0.09 ‰ to +1.17 ‰. Lower-temperature vent systems had higher  $\delta^{66}\text{Zn}$  values, suggesting that precipitation of isotopically light Zn sulfides drives much of the Zn isotope fractionation in hydrothermal systems. In cultured diatoms, a relationship was discovered between Zn transport by either high-affinity or low-affinity uptake pathways, and the magnitude of Zn isotope fractionation. We established isotope effects of  $\delta^{66}\text{Zn} = -0.2$  ‰ for high-affinity uptake and  $\delta^{66}\text{Zn} = -0.8$  ‰ for low-affinity uptake. This work is the first to describe the molecular basis for biological fractionation of transition metals. Biological fractionation of Zn isotopes under natural conditions was investigated by measuring Zn isotopes in plankton collected in the Peru Upwelling Region and around the world. Seawater dissolved Zn isotopes also reflect the chemical and biological cycling of Zn. The  $\delta^{66}\text{Zn}$  of deep seawater in the North Pacific and North Atlantic is about 0.5‰, and the dissolved  $\delta^{66}\text{Zn}$  gets lighter in the upper water column. This is unexpected based our observations of a biological preference for uptake of light Zn isotopes, and suggests that Zn transport to deep waters may occur by Zn adsorption to sinking particles rather than as primary biological Zn. The thesis, by presenting data on several important aspects of Zn isotope cycling in the oceans, lays the groundwork for further use of Zn isotopes as a marine biogeochemical tracer.

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