Germanium and silicon isotopic evolution of seawater inferred from Precambrian Iron Formations

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The metalloid germanium behaves as silicon's geochemical twin as the result of their near-identical ionic radii and coordination environments, and the behaviour of Ge and Si in modern seawater are tightly correlated. However, two important exceptions exist: (1) in hydrothermal systems where Ge/Si is elevated due to Si uptake during quartz precipitation, and (2) in continental runoff, where Ge/Si is depressed due to Ge retention during clay formation. Contrasting Ge/Si of these two major marine Ge and Si inputs has led to the suggestion that Ge/Si ratios of siliceous sediments may be used as a paleo-proxy for evolving marine Si sources and sinks. Germanium has five stable isotopes (^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, ^{76}Ge), and natural Ge stable isotope variations stand poised to provide additional constraints on marine Ge and Si cycling past and present [1]. In this work, we examine secular changes in Ge/Si and the Ge and Si isotopic compositions of Si-rich metalliferous deposits to better understand their inter-relationship and implications for the evolution of marine silicon cycling. We focus on Precambrian iron formations as they predate the modern biological silicon pump and represent >3 Gyr of inorganic marine Si cycling that remains largely unexplored. Both $\delta^{74/70}$Ge and $\delta^{30/28}$Si data demonstrate a nearly 3‰ variation over geological time and Archean IF that are isotopically light relative to later deposits. A heavy excursion in Ge isotopes alone appears to coincide with atmospheric oxygenation ca. 2.5-2.3 Ga. This new dataset will be discussed in light of the proposal that silicon isotopes in Precambrian cherts record waning hydrothermal input and cooling seawater over geological time [2].

[1] Rouxel et al. (2006) *Geochim. Cosmochim. Acta* **70**, 3387-3400.
[2] Robert & Chaussidon (2006) *Nature* **443**, 969-972.

Size-fractionated particle mass and composition during the U.S. GEOTRACES North Atlantic Zonal Transect

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Particles are a key parameter for the international GEOTRACES program because of their role in mediating the cycles of so many trace elements and isotopes (TEIs). For example, the atmospheric or margin input of lithogenic particles is a source of many TEIs to the ocean; primary producers and consumers (biogenic particles) mediate the internal cycling of TEIs; and particles of all compositions are the vector for the scavenging removal of particle-reactive TEIs to the sediments. One of the key recommendations to emerge from the 3rd GEOTRACES Data-Model Synergy Workshop was the importance of measuring total suspended mass and major particle composition for GEOTRACES. These parameters are crucial for understanding the scavenging behaviour of many TEIs.

Here we present the major particle composition and the chemically-derived particle mass of the suspended (<51μm) and sinking (>51μm) size fractions for particles collected by in-situ filtration on the U.S. GEOTRACES North Atlantic Zonal Transect in occuppied in 2010 and 2011 (NAZT'10 and NAZT'11). Results from NAZT'10 Stn 10 in the eastern tropical Atlantic, 500 km away from the Mauritanian coast, show that particulate organic matter accounts for over 80% of suspended particle mass in the euphotic zone, declining to 25% near the seafloor at 3300m. The opal and $CaCO_3$ contributions at this station were less than 8% and 27%, respectively, of the suspended particle mass. The lithogenic fraction increased with depth until it accounted for 41% of suspended particle mass by 3300m. We will contrast this station with profiles from a selection of stations that represent a wide range of particle compositions, including the oligotrophic gyres, the TAG hydrothermal site, and the western and eastern margin stations.