

Illuminating the marine sedimentary reductive iron source using iron isotopes

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Marine sediments are now well established as an important source of dissolved iron (Fe) to the oceans. In the last two decades, stable Fe isotope ratios ($\delta^{56}\text{Fe}$ relative to IRMM-014) have provided insight into the speciation, transport, and longevity of dissolved Fe sourced from dissolution of marine sediments. Studies of the ferruginous zone within sediments show that a large isotope equilibrium effect is expressed during bacterial reduction of Fe(III) minerals during oxidation of organic matter, generating a porewater dissolved Fe (dFe) pool which has lower $\delta^{56}\text{Fe}$ than sediments (-1 to -2 vs +0.1‰). Further equilibrium-driven isotope fractionation during oxidative precipitation within porewaters or overlying bottom waters may drive the $\delta^{56}\text{Fe}$ of the dFe pool even lower (-3 to -5‰). Benthic lander and bottom water $\delta^{56}\text{Fe}$ measurements from the low-oxygen Californian Margin show low $\delta^{56}\text{Fe}$ values can be preserved into marine bottom waters, despite a gradient in dFe from sediments to the water column. Recent work from the Benguela Upwelling System also shows that low $\delta^{56}\text{Fe}$ values (-4‰) in porewaters are preserved into oxygenated bottom waters. As such, reductive fluxes of dFe from sediments may have a diagnostic $\delta^{56}\text{Fe}$ signature that can be used to trace and constrain sediment addition. However, questions remain about the longevity of such signatures, fractionation associated with dFe complexation with organic matter, and kinetic isotope effects as dFe is lost via oxidative precipitation and/or scavenging. Attenuation of the sediment-derived signature may happen either at the local oxic-anoxic or sediment-water interface, or during transport through the ocean. Here, using both open-ocean GEOTRACES $\delta^{56}\text{Fe}$ studies, we will discuss the $\delta^{56}\text{Fe}$ signatures of dissolved Fe attributed to sediments, the evidence for long-distance transport of sediment-derived Fe that may maintain a diagnostic Fe isotope signatures, and the constraints on the fractionation mechanisms that may attenuate these signals. We will especially focus on work from the North Pacific where synthesis of GEOTRACES sections (GP02 & GP15) demonstrates the long-distance transport (~5000 km) of a relatively conserved $\delta^{56}\text{Fe}$ signature from reductive sediments.