

The Fe isotope case for sediments as an important marine Fe source

TIM M. CONWAY¹, HANNAH R. HUNT¹, MATTHIAS SIEBER¹, HUNG-AN TIAN², BRENT A. SUMMERS¹, NATHAN T. LANNING^{3,4}, JANELLE M. STEFFEN⁴, WILLIAM B. HOMOKY⁵, JESSICA N. FITZSIMMONS⁴, ROB MIDDAG^{2,6} AND SETH G. JOHN⁷

¹University of South Florida

²Royal Netherlands Institute for Sea Research (NIOZ)

³Massachusetts Institute of Technology

⁴Texas A&M University

⁵University of Leeds

⁶University of Groningen

⁷University of Southern California

Presenting Author: tmconway@usf.edu

Since the first measurements of stable Fe isotope ratios ($\delta^{56}\text{Fe}$ relative to IRMM-014), we have known that redox exchange between Fe(II) and Fe(III) generates large equilibrium isotopic fractionations ($\sim 3\%$). Studies of the ferruginous zone of marine sediments show that this 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 that such 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 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, with potential fractionation as dFe is complexed to organic matter, or via kinetic isotope effects as dFe is lost via oxidative precipitation and/or scavenging. Marine studies also suggest that oxidative precipitation (when dominated by kinetics) within the water column may actually drive dFe to isotopically-heavier compositions. Attenuation of the sediment-derived signature could happen either at the local oxic-anoxic or sediment-water interface, or during transport through the ocean. Additionally, based on water-column and porewater $\delta^{56}\text{Fe}$ measurements, a second mechanism of sediment dissolution, non-reductive dissolution, has been suggested. As proposed, this mechanism produces Fe(III) colloids with a lithogenic $\delta^{56}\text{Fe}$ signature, and unlike reductive fluxes, is decoupled from benthic oxygen. Here, using $\delta^{56}\text{Fe}$ from seven GEOTRACES sections or process studies in the Pacific, Atlantic and Southern Oceans, we discuss the $\delta^{56}\text{Fe}$ signature of Fe attributed to marine sediments, the evidence for long-distance transport of sediment-derived Fe