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Internal redox cycling of iron within oxygen deficient zones and its impact on the shelf to basin shuttle

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Plumes of iron(II) coincident with the secondary nitrite maximum are a ubiquitous feature within marine oxygen deficient zones (ODZs), far from reducing coastal sediments. We show that such plumes are supplied by iron(II) from reducing coastal sediments but also undergo high rates of iron(III) reduction and iron(II) oxidation internally due to microbially mediated processes. Measurements of iron(II) oxidation using an isotope tracer were carried out in situ on free-floating sediment trap arrays in the Eastern Tropical North Pacific within the ODZ. Oxidation was particle-dependent and led to the accumulation of extracellular particulate iron (probably iron oxyhydroxides). Presumably, the reaction was mediated by bacteria using nitrate as the terminal electron acceptor, consistent with measurements made in bottom waters overlying shelf sediments in Peru [1] and with Fe oxide formation within the Peruvian ODZ [2]. Iron(II) half-lives in the incubations ranged from 43 to 132 days near the shelf-slope break. Rates further offshore were slower. An inverse model (AWESOME OCIM) showed that the persistence of iron(II) within plumes cannot be explained solely by high rates of lateral advection, even when we assume an exponential decrease in oxidation rates moving offshore – there must be an in situ reduction process to balance excess oxidation. Experiments were carried out in a mesocosm simulating conditions within an ODZ, but lacking any sediment source. The mesocosm was used to investigate iron(II) production under denitrifying conditions. Replicates using unfiltered vs. 50 µm filtered seawater showed that iron(II) production occurred, but only if large particles are present in the system. This may reflect the emergence of nitrate-depleted microenvironments within such particles that create conditions thermodynamically favorable for iron reduction. Results suggest that microbial processes within the water column can have a large impact on the shelf to basin shuttle in ODZs which can ultimately control the exchange of iron between the continental shelf and ocean basin.

1. Scholz, Florian, et al. *Earth and Planetary Science Letters* 454 (2016): 272-281.
2. Heller, Maija I., et al. *Geochimica et Cosmochimica Acta* 211 (2017): 174-193.