Iron Isotope Constraints on the Archean and Paleoproterozoic Ocean Redox State

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The response of the ocean redox state to the rise of atmospheric oxygen by ca. 2.3 Ga ago is poorly constrained although deposition of BIFs until ca. 1.8 Ga suggests at least episodical deep ocean anoxia during the Paleoproterozoic. We will present a study of Fe isotope composition of sedimentary sulfides over geological time and provide evidence for a change in the ocean Fe cycle at the same time as atmospheric redox state changed.

We analyzed Fe isotope compositions of ~ 150 pyrites from 20 black shale units using a Neptune MC-ICPMS at WHOI. The emerged general pattern of Fe isotope record allows dividing the Earth's history into three stages which are strikingly similar to the stages defined by the $\delta^{34}S$ and $\Delta^{33}S$ as well as other indicators of the redox state of the atmosphere and ocean. (1) Stage 1 (>2.8 to 2.3 Ga) is characterized by highly variable and negative $\delta^{56}Fe$ values of pyrite (down to –3.5‰) that are interpreted to reflect the reservoir effects during partial oxidation of hydrothermally-derived Fe(II) and precipitation of Fe-oxides. (2) Stage 2 (2.3 to ~1.6 Ga) is characterized by $\delta^{56}Fe$ values ranging from -0.3 to 1.2‰ that might be related to the increased effect of sulfide precipitation in a redox-stratified ocean. (3) Stage 3, from 1.6 Ga through the Phanerozoic, is characterized by sedimentary pyrite having a limited range of $\delta^{56}Fe$ variations (less than 0.5‰ around igneous value at ~0‰) reflecting the establishment of an Fe-poor oxygenated ocean.