

Developing an Interpretive Framework for the Oxygen Isotope Record in Ferromanganese Crusts

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The oxygen isotope signature of atmospheric O₂ integrates several biogeochemical reactions related to the production and consumption of oxygen, including respiration, photorespiration, the Mehler reaction, and evapotranspiration. The net result of these processes is an atmospheric O₂ signature that is enriched in oxygen-18 relative to seawater. Variations in the oxygen isotope composition of O₂ can signal major changes in biogeochemical cycling of O₂. Our ability to measure the isotope composition of O₂ and the extent to which it has varied over time is limited by the availability of samples or acceptable proxies. Presently, O₂ collected from gas bubbles within ice cores is the only means by which this record has been investigated, which limits the temporal record of this signal to on the order of hundreds of thousands of years. We have shown that manganese (Mn) oxides directly incorporate oxygen from dissolved O₂ in aqueous environments. Specifically, near 50% of oxygen in Mn oxides synthesized in the lab (from biotic and abiotic origin) is derived from dissolved O₂. Here we use a suite of analytical techniques including micro X-ray fluorescence, micro X-ray absorption spectroscopy, isotope ratio mass spectrometry, and secondary ion mass spectrometry to characterize natural Mn oxide samples by their major elemental composition, redox state, mineralogy, and oxygen isotope composition. This is a preliminary step to determining if the oxygen isotope signature of Mn oxides has long term fidelity and viability as a proxy for the oxygen isotope signature of O₂.