

## **Active microbial Mn(II) oxidation mediates Cr(III) oxidation and fractionates Cr stable isotopes**

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Manganese(III,IV) oxide minerals (MnO<sub>2</sub>) are the primary naturally occurring oxidants for the oxidation of Cr(III) to Cr(VI). Since Mn(II) oxidation to MnO<sub>2</sub> requires oxygen, fractionation of stable chromium (Cr) isotopes by MnO<sub>2</sub> has been proposed as a paleoredox proxy to shed light on the oxygenation history of Earth's surface environment. However, Cr isotope fractionation during oxidation of insoluble Cr(III) to soluble Cr(VI) by manganese oxide is still poorly understood.

We investigated Cr isotope fractionation during coupled Mn(II) and Cr(III) oxidation by manganese-oxidizing bacteria in the laboratory and by natural microbial communities in water samples collected from the seasonally suboxic zone of the Chesapeake Bay, Maryland, USA. Our results show that Cr(III) oxidation catalyzed by microbial Mn(II) oxidation can induce significant Cr isotope fractionation in both laboratory cultures and in incubations with natural seawater.

Our experiments provide strong evidence for a rapid, microbially catalyzed, coupled oxidation of Mn(II) and Cr(III) in the marine environment. This suggests that, under a reducing atmosphere, the production of Cr(VI) near oxic-anoxic redoxclines by submarine weathering in shallow oceans may influence the Cr isotope signals measured in sedimentary archives.