Coupling magnetic and molecular techniques to study microbial-mediated iron and carbon cycling

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Dissimilatory iron-reducing bacteria are able to reduce iron coupled to organic carbon oxidation, often producing magnetic mineral phases. Magnetic susceptibility (MS) measurements can therefore play an important role in identifying zones where microbial-mediated iron mineral transformation is occurring so that these zones can be studied by microbiological techniques. We investigated the MS and microbial community variations in a hydrocarbon-contaminated aquifer where iron-reduction and methanogenesis are occurring. Our results show two zones of elevated MS at the contaminated locations; one occurred within the zone of water table fluctuation and coincident with high concentrations of Fe(II) and organic carbon. The second was observed in the vadose zone and associated with the methane plume. Using the polymerase chain reaction technique, *Geobacter* species were found to be present in these two zones. At the background location, *Geobacter* species were limited to the upper soil layer. Therefore, *Geobacter* species could be the main drivers of magnetic mineral formation in these zones. Using molecular methods, including denaturing gradient gel electrophoresis and DNA sequencing, we observed that *Smithella* and other syntrophic species were dominant in the zone of peak magnetic susceptibility coinciding with zones of iron reduction and methanogenesis. Our results suggest that the integration of geophysical and microbiological methods will be of value for iron and carbon cycling studies.

Post depositional transformation of Ni-rich birnessite

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Birnessite is the dominant Mn oxide in marine sediments. However, under diagenesis and mild hydrothermal conditions the phyllomanganate birnessite transforms to the tectomanganate todorokite [1-3]. Across significant areas of the seafloor birnessite is therefore a transient mineral phase. This is important because scavenging of dissolved trace metals to birnessite exerts a strong control on the concentration of these species in seawater. In particular, in the modern oceans the sorption of Ni to birnessite is the primary control on Ni oceanic concentration [4]. Ni is a bioessential element, required by primary producers and methanogenic bacteria [5]. As such understanding the sequestration of Ni to birnessite, and its fate and mobility during the transformation of birnessite to todorokite, is key to elucidating the feedbacks between Ni abundance, oceanic productivity and ultimately air-sea gas exchange. The presence of Ni in birnessite is traditionally believed to aid recrystallization to todorokite, where Ni is eventually retained in the todorokite structure, providing a potential sink for dissolved Ni [2]. Here we present the results of a novel todorokite synthesis, where we transform Ni-rich birnessite under conditions representative of marine diagenetic and mild hydrothermal settings. We have performed a time resolved study, combining XRD, BET, HR-TEM and XAS to fully characterise the transformation pathway and determine the fate and mobility of Ni during the transformation. Results facilitate our interpretation of recently collected μ-XRF and μ-XAS data, mapping Ni speciation and distribution in natural diagenetic and hydrothermal marine ferromanganese-rich sediments. We find that Ni retards the transformation of birnessite to todorokite under diagenetic and mild hydrothermal conditions, and is ultimately rejected from the neoformed todorokite during a late stage dissolution recrystallization process.

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DOI:10.1180/minmag.2013.077.5.1