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Changing chemistry of particulate manganese in the near- and far-field hydrothermal plumes from 15°S East Pacific Rise and its influence on metal scavenging

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Dissolved Mn(II) in the hydrothermal plume is known to be microbially oxidized to form Mn(III/IV) oxides, and the Mn oxides scavenge other trace elements in seawater.

In the GEOTRACES GP16 cruise, different removal rates of dMn and pMn as well as pMn size distribution were observed between the near-field (<80 km from the ridge axis) and far-field (>80 km) hydrothermal plumes from the 15°S Eastern Pacific Rise. In order to understand Mn cycling in these plumes, the spatial distribution, oxidation states, and mineral structures of Mn in small (SSF; 0.8-51 μm) and large (LSF; >51 μm) size fraction particles from the near-field and far-field plumes were examined using various X-ray based spectroscopic techniques. In the near-field plume, pMn in the SSF is dominated by oxidized Mn with Mn(III) fractions of ~30%. They are a mixture of δ-MnO_2 and triclinic birnessites that is known to be formed as a result of autocatalytic Mn(II) oxidation at the surface of freshly-formed δ-MnO_2, suggesting that both microbial and autocatalytic Mn oxidation occur in the near-field plume. The LSF pMn in the near-field plume is also oxidized and often found in large aggregates several hundreds of μm in size. In the far-field plume where Mn oxides are not newly formed, pMn in the SSF is oxidized, but their Mn(III) fractions are smaller than in the near-field pMn. The far-field plume LSF pMn is dominated by reduced Mn, implying very slow aggregation of pMn in the far-field plume. The different characteristics of pMn between the near-field and far-field plumes affect its scavenging of other trace elements. In the near-field plume, Co, Mo, ^{231}Pa are associated with pMn, but not in the far-field plume. ^{231}Pa is adsorbed to pFe rather than pMn in the far-field plume, and Pb is adsorbed to pFe in the entire plume. The result shows that freshly-formed Mn oxides in the near-field plume have higher scavenging capacity than the far-field plume pMn. Our findings suggest that the mineralogical age of Mn oxides may be an important parameter that controls the scavenging of many other trace elements and isotopes.