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Nickel release during manganese oxide transformation: The role of lattice-bound vs. surface-adsorbed Ni in Mn oxide diagenesis in the deep ocean

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Ni is an essential micronutrient for marine ecosystems, yet the processes governing its global cycling remain unresolved. Birnessite, a manganese oxide commonly found in marine sediments, is a key Mn-bearing phase that hosts Ni either as surface-adsorbed or incorporated into its crystal lattice. Over time, birnessite undergoes diagenetic transformation into todorokite, a more stable phase. Laboratory simulations of this transformation have shown that up to 50% of the surface-adsorbed Ni is released into solution. A critical, unresolved question is whether this transformation occurs rapidly enough to release Ni into seawater before sedimentation diminishes hydraulic conductivity with the overlying water column. This uncertainty arises from the fact that the in-situ kinetics of this process remain poorly constrained, largely due to the exceedingly long timescales of mineral transformation in natural settings. To address this, we simulate the process in the laboratory at elevated temperatures—accelerating the reaction—and then extrapolate the results to more realistic ocean-floor conditions (around 10 °C).

We transformed birnessite at 100°C and 75°C, pulling samples at regular intervals to extrapolate transformation rates as a function of temperature. In parallel, we performed two additional transformations using birnessite samples with differing Ni distributions: dominantly within the crystal lattice, and another dominantly adsorbed on the mineral surface. This approach allowed us to examine not only the temperature-dependent kinetics of the transformation but also how the location of Ni within the mineral structure affects its release during diagenesis. Our results show that the transformation rate at 75°C slowed by nearly 20-fold compared to 100°C. Interestingly, despite the slowed transformation kinetics, Ni concentrations released into solution were comparable to that of the 100°C transformation experiment. This suggests that Ni location within the crystal lattice likely plays a more significant role in Ni release than the bulk transformation rate. Collectively, these data demonstrate that Ni release into the water column is not directly proportional to the extent of birnessite transformation. These findings highlight the complex interplay between mineral transformation and Ni distribution within the crystal lattice, offering new insights into the timing and magnitude of Ni release in global marine systems.