

The role of trivalent manganese in transformation of layered to tunnelled manganese oxides

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Tunnelled Mn oxides (TMOs), common minerals in ferromanganese nodules of oceanic and lake sediments, host a considerable amount of transition and rare earth metals, thus mediating metal cycling in these environments. TMOs form through topotactic transformation of layered Mn oxides (LMOs), but the transformation is extremely slow at room temperature. Trivalent Mn (Mn(III)) in the LMO structure is a critical player in the transformation. However, the specific role of Mn(III) in the transformation remains unknown.

In this study, δ -MnO₂, a hexagonal birnessite analogous to vernadite, was equilibrated with Mn(II) in at pH 4 for 2 hours to prepare Mn(II)-adsorbed δ -MnO₂ (Mn(II)-bir). Then Mn(II)-bir was incubated in NaCl solution at pH 6, 7 or 8 in an anaerobic chamber or in air.

Results showed that Mn(II)-bir rapidly transformed to a 4×4 TMO. The rapid transformation was triggered by vacancy-adsorbed Mn(III) produced by the comproportionation reaction between the vacancy-adsorbed Mn(II) and Mn(IV) in δ -MnO₂. The transformation was fastest at pH 7. An incubation at pH 6 or 8 retarded the transformation due to an insufficient amount of Mn(III) (pH 6) or the formation of triclinic birnessite (pH 8) as an intermediate product. The presence of O₂ retarded at pH 8 but promoted at pH 6 the transformation. We proposed a transformation mechanism of LMOs to TMOs, highlighting the role of vacancy-adsorbed Mn(III) in the transformation.

This work changes our understanding of the TMO formation kinetics, and suggests TMOs can readily form in low-temperature redox-fluctuating environment, such as lake and oceanic sediments where Mn(II) often coexists with LMOs.