Abiotic geochemical processes forming diverse Mn oxides through various redox reactions

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Mn oxides, widely distributed in soils, are one of the most reactive minerals in the environment by controlling the fate and transport of various nutrients, contaminants, and other elements through sorption and redox reactions. Over 30 different types of natural Mn oxides exist near the Earth's surface environment with different atomic arrangement, crystallinity, and structural Mn valence, which are accounting for unique physico-chemical properties of each Mn oxide. Previoius studies focused on the reactivity of the sorption and redox reactions of specific Mn oxides with various contaminants. However, the geochemical processes controlling the formation of diverse Mn oxides have not been clearly understood yet. This study examined the formation and phase transformation of Mn oxides through various redox reactions between Mn and common redox sensitive contaminants.

Formation and phase transformation of various Mn oxides were examined through homogeneous or heterogeneous Mn(II) oxidation, and during the redox reactions between birnessite and $Cr(OH)_3(s)$. The results showed that homogeneous Mn(II) oxidation ($[Mn(II)]_0$ = 50 – 994 μM) conducted at pH 9.0 open to the atmosphere produced hausmannite (Mn_3O_4), whereas heterogeneous Mn(II) oxidation in the presence of 1.0 g/L $Cr(OH)_3(s)$ otherwise under the same conditions produced mixed valence Mn oxides analogous to birnessite. During the redox reactions between birnessite and $Cr(OH)_3(s)$ under common groundwater pH conditions (pH 7.0 – 9.0) open to the atmosphere, feitknechtite (β-MnOOH) was produced as a secondary Mn oxide phase. These results suggested that various Mn oxides can be formed through various redox reactions, and the factors controlling the formation and the phase transformation of various Mn oxides should be further investigated.