

Surface site-specific reactivity of δ -MnO₂ probed by Co(II) and quick X-ray absorption spectroscopy

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Birnessite is among the most oxidizing solid-phase species in the environment. Natural birnessite and its synthetic analog, δ -MnO₂, possess a layer-type structure with reactive vacancy or edge sites. In addition, they can contain up to 35% of Mn(III) located in the MnO₂ layers or adsorbed in the interlayer space above vacancy sites. Due to different redox properties between Mn(III) and Mn(IV) and different reactivity of surface oxygen at interlayer, vacancy and edge sites, birnessite can oxidize a range of organic and inorganic contaminants. However, the factors controlling the site-specific reactivity of birnessite are still unclear.

In a previous study using Co(II) to probe the site-specific reactivity of Mn(III)-rich δ -MnO₂ [1], we showed that Mn(III,IV) at the particle edges were mainly responsible for Co(II) oxidation in the initial fast kinetic step ($t < 10$ min), whereas interlayer Mn(III) was the main oxidant at longer reaction times ($t > 10$ min). However, the reactivity of different surface sites in a Mn(III)-free δ -MnO₂, their pH-dependency, and the oxidation reactivity of Mn(IV) compared to that of Mn(III) remained unexplored.

Here we used quick X-ray absorption spectroscopy (QXAS) to investigate site-specific reactions between Co(II) and δ -MnO₂ at pH 8, 6 and 4. At $t < 11$ min, Co(II) sorption and oxidation occurred almost exclusively on edge sites at pH 8, but reactions on vacancy sites were also significant at pH 6 and 4. At longer reaction times (< 24 h), while Co continued to be adsorbed or incorporated at vacancy sites, the amount of edge species decreased (pH 8) or remained stable (pH 6 and 4). This site-specific and pH-dependent reactivity of δ -MnO₂ could be explained by diffusion-limited adsorption processes, higher thermodynamic stability of Co vacancy species and the pK_a of the singly-coordinated O atoms on the edges lying between 6 and 8. Moreover, vacancy sites in δ -MnO₂ are much more reactive than those in Mn(III)-rich δ -MnO₂, passivated by interlayer Mn(III). These results reveal the role of different crystallographic sites and solution pH on the adsorption and oxidation reactivity of Mn oxide minerals.

[1] Simanova & Peña (2015) *Environ Sci Technol* **49**, 10867-10876.