The metal sorption capacity of biogenic birnessite is directly linked to the Mn(II) concentration present during mineral formation.

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Biogenic birnessite minerals (layer-tpe MnO_2) display a remarkable affinity for binding metals, and are thus of considerable importance towards directing the fate and transport of contaminant metals. The significant metal sorption capacity of biogenic birnessite phases is largely due to cation vacancy sites in the mineral. However, the presence of Mn(II/III) during the formation of biogenic birnessite may be a key factor in governing the reactivity of the mineral phase by sorbing to these vacancy sites. We hypothesize that increasing the initial concentration of Mn(II) during biogenic birnessite formation decreases the fraction of free vacancy sites due to the sorption of Mn(II/III).

We investigated the impact of the initial Mn(II) concentration (0.05 – 1.0 mM) supplied to the Mn-oxidizing bacterium *Pseudomonas putida* on the structural properties and metal sorption capacity of biogenic birnessite. Characterization of the solid phase was carried out by measuring the average manganese oxidation number (AMON) and the Mn(III) content. The sorption capacity of the mineral phase was determined by combining Ni sorption isotherms with Ni K-edge extended X-ray absorption fine structure spectroscopy. Our results show that the proportion of vacancy sites on biogenic birnessite that bind Ni in inner-sphere surface complexes decreases with increasing initial Mn(II) concentration present in the growth medium. The decrease in the reactivity of the mineral phase towards Ni sorption is correlated positively with an increase of the Mn(III) content and a decrease of the AMON of the mineral phase. These results indicate that the formation of biogenic birnessite in an environment containing large quantities of Mn(II) diminishes its reactivity towards metal sorption due to incomplete biological Mn(II) oxidation and the sorption of Mn(II/III) on vacancies. Our results suggest that limiting the initial Mn(II) concentration during biogenic birnessite formation or limiting the Mn(II) concentration in contact with nascent biogenic birnessite particles is key to maximize the metal sorption reactivity of the mineral phase.