pH Effects on the structure of biogenic Mn-oxides

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Mn-oxides play important roles in controlling the behavior of heavy metal(loid)s, nutrients, and organic compounds in the environment. Microbially -mediated biogenic Mn-oxides (BioMnOx) are believed to be one of the major sources of manganese oxides in soils. The reactivity of manganese oxides strongly depends on the mineralogy. Previous studies revealed that the structure of biogenic Mn-oxides is determined by the solution chemistry during formation, such as the effect of alkaline and alkaline earth metals. In this study, pH effects were investigated in CaCl2 and NaCl solutions at pH 6, 7 and 8 for 48 hours and one week reaction time during the formation of biogenic Mn-oxides (pseudomonas putida strain GB-1) using XAS and synchrotron XRD. After the formation of biogenic Mn-oxides at pH 8, the oxides were subjected to lower pH solutions (pH 7, 6 and 5) for possible pH-induced modifications, since pH changes are prevalent in the natural environment. Results indicated that at pH 8, triclinic birnessite or hexagonal birnessite with a high content of Mn(III) were formed, while at pH 6, hexagonal birnessite with low content of Mn(III) occurred. The pH 7 samples exhibit intermediate properties. One week reaction time favored the formation of triclinic birnessite or increased Mn(III) content in hexagonal birnessite. The structure of BioMnOx preformed at pH 8 in a CaCl2 solution was not modified by lower pHs of the CaCl2 solution until the solution pH decreased to pH 5. However, the structure of BioMnOx preformed at pH 8 in a NaCl solution was altered even by a pH 7 NaCl solution. This study indicates that the geochemistry of biogenic manganese oxides can be substantially affected by environmental pH.

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