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LETTER

Continuous time-resolved X-ray diffraction of the biocatalyzed reduction of Mn oxide

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ABSTRACT

Here we report the first continuous time-resolved X-ray diffraction analysis of a biologically mediated mineral reaction. We incubated total membrane (TM) fractions of the facultative anaerobe *Shewanella oneidensis* in an anoxic environmental reaction cell with formate (as electron donor via formate dehydrogenase) and powdered birnessite, a layered $Mn^{3+,4+}$ oxide common to many soils. Using both synchrotron and conventional X-ray sources, we irradiated the reaction mixtures for up to two weeks and observed bioreduction and dissolution of birnessite and the concomitant precipitation of rhodochrosite [$Mn^{2+}CO_3$] and hausmannite [$Mn^{2+}Mn_2^{3+}O_4$]. The high time resolution of these experiments documented systematic changes in crystal structure during the breakdown of birnessite and the emergence of nanocarystalline rhodochrosite. In addition, the relative abundances of birnessite and rhodochrosite were quantified over time for different concentrations of TM fraction, allowing for the determination of rate equations that govern this bioreaction. Importantly, constant irradiation for two weeks did not stop the enzymatic reaction, suggesting that enzymes may be more resilient than whole cells when exposed to X-ray radiation.

Keywords: Mn oxide, biological-mineral interactions, time-resolved XRD, birnessite, rhodochrosite, hausmannite