

# Effects of Structural Impurities on the Reactivity and Transformation Process of Hausmannite (Mn<sub>3</sub>O<sub>4</sub>)

BOJEONG KIM<sup>1</sup>, BOYOUNG SONG<sup>2</sup>, MOHAMMAD RASHID<sup>1</sup> AND EVERT ELZINGA<sup>3</sup>

<sup>1</sup>Temple University

<sup>2</sup>University of Arizona

<sup>3</sup>Rutgers, The State University of New Jersey

Presenting Author: [bkim@temple.edu](mailto:bkim@temple.edu)

Manganese (Mn) oxides are among the most ubiquitous and reactive mineral phases in natural environments, and significantly influence the speciation and distribution of trace metals and metalloids, as well as the cycles of essential nutrients. Natural Mn oxides typically contain structural impurities, such as nickel (Ni), cobalt (Co) and zinc (Zn); however, the effects of structural impurities on the reactivity and stability of Mn oxides have not been experimentally assessed. In the present work, we used hausmannite (Mn<sub>3</sub>O<sub>4</sub>), the most widely distributed spinel-structured Mn(II/III) oxide, with impurities of Ni, Co, or Zn at trace levels (up to 2 wt%) and investigated the oxidizing ability of pristine and metal-substituted hausmannite toward arsenite (As(III)). To quantify these effects, the present study integrated laboratory batch experiments, synchrotron-based X-ray absorption spectroscopy (XAS) and transmission electron microscopy (TEM) analyses. First, structural analysis by XAS indicated that Ni substitution occurred at Mn(III) octahedral sites, whereas Zn positioned at Mn(II) tetrahedral sites. Substitution of Co(II) and Co(III) occurred at Mn(II) and Mn(III) sites, respectively, with Co(II) dominating in hausmannite structure. All metal substitution in hausmannite produced changes in the lattice parameters of the pristine phase, and Ni causing the most noticeable structural modification. Secondly, both pristine and metal-substituted hausmannite minerals effectively oxidized As(III) to arsenate (As(V)) at pH 5. However, when the concentration of As(V) produced was normalized by surface area, metal-substituted hausmannite showed a higher oxidizing potential than pristine phase. Unlike redox-inactive Ni and Zn, Co(III) can contribute to the oxidizing ability of the mineral; however, due to its trivial quantity, Co(III) does not seem to be actively involved in As(III) oxidation. During the As(III) oxidation, concurrent release of structural Ni, Co, or Zn was also observed, and their release increased with substitution percentage. Finally, TEM analysis presented the changes in the mineral morphology and the formation of manganite (MnOOH) from the As(III)-reacted hausmannite. Thus, this study showcases that it is important to consider the effects of structural impurities to better predict the behavior and reactivity of natural Mn(II/III) oxides and related phases in complex surficial environments.