

Nanocrystalline features of birnessite, a layered Mn oxide, with high Ca and Zn content

EVA PROROKOVÁ¹, KORNÉL RÁCZ², LUKÁŠ
FALTEISEK³ AND TOMÁŠ MIKUŠ⁴

¹Slovak Academy of Sciences

²University of Pannonia

³Faculty of Science, Charles University

⁴Earth Science Institute, Slovak Academy of Sciences

Minerals belonging to the layered birnessite family are widely studied for their role in metal cycling in a range of terrestrial settings, for their chemical reactivity, and for their eventual biogenicity [1, 2, 3]. In addition to Mn, the cations typically occurring in terrestrial birnessites include Na⁺, Mg²⁺, K⁺, Zn²⁺, and Ca²⁺ [1]. In this work we describe the properties of a homogeneous occurrence of birnessite with an unusually high content of Ca and Zn, and only traces of other interlayer cations.

We obtained a series of nanocrystalline manganese oxide (MnO_x) samples from an abandoned mine in the Banská Štiavnica stratovolcano region, Slovakia, hosting hydrothermal, polymetallic Pb-Zn-Cu-Ag veins. One of the samples was a 15 cm-long, continuously growing MnO_x stalactite, intergrown with calcite. The MnO_x contained an uncommonly high Ca and Zn content, with the Ca/Zn ratio in the range of 1.9–2.6. Based on TEM and EMPA-WDS studies, the MnO_x material is homogeneous, consists of entangled nanosheets with a disordered, birnessite-like structure, and has a homogeneous distribution of Ca and Zn cations with an average composition of Ca_{0.31}Zn_{0.12}Na_{0.04}Mg_{0.03}Mn_{1.74}O₂·2H₂O. An inverse correlation of Zn and Ca suggests that they occupy the same position, probably above and below the Mn(IV) vacancy sites of the oxide layers [3]. Using NEXAFS, the average oxidation state (AOS) of Mn was determined as 3.90, within the range of biotic MnO_x [4]. The nanocrystallinity, high AOS of Mn, and layered structure suggest a possible biogenic influence over mineral formation. Amplicon sequencing of prokaryotic 16S rRNA gene found high microbial diversity with high relative abundance of chemolithotrophic microorganisms suspect from Mn²⁺ oxidation.

References:

- [1] Ling T.F. et al. (2020) *American Mineralogist*, 105, 833–847.
- [2] Post, J.E. (1999). *Proceedings of the National Academy of Sciences*, 96, 3447–3454.
- [3] Toner B. et al. (2006) *Geochim. Cosmochim. Acta* 70, 27–43.
- [4] Villalobos M. et al. (2003) *Geochim. Cosmochim. Acta* 67, 2649–2662.
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