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Oxalate formation by *Aspergillus niger* on minerals of manganese ores

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Abstract

Microscopic fungi (micromycetes) play an important role in rock alteration, often leading to the formation of insoluble biogenic oxalates on their surface. Oxalate crystallization under the influence of fungus *Aspergillus niger* (one of the most active stone destructors) was studied in vitro conditions on following Mn,Ca-bearing minerals of manganese ores: todorokite $(Na_{0.36},Ca_{0.09},K_{0.06},Sr_{0.03},Ba_{0.02})_{0.56}(Mn_{5.53},Mg_{0.47})O_{12}\cdot 3–4H_2O$ and kutnohorite $(Ca_{0.77},Mn_{0.23})(Mn_{0.74},Fe_{0.14},Mg_{0.11})(CO_3)_2$. The underlying minerals and the products of their alteration were investigated via powder and single-crystal X-ray diffraction, optical microscopy, SEM and EDX methods.

It was shown that more intense leaching of Ca-ions (compared to Mn-ions) from todorokite and kutnohorite leads to an earlier crystallization of calcium oxalates (predominantly whewellite) compared to manganese (lindbergite, falottaite). Crystallization of manganese oxalates on the surface of kutnohorite occurs in a more acidic (compared to todorokite) medium through the formation of mycogenic Mn,Ca-bearing oxides, which are close in composition and structure to todorokite. The possibility of structural evolution within the manganese oxalate crystalline phases caused by hydration and dehydration processes, which are responsible for changes in proportions of lindbergite and falottaite, derives from the similarities of falottaite and lindbergite crystal structures. The amorphization of falottaite in the temperature range of 70–80 °C suggests that formation of linbergite by falottaite dehydration occurs via amorphous precursor.

The result can be used for developing efficient biotechnologies using fungi for industrial enrichment of poor manganese ores and environmental bioremediation.

Keywords: Fungal biomineralization, *Aspergillus niger*, manganese oxidation, todorokite, kutnohorite, falottaite, lindbergite, whewellite, weddellite