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<sub>0.36</sub>Ca<sub>0.09</sub>K<sub>0.06</sub>S<sub>0.03</sub>Ba<sub>0.02</sub>)<sub>6</sub>(Mn<sub>5.53</sub>Mg<sub>0.47</sub>)<sub>12</sub>·3–4H<sub>2</sub>O and kutnohorite (Ca<sub>0.77</sub>Mn<sub>0.22</sub>)(Mn<sub>0.74</sub>Fe<sub>0.14</sub>Mg<sub>0.11</sub>)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>·5.53H<sub>2</sub>O. 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, falloitaite). 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 falloitaite, derives from the similarities of falloitaite and lindbergite crystal structures. The amorphization of falloitaite in the temperature range of 70–80 °C suggests that formation of linbergite by falloitaite 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, falloitaite, lindbergite, whewellite, weddellite

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**Introduction**

Microscopic fungi (micromycetes) play an important role in rock alteration often leading to a formation of insoluble biogenic oxalates on their surface (Sterflinger 2000; Burford et al. 2003; Gadd 2007, 2010; Gadd et al. 2014; Gorbushina 2007; Vlasov et al. 2020). Investigation of these processes contributes to the understanding of biomineralization mechanisms under the influence of lithobiotic microbial community and biogeochemical cycles. These create a basis for the potential biotechnological applications using fungi (Gadd 2010; Mulligan et al. 2004; Das et al. 2011, 2015, 2016; Acharya et al. 2004).

Simulation experiments with microorganisms (in particular microscopic fungi) are of great importance because they help obtaining the patterns of rock alteration by microbial action and identification of the factors controlling these processes (Sayer et al. 1997; Burford et al. 2006; Wei et al. 2012; Ferrier et al. 2019; Vlasov et al. 2020).

Manganese is a technologically important metal that has a few direct primary sources and is often mined in conjunction with other metals (Cu, Ni, and other), as well as from the low-grade manganese ores (Das et al. 2011, 2015; Acharya et al. 2004; Ghosh et al. 2016). Genuine interest in biotechnologies using diverse microbes, which leach manganese and other metals from the ores, including low-grade ores, lies in biomining, which is a superior green alternative to the current pyro-metallurgical techniques (Mehta et al. 2010; Pattnaik et al. 2019; Acharya et al. 2004; Huerta-Rosas et al. 2020; Ghosh et al. 2016; Mulligan et al. 2004). Micromycetes, which are active producers of various organic acids, are often used in biолeaching. For example, the leaching of metals from Indian ocean nodules was produced with *Aspergillus niger* (Mehta et al. 2010), the leaching of manganese from manganese ore with *Penicillium citrinum* (Acharya et al. 2003), and *Aspergillus* sp. (Mohanty et al. 2017), the leaching of heavy metals from mine tailings with *Aspergillus fumigatus* (Seh-Bardan et al. 2012). The biotechnologies for bioremediation of the environment from Mn and other toxic metals are also developed (Mota et al. 2020; Tsekova et al. 2010; Ren et al. 2009; Barbosa et al. 2016; Das et al. 2015).

The interest of the mineralogical community in studying the bioalteration of Mn-bearing minerals is caused by the significant role of manganese in terrestrial and marine biological systems as it is used by photosynthetic microorganisms for oxygen evolution (Tebo et al. 2005; Ehrlich and Newman 2009). In nature, Mn ions

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