

## SUBMICROMETER-SCALE TEXTURAL RELATIONS OF MANGANESE-BEARING MINERALS IN THE ÚRKÚT MANGANESE ORE DEPOSIT, HUNGARY

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The Toarcian Oceanic Anoxic Event (T-OAE) related geological and biogeochemical processes led to the deposition of manganese ores at Úrkút (Hungary), where both carbonatic and oxidic ore types occur. Both types have been intensively studied in the last decades and fundamental discoveries of POLGÁRI *et al.* (1991, 2012) changed our views on the genesis of the carbonatic ore. The characterisation of the oxidic ore was hindered because of the complex textural relations and the large variety of the micro- and nanometer sized manganese oxide and oxide hydroxide minerals, leaving open questions about some mineralogical processes. Thanks to the intense scientific interest and the mining activities – despite the closing of the mine in 2016 – well documented samples are still available for further research. In this study we focused on the fine micro- and submicro-scale textural relations of ore minerals with the help of samples collected from a geological profile representing an alternating sequence of both oxidic and carbonatic ore layers.

To identify the mineral species and reveal the textural features we combined X-ray powder diffraction (XRD), scanning electron microscopy (SEM), electron beam microanalysis (SEM+EDX) and Raman spectroscopy. Few hundred nanometer thin slices were cut with plasma focused ion beam technique (PFIB-SEM). EDS elemental mapping and line scans were performed for tracing the chemical (thus mineralogical) changes of resolution of a few micrometers, while SEM-BSE images allowed textural resolution even in the submicrometer range. The dominant manganese-bearing mineral phases of the deposit are manganite:  $Mn^{3+}O(OH)$ , cryptomelane:  $K(Mn^{4+}, Mn^{3+})_8O_{16}$  and rhodochrosite:  $MnCO_3$ , but other manganese-oxides and carbonates with different manganese and calcium content are also important part of the system. The three main mineral phases represent different oxidation states of manganese, so the diversity of their presence indicates geochemical changes in the environment. Tracking the various textural positions of these minerals could help the better understanding of the pre-, sin- and/or post-diagenetic mineral formation processes.

One of these key characteristic features is the bioclast-related textural position of the manganese-bearing minerals. Remnants of these – originally manganese-free – shells can be classified as follows: #1 manganese-free calcite shells surrounded and filled by oxidic manganese matrix and/or veins, #2 manganese-free calcite shells partly replaced by manganite and/or manganese oxides, #3 originally calcite shells fully

replaced by manganite and/or manganese oxides. In all cases the shape of the bioclasts is well preserved, indicating substitution processes gentle enough for resulting perfect pseudomorphs. Different degrees of replacement (#1 and #3) may occur even within the same fossil with sharp boundary. The replacement process usually starts with the formation of 1–3 micrometer thin potassium-bearing manganese oxide filling (“veinlets”) in the fissures and/or along the borders of the original shell building calcite crystals. The next step of the shell replacement is the complete exchange of calcite for manganite.

Another typical textural feature of the layers occurring through the whole profile is the presence of non-bioclast-replacing veinlets varying from a few to a few hundreds of micrometers in width. The veinlets may be monomineralic or may show a complex, submicrometer range, intimate intergrowth pattern of minimum two manganese oxides and/or oxide hydroxides of different manganese valance states ( $Mn^{3+}$ ,  $Mn^{4+}$ ), hindering the direct genetic interpretation.

Detailed analysis of the features of these mineral assemblages could help the understanding of essential mineralogical processes and the environmental conditions during accumulation and crystallization.

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