

# Oxidické minerály manganu z jihomoravských andezitoidních hornin (Západní Karpaty)

## Oxide manganese minerals from the Southern Moravian andesitic rocks (Western Carpathians)

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### Abstract

In the Tertiary andesitic rocks from the Outer Western Carpathians (ca. 15 to 11 Ma) several dikes and sills were opened for construction material extraction. Four studied samples containing manganese oxides came from the still operating Bučník Quarry near Komňa village (GPS N 48° 58.767' E 017° 47.480') and abandoned U Kyselky (Sauerbrunn) Quarry at Nezdenice (N 49° 00.594' E 017° 45.313'). All of them were collected during the second half of the 20<sup>th</sup> century and are deposited in the Museum of the South-eastern Moravia (Zlín). Samples from the Bučník Quarry form loose botryoidal aggregates of manganese minerals up to several centimetres large or fillings of fissures in the hydrothermally altered andesitic rock. Sample from the Nezdenice Quarry is formed by a brownish-black powder mixed with few goethite ochre particles. X-ray powder diffraction analysis proved mixtures of manganese oxides in all cases: birnessite with todorokite from Nezdenice and birnessite, todorokite, ranciéite, and possibly also vernadite from Bučník. Very small size of the crystal domains can be interpreted from the diffractograms, resulting from the poor crystallinity of mineral phases. Strong texturation of the powdered samples emphasizes structural planes 001 and 002 in the record. Electron microscopy shows mostly sphaerulitic aggregates, frequently with concentric zoning caused by both irregular Ba and Zn distribution and the distribution of empty spaces between the extremely thin and twisted mineral lamellae. Average birnessite chemical formula from WDS is  $\text{Na}_{0.012}\text{K}_{0.022}\text{Ca}_{0.096}\text{Sr}_{0.002}\text{Ba}_{0.104}\text{Fe}_{0.004}\text{Mg}_{0.047}\text{Zn}_{0.002}(\text{Al}_{0.034}\text{Si}_{0.012}\text{Mn}^{3.75+})_4\text{O}_{1.949}\cdot 1.462\text{H}_2\text{O}$ . Average formulae of todorokite samples are  $(\text{Ca}_{0.241}\text{K}_{0.132}\text{Na}_{0.091}\text{Mg}_{0.121}\text{Ba}_{0.017}\text{Sr}_{0.017}\text{Zn}_{0.244}\text{Pb}_{0.002})_{\Sigma 0.918}(\text{Mn}^{4+}_{5.518}\text{Al}_{0.065}\text{Fe}^{3+}_{0.009}\text{Si}_{0.024})_{\Sigma 5.616}\text{O}_{12.000}\cdot 2.800\text{H}_2\text{O}$ ,  $(\text{Ca}_{0.255}\text{K}_{0.106}\text{Na}_{0.062}\text{Mg}_{0.125}\text{Ba}_{0.165}\text{Sr}_{0.020}\text{Zn}_{0.102}\text{Pb}_{0.002})_{\Sigma 0.837}(\text{Mn}^{4+}_{5.604}\text{Al}_{0.019}\text{Fe}^{3+}_{0.010}\text{Si}_{0.015})_{\Sigma 5.661}\text{O}_{12.000}\cdot 2.815\text{H}_2\text{O}$ , and  $(\text{Ca}_{0.276}\text{K}_{0.133}\text{Na}_{0.055}\text{Mg}_{0.129}\text{Ba}_{0.087}\text{Sr}_{0.042}\text{Zn}_{0.149}\text{Pb}_{0.014})_{\Sigma 0.886}(\text{Mn}^{4+}_{5.553}\text{Al}_{0.025}\text{Fe}^{3+}_{0.013}\text{Si}_{0.023})_{\Sigma 5.614}\text{O}_{12.000}\cdot 2.807\text{H}_2\text{O}$ . Described oxidic manganese minerals probably originated during near-surface weathering of hydrothermal veins, when manganese was released during the decomposition of carbonates (Mn-rich siderite etc.), and was fixed in more stable  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  oxide minerals.

**Key words:** Outer Carpathians, andesite, supergene zone, mineralogy, birnessite, todorokite, ranciéite, vernadite

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