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Thalliomelane, $TlMn^{4+}_{7.5}Cu^{2+}_{0.5}O_{16}$, a new member of the coronadite group from the preglacial oxidation zone at Zalas, southern Poland

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ABSTRACT

Thalliomelane, a new member of the coronadite group (hollandite supergroup), was discovered at Zalas near Kraków in southern Poland (the southern margin of the Kraków-Silesia Monocline) in relics of a preglacial supergene mineralization disseminated in a fault breccia in Middle Jurassic sandy limestone. The mineralization formed at the expense of a sulfide assemblage, which was most likely the source of thallium, related to rejuvenation of Early-Paleozoic fault zones in the Sava phase of the Alpine orogeny. Thalliomelane occurs rarely and exclusively in the form of fibrous and highly porous tiny aggregates <50 μm in size that fill small fractures and voids in the sandy limestone host rock. Microprobe analyses based on 16 O and 8 octahedral cations per formula unit resulted in the mean empirical formula $[Tl_{0.77(10)}Ba_{0.21(3)}K_{0.03(1)}Na_{0.01(0)}Pb_{0.01(0)}]_{\Sigma 1.03(7)}[Mn^{4+}_{7.15(11)}Cu^{2+}_{0.63(4)}Co^{2+}_{0.08(3)}Fe^{3+}_{0.06(3)}Ni^{2+}_{0.03(1)}Si_{0.03(2)}Mg_{0.01(1)}]_{\Sigma 8}[O_{15.67(24)}(OH)_{0.33(24)}]$, corresponding to the formula $Tl(Mn^{4+}_{7.5}Cu^{2+}_{0.5})O_{16}$ for the thalliomelane end-member. The mineral crystallizes in the tetragonal system, space group $I4/m$, and has unit-cell parameters $a = 9.8664(12)$, $c = 2.8721(4)$ Å, $V = 279.59(8)$ Å^3, $Z = 1$. The crystal structure of thalliomelane, measured with 3D electron-diffraction, was refined to an R_1 index of 23.74%. Thalliomelane has the hollandite-type structure. The Mn^{4+} cations, substituted by Cu^{2+} at an amount of ~0.5 apfu, are octahedrally coordinated by oxygen atoms. Four double chains of edge-sharing (Mn,Cu)-O octahedra share corners with each other to form tunnels along the [001] direction. Tl^+ cations are located in the tunnels, occupying partially the origin and center of the unit cell. The formation of thalliomelane was most probably connected to the weathering of a sulfide mineral assemblage under semi-arid to arid climate. It resulted in the release of Tl and other components of the mineralization into water under the influence of Cl-, Br-, and I-bearing brines and pore waters from the Carpathian flysch or from sediments of the Carpathian foredeep mobilized by compaction during the Sava phase. Via the interaction of these waters, the primary ores altered mainly into goethite, cuprite, malachite, Mn oxides of the coronadite type, with subordinate Cu sulfates, Pb arsenates, Bi oxy-chlorides, and traces of iodargyrite. This assemblage indicates oxidation at a progressively increasing pH of ~8–10 and Eh of the order of +0.4–0.5 V. In this setting, thalliomelane could have formed from a cryptomelane-type Mn oxide in contact with Tl-bearing aqueous solutions through Tl-for-K exchange over time.

Keywords: Thalliomelane, thallium, Mn oxide, hollandite supergroup, coronadite group, chemical composition, crystal structure, supergene Tl mineral