Manganese oxides from Zalas, Kraków area, southern Poland

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The Zalas quarry is located in the southern, marginal part of the Silesian-Cracovian Monocline. Permian rhyodacite laccolith has been exploited here for over 70 years. The intrusion was formed about 260–280 Ma during the Early Permian transtensional, sinistral tectonic regime predominating in central Europe at that time (Nawrocki et al. 2005). Permian volcanic rocks are overlain by a Middle–Upper Jurassic sedimentary sequence, built from sands and sandstones, substituted with the passing of time by limestones and sandy limestones rich in fossils (Matyszkiewicz et al. 2006).

Quarrying operations carried out approximately 10 years ago uncovered a fault zone cutting the Middle Jurassic sandy limestones. Exposed breccias was locally encrusted by a hydrothermal mineralization forming thin veinlets cutting the limestone, or surrounding the breccia clasts. Primary mineralization contained small relics of pyrite, chalcopyrite, chalcocite, galena, native bismuth and barite and was significantly replaced by supergene minerals e.g. Fe and Mn oxides, malachite, cuprite, Cu sulphates, iodargyrite, Bi oxychlorides and Na, K chlorides (Gołębiowska et al. 2006, 2010, 2015). The mineralization is most likely connected with rejuvenation of Early-Paleozoic fault zones during the Sava phase of the Alpine orogeny, and subsequent intensive weathering under semi-arid and arid climate in a period between the Oligocene and Middle Miocene (Gołębiowska et al. 2010). In the sandy limestone encrusted by the oxidized mineralization, very interesting Mn-oxides, enriched in numerous heavy metals were encountered. They filled small fractures and voids within the fault breccia. Among them, Tl-rich varieties have been recently reported. Extremely high thallium content, reaching 20.82 wt% Tl_2O, makes the oxides unique on a world scale (Gołębiowska et al. 2015). In this paper we focused on the variable admixtures in Mn oxides from oxidation zone in Zalas; for this purpose, SEM-EDS and WDS analyses were carried out.

Mn oxides in Zalas are accompanied by malachite, Fe oxides (goethite and hematite) and relics of primary mineralization (Matyszkiewicz et al. 2015). Mn and Fe oxides commonly form the yellowish to red-brownish or black tiny grains or cryptocrystalline aggregates with sizes up to a few millimetres across.

Manganese oxides contain variable admixtures of Cu, Ca, Pb, Ba, Fe, Ni, Co and Tl. On the basis of chemical analyses, three major Mn oxide types have been distinguished: those enriched in (i) Ni and Co, (ii) Pb and (iii) Ba and Ca.

Co-Ni-bearing Mn oxides, probably asbolane-type, contain 17.01–21.58 wt% CoO and 3.05–8.33 wt% NiO. These phases contain also admixtures of Cu (up to 10 wt% CuO) and Al (up to 7 wt% of Al_2O_3), as well as traces of Fe, Ba, Zn, Mg and Tl (up to 0.5 wt%). Interestingly, in Mn oxides of this type, the admixtures of lead are absent. Pb-bearing Mn oxide, probably coronadite, contain up to 21.48 wt% PbO. In its composition various other elements were also noticed: up to 2 wt%

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CoO, 0.4 wt% NiO and very high concentrations of CuO up to 8 wt%, as well as up to 1 wt% BaO, FeO, CaO Tl_2O, Al_2O_3 and traces of Zn and Mg. Chemical mapping indicates that the Ba- or Ca-bearing Mn oxides occur only in marginal parts of zoned MnO_2 aggregates with almost pure MnO_2 in their cores. They contain 78–84 wt% MnO_2, 3–10 wt% BaO and 2.5–4.5 wt% CaO.

High contents of Co, Ni, Pb, Cu and Tl in Mn oxides from Zalas indicate a direct link with the primary ore assemblage. High concentration of cobalt and nickel might suggest some connection with Co and Ni mineralization known from nearby Karniowice Travertine (Czerny 1992). Mineral association, as well as crystal morphologies and sizes could indicate hydrothermal origin of at least part of the Mn oxides. However, identification of the particular minerals as well as concluding on the details of their origin is quite difficult on this stage of research.

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