MANGANESE MINERALIZATION IN JURASSIC SEQUENCES, SLOVAKIA

I. ROJKOVIČ

Comenius University, Bratislava, Slovakia

Abstract: Manganese mineralization is bound to Jurassic black shale, limestone and radiolarite chert. Diagenetic manganese ore forms beds and lenses in Toarcian or Aalenian shale and marl. Hydrogenetic manganese crusts and nodules occur in limestone and radiolarite chert of different age. Younger supergene manganese mineralization of Cretaceous age fills cavities and fissures in Jurassic limestone.

Key words: manganese minerals, trace elements, organic matter

Geological position

Jurassic sequences contain black shale, limestone and radiolarite chert with manganese mineralization. The Toarcian Mariatal marly shale contains manganese mineralization in the Malé Karpaty Mts. between Jablonové and Borinka. Lenses of manganese ore (5 to 8 m thick) occur in several tens of meters thick zone with increased manganese contents Manganese deposits near Lednické Rovne and Zázrivá are related to the Aalenian Posidonia Beds of the Klippen Belt represented by shale and marl (Fig.1).

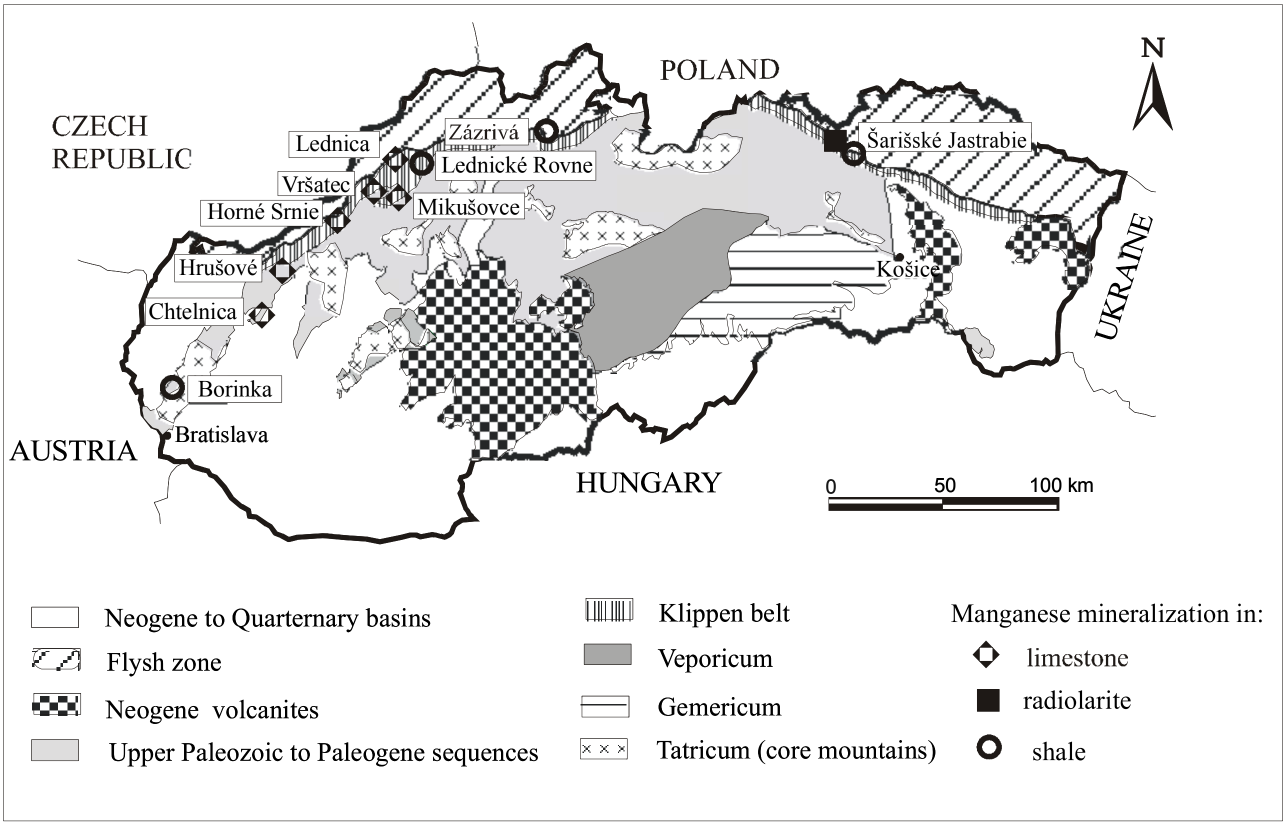

Fig. 1. Manganese mineralization in the Jurassic rocks of the Western Carpathians.

Tectonic contact of radiolarite chert with underlying shale and marly shale is mineralized near Šarišské Jastrabie. Weathered marly shale shows zoned crusts formed by iron and manganese oxides and hydroxides on lenticular fresh cores consisting of Mn-Fe carbonates. Mn-Fe oxides and hydroxides penetrated along the tectonic contact into fissures of overlying radiolarite.

Manganese hardgrounds of small extension and mostly of several cm thick occur in the Klippen Belt near Bolešov, Horné Srnie and Vršatec (Mišík 1979, Aubrecht et al. 1998, Rojkovič 1999). Manganese crusts and nodules are bound to Upper Callovian – Lover Oxfordian limestone of Czorstyn Unit. The manganese hardground (rarely up to 15 cm thick) is thin bedded in the upper part, massive in the central part (5 to 10 cm thick) and it fills the fissures in underlying limestone with ammonites. Manganese hardgrounds occur also in Toarcian limestone of the Nedzov Nappe near Hrušové in the Brezovské Karpaty and in the Choč Nappe near Chtelnica in the Malé Karpaty.

The high-grade manganese ore fills fissures and cavities in the crinoidal Bathonian limestone at the locality Mikušovce and in the Kimmeridgian – Lower Tithonian limestone at the Lednica castle. The high-grade manganese ore in Mikušovce is composed from redeposited residual sediments originated by the dissolution of the mentioned crinoidal limestone and red nodular limestone with hardground mineralization. No marine fossils are present but cavities and fissure in the Kimmeridgian – Lower Tithonian limestone at the Lednica castle contains manganese ore with abundant non-marine algae (Dragastan & Mišík 2001). Clasts of *Saccocoma* limestone from the walls and fragments of *Calpionella* limestone date the origin of these redeposited Mn-ores as post Upper Tithonian.

Mineralogy

Minerals were identified by the help of wave-dispersion analysis, energy dispersion X-ray analysis and by the X-ray diffraction analysis.

Manganese ore in the Jurassic shale consists of carbonates, oxides and hydroxides of manganese. Primary ore is represented by manganocalcite, calcite, dolomite, kutnahorite and rhodochrosite. They often form zoned aggregates with manganese rich phase, especially rhodochrosite, forming marginal part. Manganese oxides and hydroxides are mostly oxidation products of carbonates. They form beds or veinlets in dominantly carbonate rocks. They are represented by pyrolusite, manganite and todorokite. They are accompanied by pyrite, marcasite, illite, smectite, quartz, opal, barite, goethite and other iron hydroxides.

Manganese ore in Šarišské Jastrabie is composed according to Ilavský (1955) by rhodochrosite-dialogite, psilomelane and limonite. Marly shale underlying radiolarite is according our results dominated by Fe-rhodochrosite. It is replaced by todorokite, romanèchite, cryptomelane and pyrolusite. Pyrite is disseminated in marly shale as well as in radiolarite chert often in framboidal form. Goethite and other iron hydroxides replace Fe-rhodochrosite and pyrite.

Pyrolusite, „psilomelane“ and wad were described mostly as manganese minerals of oxidic ore in limestone (Andrusov et al. 1955). Recent study has confirmed pyrolusite as dominant mineral in Hrušové, Horné Srnie and Vršatec. It is accompanied by romanèchite, manganite and todorokite. Columnar stromatolites are replaced mostly by pyrolusite. Manganese minerals form colloform aggregates and they often replaced foraminifers, lamellibranches, echinoderms, ammonites and also fossil traces. Iron hydroxides dominate brown coloured hardgrounds conform to black manganese hardgrounds. Manganese nodules in Polish part of the Klippen Belt similarly as in Sicily consist of Fe-Mn minerals as hematite, goethite and todorokite (Jenkyns 1970, Zydorowicz a Wierzbowski 1986).

Younger high-grade ore in Mikušovce is characterised by dominant coarse-grained pyrolusite and manganite. The manganese mineralization filling cavities in the Lednica castle consist of dominant manganite accompanied by romanèchite and replaced by younger pyrolusite.

Geochemistry

Chemical composition of the mineralized rocks is documented by X-ray fluorescence analysis and by optical emission spectroscopy. Rare earth elements were determined by atomic emission spectroscopy with induction-coupled plasma.

Analyses of ores in shale and marl from recent dumps show (in weight %) 10 to 20 of Mn, 5 to 11 Fe in Borinka, up to 26 of Mn and up to 11 of Fe in Lednické Rovne and 6 to 10 Mn and 3 to 10 Fe in Zázrivá. Contents of organic carbon are increased up to 3 weight % in all above-mentioned deposits (Fig. 2). Co, Cu and Ni contents are very low with total mostly below 100 ppm. It is increased up to 300 ppm in rocks with pyrite accumulation only. However it is still much lower as in hardgrounds in Jurassic limestone (Fig. 3).

Chemical composition of ore from the contact between radiolarite and shale in Šarišské Jastrabie is according to Ilavský (1955) Mn - 18,9, Fe - 15,23, S - 0,16, SiO_2 - 30,6 and Al_2O_3 - 14,11 weight %. Our results show in marly shale and shale (in weight %) 14 to 23 of Mn, 4 to 16 of Fe, 30 to 65 of SiO_2, 8 to 11 of Al_2O_3 and up to 18 of CO_2. Radiolarite chert shows over 90 weight % of SiO_2 but less than 0,5 % of Mn and 0,7 % of Fe. Total content of Co, Cu and Ni in radiolarite chert as well as in shale and marly shale is less than 160 ppm.

Iron content is distinctly higher (often over 10 weight % of Fe) and Mn/Fe ratio is lower in hardgrounds and nodules than in manganese ores in shale and marl. Manganese hardgrounds in studied localities show Mn/Fe ratio 2,59. Presence of romanèchite is confirmed also by contents of Ba over 2000 ppm). Increased contents of Co, Cu and Ni are characteristic for hardgrounds and nodules in the Jurassic limestone (Fig. 3). Co shows positive correlation to Mn. Increased content of Pb and V (Hrušové and Vršatec) indicate their bond to iron hydroxides. Sr is associated with carbonates. Content of organic carbon is low (0,16 weight %).

The highest content of Mn in ore was found in manganese ore in fissures and cavities in Mikušovce and Lednica reaching up to 48 weight % with higher Mn/Fe (Nx10) comparing to sedimentary manganese mineralization in the Callovian-Oxfordian red limestone with low Mn/Fe ratio (Nx1). Increased contents of SiO_2 reflect presence of clastic quartz or secondary silicification. Relatively high contents of Ni, Co and Cu (with totals close to 1500-2000 ppm and with contents of Co close to 1000 ppm) are closer to primary hydrogenetic ore in hardgrounds of the same locality. REE distribution with dominant proportion of light REE does not indicate the presence of volcanic source for the formation of manganese ore.

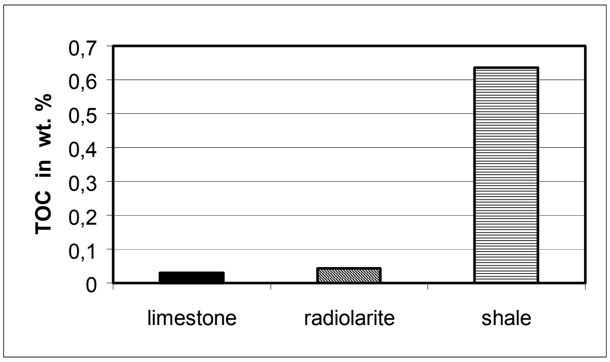

Fig. 2. Average content of organic carbon (TOC) in manganese ores.

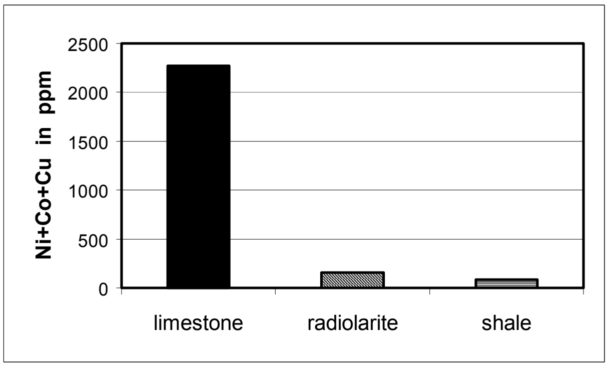

Fig. 3. Average content of Co+Cu+Ni in manganese ores.

Origin

The Toarcian anoxic event in Tethys ocean (Bellanca et al. 1999, Corbin et al. 2000) formed carbonates of manganese associated with black shale in rifted basins in on continental margin. The Toarcian Mariatal shale and the Aalenian Posidonia Beds represent black shale sediments enriched of organic matter. Manganese mineralization is closely associated with sedimentation in epicontinental anoxic environment. There is no sufficient evidence for volcanic origin (Polák 1957). The origin of manganese deposits in the Aalenian shale was explained mostly as sedimentary (Andrusov et al. 1955, Polák 1955). High content of organic carbon, low Ni, Co and Cu as well as higher Mn/Fe ratio comparing to the Jurassic hardgrounds in limestone suggests diagenetic accumulation of manganese in shale and marly shale. Their diagenetic origin may be similar as manganese concentration in Baltic Sea (Huckriede a Meischner 1996).

Ilavský (1955) presumed in Šarišske Jastrabie redistribution of disseminated manganese mineralization from radiolarite chert to its base on the contact with underlying shale. Our results suggest only redistribution of manganese and iron oxides and hydroxides during weathering from layer of Fe-rhodochrosite in marly shale.

Manganese hardgrounds and nodules formed in continental margin in topographic highs in relatively shallow water are characteristic for Jurassic of Tethys region (Jenkyns 1970, Jenkyns et al. 1991, Roy 1980). Most of the authors consider them of sedimentary origin formed according to fossils 50 -200 m below sea level (Andrusov et al. 1955, Čechovič 1942). They are associated with algae stromatolites and cover foraminifers, ammonites and echinoderm fragments. Bedding and their alternations with iron hydroxides and calcite suggest hydrogenetic up to early diagenetic origin of Fe-Mn accumulation.

Secondary high-grade ore in Mikušovce and Lednica was formed in fissures and cavities by circulating meteoric water from the manganese hardgrounds of dissolved Callovian-Oxfordian red limestone during Barremian-Aptian time.

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