OCCURRENCE OF RANCIEITE IN THE POLISH FLYSCH CARPATHIANS

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Four horizons with Mn oxide concretions were encountered in Nowa Wies near Rzeszów in the profile of the Variegated Shales Formation (RAJCHEL, 1990) of the Flysch Carpathians. These horizons occur in the upper part of the profile, in the so-called clinoptilolite–montmorillonite clays (WIESER, 1994; FRANUS & DUDEK, 1999). Up to now only diagenetic carbonate (rhodochrosite, Fe-rhodochrosite, and oligonite-ankerite) macro- and microconcretions were reported from the Lower Eocene part of the Variegated Shales (MUSZYNSKI *et al.*, 1978; WIESER, 1982). The predominating mineral of the examined concretion horizons is rancieite (Mn oxyhydroxide rich in Ca^{2+}), as it was demonstrated by scanning microprobe analysis:

I – $(Na_{0.04}K_{0.07}Ca_{1.731}Mg_{0.133}Ba_{0.004}Al_{0.014}Fe^{2+}_{0.06})_{2.052}Mn^{4+}_{5.947}O_{13.93}(H_2O)_{5.67}$;

II – $(Na_{0.03}K_{0.075}Ca_{1.755}Mg_{0.148}Ba_{0.001}Al_{0.014}Fe^{2+}_{0.052})_{2.048}Mn^{4+}_{5.98}O_{13.94}(H_2O)_{5.72}$.

Increasing activity of oxygene and Ca^{2+} ions upwards the profile is expressed by the increase of ratio: Ca^{2+}/cations < 4+ = 0.844; Ca^{2+}/cations<4+ = 0.857.

With this context in mind it should be pointed out that the Lower Eocene rancieites from Nowa Wies exhibit by far the greatest known content of calcium ions (ca. 85 %) in interstratal positions and completely oxygenated manganese in form of Mn^{4+} ions.

Weakly cemented Mn rich, gel-like material was subjected in greater degree than Mn nodules included in turbidite type sediments to granulation and redeposition by oxygen rich bottom currents. The contact with bottom water was not long enough to allow a marked enrichment in heavy metal ions, as in typical recent, hydrogenous Mn nodules, called, not without reason, metal scavengers.

Rancieite seems to be a final stage of Mn nodule transformations relying on substitution, esp. of calcium in place of alkalies with simultaneous oxidation of Mn^{2+}, Mn^{3+} to Mn^{4+} stage.

References

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