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ABSTRACT OF PhD THESIS

MINERAL AND CHEMICAL COMPOSITION, CONDITIONS OF FORMATION AND POSSIBILITIES OF USE OF OCHREOUS SEDIMENTS FROM ZABRATÓWKA NEAR DYNÓW

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Kraków 2016

The subject of the doctoral dissertation is accumulation of ochreous sediments in Zabratówka village located about 20 km north from Dynów. The area is situated in the eastern part of the Outer Carpathians, within the Dynowskie Foothills which are built of the Skole Unit formations (flysch sediments of the Lower Cretaceous - Lower Miocene age). It is characterized by a diversified relief with gentle hills and cut-up stream valleys.

The essential aim of the doctoral dissertation was to establish the mineral and chemical composition, conditions of formation and possibilities of use of ochreous sediments from Zabratówka.

The scope of research:

- field work and geophysical surveys – first of them was used to perform wells and pits, as well as collect sediment samples for further studies. The geophysical measurements were also aimed at analysis of the detection possibilities of the GPR method for outlining accumulations of Carpathian ochre. The GPR data have been interpreted on the basis of synthetic radargram obtained from numerical modeling and the results of petrophysical measurements. The results of geophysical surveys were correlated with information from boreholes and geochemical analysis;
- mineralogical and geochemical studies – e.g. chemical analyses, selective extractions, X-ray diffraction (XRD) analysis, scanning electron microscopy observations with chemical analyses in microarea (SEM-EDS) as well as Mössbauer spectroscopy have been carried out;
- microbiological tests, aimed at quantitative and semi-quantitative identification of microorganisms present in water and ferruginous precipitates;
- determination of the attributes and physicochemical properties of ochreous sediments – it allowed to propose potential and real possibilities of their practical use, e.g. as mineral sorbents or natural dyes.

In the area 49 samples were collected from 14 boreholes for further laboratory measurements. Accumulations of ochreous sediments from Zabratówka are represented by different types: typical ochre, ferruginous ochre and ochreous clay. They are characterized by variable admixtures of clastic material and various colors, from yellow through different shades of red to brown. Cemented ferruginous concretions, up to several centimeters in

diameter, were also observed in several cases. The ochreous sediments were covered with the layer of younger deluvial clays and in its bedrock there were found fragments of the Menilite Formation. Moreover, there were observed yellow and rust-coloured eruptions (ferruginous precipitates) of iron compounds emerging during outflows of underground waters.

The extent of ochre cover in Zabratówka, its form and shape, as well as the lateral and vertical borders were difficult to establish due to the lithological variability occurring in the accumulation of sediments. In order to solve these problems ground-penetrating radar method (GPR) was used for the first time for outlining accumulations of the Carpathian ochre. The results of geophysical surveys were correlated with information from boreholes and geochemical analyses (mainly based on iron content analyses). The main conclusion from this study is that the GPR method can be successfully applied, in addition to traditional geological methods, to outline accumulations characterized by an increased concentration of iron compounds.

Shales from the Menilite Formation are characterized by low content of SiO_2 and Al_2O_3, and relatively high values of Fe_2O_3, CaO and loss on ignition (LOI). This proves calcium nature of these rocks and significant ferrous concentrations, probably resulting mainly from the presence of pyrite and glauconite.

Several different classifications were applied for ochreous sediments, basing on the sieve analysis. Plotting these results on a triangular diagram by Stevens (1984) allowed to classify them into groups of sandy silt and clayey sandy silt. According to the classification of Picard (1971), they are termed sandy mud, silty mud and silty sand. On the other hand, according to the Polish construction norm PN-B-02481:1998 the sediments studied are classified as sandy silt.

The geochemical characteristics of ochreous sediments show that their composition is dominated by Fe_2O_3 and SiO_2. The amount of iron decreases with simultaneously increasing silica during the transition from the typical ochre, through the ferruginous ochre to ochreous clay. Calcium and magnesium concentrations are low but varying. Also concentrations of sodium, potassium, aluminum and titanium (and SiO_2) are significantly mutually correlated. This shows that these elements occur mainly in clastic material. The chemical composition of studied types of deposits pay attention to large values of P_2O_5 (up to 7.82 wt.%) and loss on ignition ranging from 12.21 wt.% to 23.79 wt.%. Such treatment may indicate the presence of hydrated forms of mineral or organic matter in the studied works. The trace metal

concentrations in the ochreous sediments are similar to their average concentrations detected in the earth's crust, rocks and clay soils. Most of the elements are in the range of values considered as representative for these environments. Sediments are enriched in cobalt, copper, nickel, zinc and - intensively - in arsenic, cadmium and selenium. On the other hand, the concentrations of barium, strontium, and above all beryllium display the lowest values.

Results of the mineralogical research (scanning electron microscopy and XRD analyses) indicate that goethite is the dominant iron mineral phase present in the ochre. It is poorly crystalline and accompanied by small amounts of quartz and alkali feldspars. The presence of small amounts of jarosite is possible as well. It was also found out that ferrihydrite predominates as Fe carrier in ferruginous precipitates. Such complicated mineralogy of iron is the result of progressive weathering of primary components of the menilite layers, upon which the ochre cover developed. The ochre of Zabratówka is also composed of allogenic components of which the most important are quartz, and in smaller quantities also feldspars, clay minerals and organic matters.

Analyzing the processes of weathering, migration or precipitation of iron compounds we cannot skip an important issue, which is the role of microorganisms. Results of measurements of pH, Eh and iron ions concentrations can be considered as compatible with physicochemical conditions indispensable to the functioning of bacteria *Galionella sp.* or *Leptothrix sp*., which accumulate oxidized form of iron outside cells.

Sorption properties of ochreous sediments have been also presented in the doctoral dissertation. Their sorption capacities towards Pb^{2+}, Cu^{2+}, PO_4^{3-} and CrO_4^{2-} have been evaluated in batch sorption experiments. The degree of desorption has been used for estimation of the bonding strength. Four samples representing different types of ochreous sediments (typical ochre, ochreous concretion, ferruginous ochre, and ochreous clay) have been analyzed. The selected samples differ in chemical and mineral composition, as well as in surface properties. It turned out, that the amounts of adsorbed components varied, depending on the sediment type, as follows: 10230-50753 mg/kg for lead, 1183-17848 mg/kg for copper, 3704-19703 mg/kg for phosphate, and 1607-6060 mg/kg for chromate. The experiment indicated that the cations adsorption is best modeled by the Langmuir isotherm, whereas the anions binding by the Freundlich equation. Desorption experiments have suggested that the studied cations were stronger bound to the samples richer in iron compounds. Anion desorption did not reveal such a trend. Therefore ochreous sediments from Zabratówka can be

treated as natural sorbents because those deposits bond tested ions better than clay and zeolite deposits, a natural palygorskites or fly ashes, and back down even bog irons.

On the basis of the field observations and laboratory research a conclusion can be made that ochreous sediments were probably formed as a result of chemical weathering of the lid sludge ochre menilite formation. Iron present in those layers in the form of sulfides and glauconite was mobilized and washed with sediments by chemical processes, possibly with the help of micro-organisms. After transferring into mobile forms it came out on the land surface, where it underwent precipitation in the form of hydroxides, which with time crystallized into goethite.