

Deposits in carbonated waters from selected springs of the Polish Carpathians

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Abstract: Deposits associated with the outlets of carbonated waters in the Magura Unit of the Polish Carpathians occur within spring niches and along headwater outflows. Mineralogical investigations of these deposits have identified a rusty-coloured, abundant precipitate of goethite and ferrihydrite, accompanied by calcite, dolomite, siderite and native sulphur.

Key words: the Carpathians, carbonated water, goethite, ferrihydrite

INTRODUCTION

The authors studied deposits formed at the outlets of carbonated waters, i.e. waters that contain in 1 dm³ more than 1 g of free CO₂. The springs dealt with are situated in the Magura Unit in the Polish part of the Outer Flysch Carpathians. Mineralization (TDS content) of their waters is up to 8 g/dm³ and the content of free CO₂ up to 3 g/dm³. Anions are represented by HCO₃⁻ and insignificant amounts of Cl⁻, while cations by main Ca⁺⁺ and Mg⁺⁺ and lesser Na⁺. These waters belong to the hydrogeological outer-Carpathian region DII (PACZYŃSKI ET AL., 1996) and their occurrences is limited to the Magura Unit. The sediments of this Unit represent a profile from the Middle Jurassic to Lower Oligocene and are developed as flysch, sandstone-shale complexes with intercalations of conglomerates and marls, deformed during Upper Cretaceous-Middle Eocene times. The carbonated waters of the

Polish Carpathians are associated with zones of tectonic deformation, mainly with discontinuous dislocations.

The deposits studied occur within spring niches and along headwater outflows, covering their bottoms and walls either as thin coats, a foaming gel or a jelly-like suspension (RAJCHEL ET AL., 1999, ŚWIDZIŃSKI, 1972). The thickness of these deposits varies from several millimetres to fifteen or so centimetres. The deposits resemble ochre and have colours grading from yellow to red, but most often they are rust coloured. Dry deposits are brownish-yellow and are earthy, brittle and knotty. Their presence in fields mark the existence of former springs that have disappeared due to a change in hydrogeological conditions. Such deposits were described in the area of the Carpathians in the 16th century (ZEUSCHNER, 1836). In recent times they were

recorded in the Poprad river valley (HUBICKA-PTASIŃSKA ET AL., 1984, KOSTECKA & WĘCŁAWIK, 1987, RAJCHEL & RAJCHEL, 1999, RAJCHEL ET AL., 1999). Ochres of other genesis, i.e. not associated with mineral waters, were described in the Skole Unit of the Outer Carpathians (KOTLARCZYK ET AL., 2002).

Mineralogical investigation included X-ray and thermal methods, supported by scanning microscopy. Samples were X-rayed with a Phillips APD X'Pert diffractometer, equipped with a graphite reflection monochromator. Thermal analyses were carried out with a „Derivatograph C” apparatus (Paulik-Paulik-Erdey system). Microstructural observations and chemical analyses in microareas were made with a JEOL ISM5200 scanning electron microscope with an EXL EDS-Link attachment. The amount of iron contained in ferrihydrite and in amorphous phases (Fe_{ox}) was estimated following the SCHWERTMANN (1959) procedure in an acetate buffer. The total amount of iron contained in hydro-oxides (Fe_{DCB}) was determined using the DCB method (MEHRA & JACKSON, 1960).

RESULTS AND DISCUSSION

The deposits were collected from 17 springs from the Dunajec and Poprad river valleys (RAJCHEL ET AL., 1999). Within the components of the deposits studied two genetic types of minerals can be distinguished: allo-genic, those carried away mechanically by water flowing out from rock masses, and authigenic, those of chemical origin in the form of precipitates. Another important component occurs as organic substances, associated mainly with accumulations of micro-

organisms that proliferate in water flowing out of the flysch strata. They are represented by bacteria (ferruginous and sulphurous), cyanoprocariota and algae. Among the organisms mentioned, the most important for the formation of the spring deposits in question are the ferruginous bacteria that stimulate precipitation of iron hydro-oxides. The allogenic minerals found include quartz, feldspars (potassium feldspars and sodium plagioclases), clay minerals (illite, kaolinite, chlorites). They occur in variable proportions and have not been studied in detail.

Iron occurs in the spring deposits studied in amounts from about 20 to 40 wt.% and is mainly contained in ferrihydrite and goethite. The amount of these iron minerals is usually proportional to the iron concentration of water. Almost amorphous ferrihydrite $5\text{Fe}_2\text{O}_3 \times 9\text{H}_2\text{O}$ was present in almost all samples. The $\text{Fe}_{\text{ox}}/\text{Fe}_{\text{DCB}}$ ratio, expressing the proportion of the iron contained in ferrihydrite to the total iron content in hydro-oxides, ranges from about 0.5 to 1.0. These figures prove that at least half, and sometimes all, the iron present in the spring deposits is contained in ferrihydrite. Goethite ($\alpha\text{-FeOOH}$) can be identified by the X-ray method only in deposits with lower $\text{Fe}_{\text{ox}}/\text{Fe}_{\text{DCB}}$ ratios. The width of the goethite reflections at the half-length as well as the intensity ratio of its 110 and 111 reflections prove that the goethite of the spring deposits is fine-crystalline, with a poorly ordered internal structure. Iron hydro-oxides occur most often as platy aggregates with sizes in the range of 1-2 mm. They frequently contain admixtures of Si, Ca and Mn. Minerals containing bivalent iron are represented by sporadically occurring carbonates: ferric dolomite and siderite.

In most of the samples authigenic calcite was found in the form of rhombohedral, micrometer-sized, isometric grains. Its contents, estimated on the basis of the mass loss during thermal dissociation, is from about 1 to 30 %, being significantly higher in the spring deposits precipitating from waters with higher concentrations of Ca and hydrogen carbonates. Small amounts of native sulphur were found in single samples. Organic substance is a significant component of the spring deposits; the degree of its alteration is variable.

Besides the correlations mentioned above, no simple relations between the chemical composition of the carbonated waters and the mineral composition of the respective precipitates have been found. It particularly refers to mutual proportions among iron hydro-oxides, as their genesis results from the superposition of various factors. The variables include not only concentrations of Fe, but also the form in which iron occurs in water (e.g. the type of iron-bearing complexes) and the presence of other ions that can promote or hamper precipitation of one of the iron minerals. For instance, the formation of ferrihydrite is favoured by elevated concentrations of silicate, phosphate, or some organic ions (CORNELL & SCHWERTMANN, 1996), while goethite precipitates more often in the zones enriched in dissolved CO₂. It is also worth mentioning that iron hydro-oxides can evolve after their formation, being prone to various transformations. It is particularly characteristic of ferrihydrite that it is thermodynamically metastable and with

the passage of time should recrystallize into goethite and/or hematite. The time of this transformation and the type of end product (mineral) strongly depend upon the conditions of the environment. Finally, it should not be forgotten that the formation of iron minerals under hypergenic conditions is inherently associated with microbiological processes, resulting particularly from the amount and type of ferruginous bacteria. These bacteria develop with variable intensity in the waters even with insignificant differences in their physical and chemical properties, such as pH, temperature or the content of total dissolved solids (LUNDGREN & DEAN, 1979).

CONCLUSIONS

The main minerals precipitating from the carbonated waters of the Carpathians include iron hydro-oxides: ferrihydrite and goethite, accompanied usually by calcite and sometimes by dolomite and siderite. The concentration of the main phases, i.e. of the iron hydro-oxides and calcite are, in most cases, proportional to the concentrations of Fe and Ca in the parent waters.

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