

## EUHEDRAL CALCITE IN CARBONATIC CONCRETIONS FROM QUATERNARY PALEOSOL ENVIRONMENT, GYÖNGYÖSVISONTA, HUNGARY

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Carbonate concretions, including grown up, fine, euhedral crystals of calcite were discovered in the open cast lignite mine at Gyöngyösvisonta, in the southern foreland of the Mátra Mountains, Hungary. The concretions are embedded in a thick (8–10 m) paleosol (red clay) sequence sedimented on Pannonian age strata. They attracted our attention because such calcite crystals are very common in hydrothermal environments, but seemed to be unusual in a soil-related environment.

Our aim was to describe the morphological appearance of the crystalline calcite in the concretions and to obtain information about their formation.

In order to get morphological data we applied stereomicroscopy, scanning electron microscopy and two-circle reflecting goniometer measurements. Two main morphological types of calcite were found. The rhombohedral type is built up of the combination different rhombohedra, while the scalenohedral type is built up of the combination of rhombohedra and scalenohedra.

X-ray powder diffraction patterns showed two types of calcite. The micritic wall of the concretions and the root zone of the euhedral crystals consisted of pure calcite. In the coronal zone of the crystals, beside the pure calcite, another, slightly substituted calcite of shorter lattice parameter ( $d_{104} = 2.98 \text{ \AA}$ ) can also be detected.

That substituted calcite region was studied in detail by cathode luminescent microscopy and by SEM+EDX. We found growth zoning of calcite in that part of the samples. The width of the individual zones varies between 50 and 150  $\mu\text{m}$ . The zoning is caused by chemical substitution. In the cathode luminescent microscope an unusually strong luminescence of these zones (in "pure" calcite) could be seen. Back scattered electron images showed the presence of cation(s) of larger average atomic number than calcium in the luminescent zones. Based on EDX measurements the substituting element is manganese (3–6 cation%). Pure calcite and manganese bearing calcite are separated by sharp boundaries. The oscillatory precipitation of the two phases resulted in the formation of several, sometimes many tens, manganese free and manganese containing zones.

Carbon and oxygen stable isotope analysis was carried out on a set of samples representing 1) the micritic wall of

the concretions, 2) the root zone and 3) the coronal zone of the euhedral calcite crystals. The results can be interpreted as the euhedral crystals precipitated in a closed system inside the concretions. There is no data indicating any elevated temperature (hydrothermal) formation condition.

The closed system crystallization raises the question on the origin of the growth zoning of calcite. In an open system chemical changes of the fluid could be assumed, in a closed system physical environmental parameters, in our case mainly temperature and maybe temperature related biological activity could be responsible for the entrance of manganese in the calcite lattice.

For a better understanding of the genetic conditions we studied also the black, mm sized nodules to be found both in the paleosol (red clay) environment of the concretions and encapsulated in the micritic wall of the concretions themselves. Based on X-ray diffractometry and optical emission spectroscopy they turned out to be mixtures of (detrital) quartz and poorly crystallized oxides and oxy-hydroxides of iron (goethite and hematite). Their manganese content is in the 1000–10000 ppm range. There was no significant difference between the nodules separated from the micritic wall and from the red clay, thus we consider the former ones as relicts of the red clay environment in the concretions.

Based on our data we reconstruct the formation of the concretions as follows:

In the first phase loose, calcareous concretions formed in the red clay sequence. In a second step volume changes, coming from alternation of dry and humid climatic periods caused cracks in the concretions within the soil. In these cracks calcite growth started, resulting both the thickening of the wall of the concretions and, simultaneously or subsequently, the precipitation of the root zone of the euhedral crystals. Concretions became thick-walled, at most 35–40 cm in diameter, bodies due to subsequent solutions and final desiccation. Inside the concretions, in the closed cavities crystallization of euhedral calcite continued, resulting bigger and bigger crystals towards the inside of the concretions.

We hope that our results contribute not only to the better understanding of the formation of concretions, but also to that of the development of the whole soil environment.