Physico-chemical constraints of apatite and crandallite formation in phosphorites from Ervenik, Croatia

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Apatite group minerals and their secondary alteration phases were studied of Upper Cretaceous phosphorite-bearing deposits. Outcrops of these deposits are situated at the foot of the SE part of Mt. Velebit near Ervenik, Croatia. Phosphorite deposits can be found in fossil caves, caverns and other karstic phenomena in limestone, generally of Cretaceous age. The exact age of the deposits is not known but is assumed to be Pleistocene. The source of phosphorus could be the phosphate-rich guano material originating from bats and birds (Marković 2002).

Collected sediment samples were disintegrated, or cut and polished and analyzed by optical microscopy, SEM, EDS, and XRD. Phase stability diagrams were constructed on the basis of mineral phases identified in the samples. The aluminum, calcium and phosphate concentrations chosen for stability field calculations are considered normal for pore fluids in contact with soil and sediments (Nriagu 1976). The phosphate minerals occur as white to greyish spherulitic aggregates or single crystals up to 2 mm in size. Cave sediments are usually compact and reddish or greyish in colour, with a high Al₂O₃ and FeO content, but low in carbonate. Optical microscopy and SEM of spherulitic aggregates showed at least two different phosphate phases identified by EDS and XRD as hydroxylapatite and crandallite. In the inner core of the spherulites, apatite is precipitated in the form of sprays up to 1.5 mm in length; outer parts of the spherulites volume is contain very fine grained radial to fibrous crandallite. Some spherulites are banded and composed of alternating apatite and crandallite layers.

Apatite and crandallite spherulites were formed during early diagenesis of the cave sediment; each single spherulite was precipitated in partially closed microenvironment of the sediment voids and pores. Apatite occupying the central portions of the spherulits centre was formed prior to crandallite in the outer spherulite sector. The calculated stability fields for apatite and crandallite may be used to explain the bi-phase precipitation in the spherulites. Higher phosphate and lower aluminum concentrations with higher pH will favour apatite precipitation; such conditions prevailed during precipitation of the spherulite core. As a consequence of apatite precipitation, phosphate concentration is decreased and aluminum is increased, the stability field of crandallite prevails and crandallite becomes stable phase precipitating in the spherulite outer volume.
