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**18th INTERNATIONAL KARSTOLOGICAL SCHOOL
"CLASSICAL KARST"**

DINARIC KARST



GENERAL INFORMATION, PROGRAMME, FIELD TRIPS, ABSTRACTS

Postojna, 2010

CAVE SEDIMENTS DIAGENETIC HISTORY RECORDED IN PHOSPHATE MINERAL ASSOCIATION

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Cave sediments are regularly enriched in phosphates, mainly originating from bat guano or vertebrata skeletal remains. One of such deposit, rich in phosphates, is situated near Ervenik, at the foot of the SE part of Mt. Velebit, Croatia. The phosphates are probably Lower Pleistocene in age, situated in caves within Cretaceous limestones. The phosphorus source is phosphate-rich guano material originating from bats and birds. These primary phosphates, in relatively short time (days or weeks) during sedimentation and early diagenesis, transform into geochemically most stable mineral phase. Stability of new mineral phases is result of physical and geochemical conditions in the cave sediment in the time of their formation. The main factors controlling phosphate phase stability in the cave environment are pH, Eh and ion activities (Nriagu, 1976). In described case, phosphate infillings determined as hydroxylapatite and crandalite in spherulitic form were found inside cave deposit. To explain the precipitation in the spherulites and diagenetic environment the stability fields for apatite and crandalite were calculated. Environmental conditions favoring apatite precipitation, with high phosphate, lower aluminum and higher pH, prevailed during precipitation of the spherulite core. Crandalite was formed during higher aluminum and lower phosphate concentrations, and lower pH. Variation in pH was probably caused by guano and other organic material decay during sedimentation and early diagenesis. Apatite was formed in the first phase of the sediment diagenesis during organic material decomposition which released significant amount of phosphate, carbonate in the environment buffered solution to higher pH values. Crandalite precipitated after apatite, when phosphate activity was lower. Due to the given example, associations of authigenic phosphate minerals can be used to reveal sedimentary and diagenetic conditions during fossil cave sediments formation.

References:

- Nriagu, O. J. (1976): Phosphate-clay mineral relations in soils and sediments. *Canadian Journal of Earth Sciences* 13, 717–736.

Keywords: cave sediments, phosphate, diagenesis, phosphorite