The complex mineralogical and physical-chemical investigation of Cretaceous vertebrate remains from the Hațeg Basin, Romania

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Detailed information concerning the pre- and post-burial modifications that affect the remains of ancient organisms (i.e. their taphonomy) are instrumental in appreciating the ways the fossil record is biased by biological and geological processes. Reconstructing taphonomic history also allows a more accurate understanding of the paleoenvironmental and paleoecological conditions that controlled different ancient ecosystems. The uppermost Cretaceous (Maastrichtian) deposits of the Hațeg Basin (western Romania) yielded a rich and diverse vertebrate assemblage with dwarf dinosaurs. Unlike recent advances in reconstructing the environment this fauna lived in, very few information is available about the diagenesis of the vertebrate fossils. Here, we investigate small samples of vertebrate (including dinosaur) remains from two important fossiliferous sites of the Hațeg Basin, belonging to different formations, and representing different sedimentary environments, with the aim to identify the diagenetic processes that led to their preservation.

Microscopic study of the fossil bone remains revealed the quasicentric texture of the primary phosphates. Osteon remodeling (phosphates) around the Haversian system led to concentric arrangement of phosphate, subsequently being filled with calcite during diagenesis. Primary lamellar, gray-colored phosphates often show later carbonation phenomena that replace the phosphates. Brown to red-purple secondary (anisotropic) phosphate appear among primary phosphate lamellae. Secondary phosphate occurs within carbonate matrix, which represents the mineralogical evidence of secondary phosphate crystallization after that of the carbonates. The presence of fine-grained cryptocrystalline collophane (isotropic) near primary concentric phosphate could by interpreted as a diagenetic phosphate recrystallization.

Angular clasts suggest a practically non-existent transport. Quartz (with undulose extinction) and feldspar (polysynthetic twinning, albite, oligoclase) are reworked from metamorphic (quartz) or magmatic (feldspar) rocks. Bones are not enveloped by a thick mineral matrix (determined by environmental conditions), suggesting that they were drawered of water and quickly buried, without being transported over long distances.

The RX diffractometry (XRD) performed on powders of global aggregate samples revealed the massive presence of calcite in all samples, confirming the conclusion of microscopic examination related to the substitution of primary phosphates by carbonates. Diffraction patterns obtained on each of fossilized bone samples showed that mineralogy is roughly the same (fluorapatite, hydroxylapatite, francolite, dahllite, chlorapatite, and calcite - present in all samples). The only difference is observed on samples of Tuștea, where monetite from juvenile bones occurs.

FT-IR absorption spectra on the paleontological samples show the characteristic band PO₄³⁻ of hydroxylapatite structure. It is significant that the CO₃²⁻ group from the hydroxylapatite structure could not be isolated in any sample, meaning that replacement processes of the PO₄³⁻ and OH⁻ groups by carbonate in apatite have not occurred. We consider that the carbonate-bearing apatite documented by diffraction is in fact related to the primary bone constituent, the so-called bioapatite (i.e. carbonate-
hydroxylapatite). On the other hand, the presence of characteristic IR bands for CaCO$_3$ in all samples proves the calcification of the bones as another effect of fossil-diagenesis.