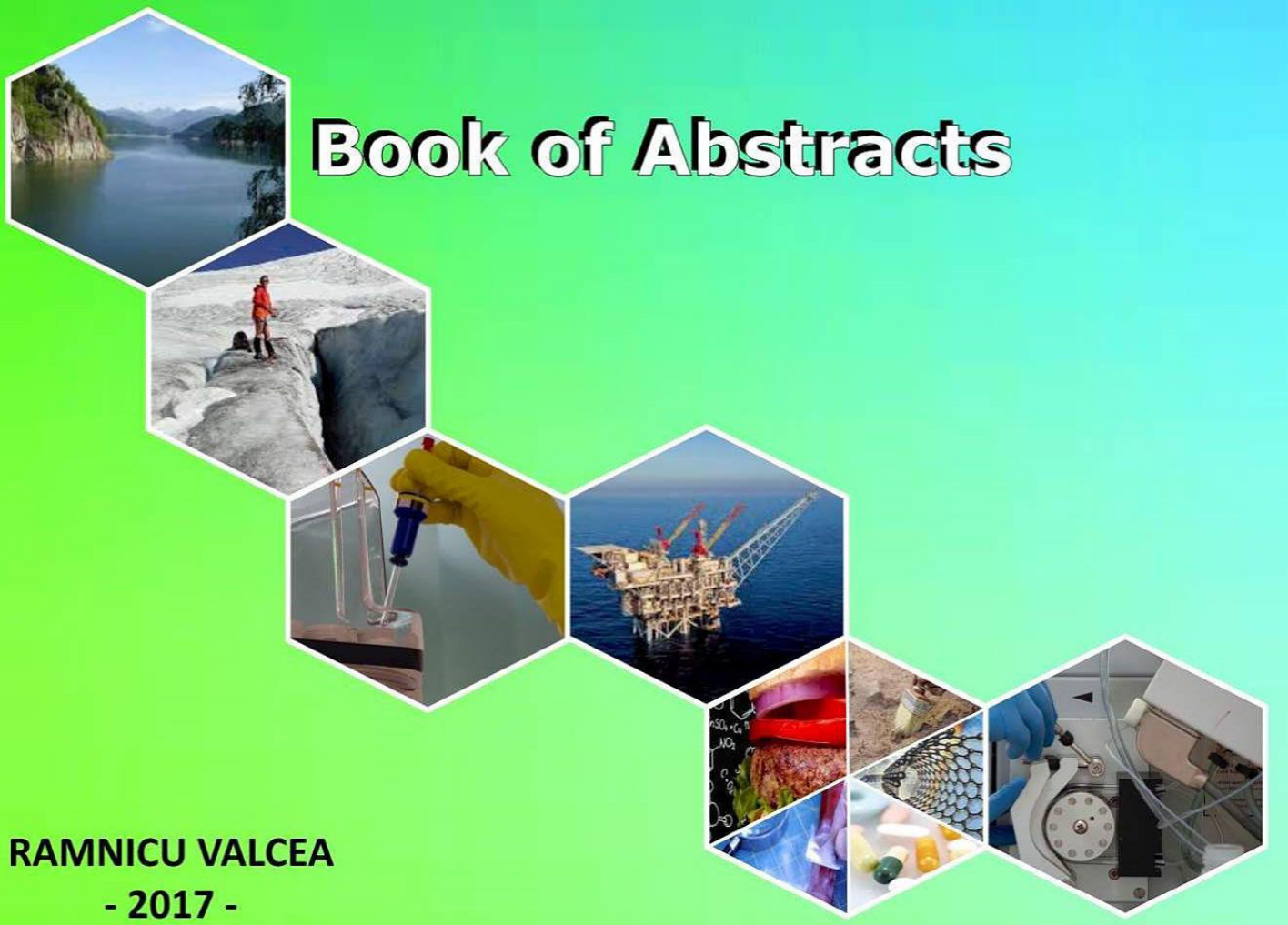
The XIVth Workshop of the European Society for Isotope Research - ESIR 2017 -

Băile Govora, ROMANIA
25-29 June, 2017



Book of Abstracts

RAMNICU VALCEA
- 2017 -

AUTHIGENIC FORMATION OF NANOSTRUCTURED CALCITE IN A LACUSTRINE KARSTIC ENVIRONMENT (KUTI LAKE, CROATIA): STABLE ISOTOPE AND *FESEM* STUDY

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The formation of authigenic calcite and isotopic composition of the sedimentary organic matter (SOM) and carbonate in a unique semi-enclosed lacustrine sedimentation system of a transitional deltaic land-sea environment of the Kuti Lake were investigated. The primary objective of this study was to determine the source of carbonaceous materials in recent sediments, particularly the relationship between the authigenically precipitated calcite and the allochtonous detrital carbonate.

The Kuti Lake is a karstic cryptodepression (altitude of the water table 0 m a.s.l.), situated in a karstic valley in the south-eastern part of the Neretva River delta plain in southern Dalmatia, Croatia. This semi-enclosed environment is part of a pristine wetland, subjected to riverine influence through porous karstic bedrock, deltaic deposits and occasional floods. The surrounding rocks are Triassic and Eocene carbonates (limestone, dolostone) and flysch. The lake is shallow (up to 4.5 m), non-stratified and predominantly freshwater, with occasional intrusions of seawater through the karstic bedrock (salinity up to 5 PSU). The trophic status of the lake is unclear, since it was characterised as eutrophic or oligotrophic by different authors within a period of few years.

Two sediment cores were analysed - one from the deepest part of the lake (sampling depth 4.5 m, length of the core 1 m) and another, from the secluded shallow area (sampling depth 1 m, length of the core 0.8 m). Redox potential and pH were measured on site in the sediment core immediately after retrieval. The sediments were cut into 2 cm segments and frozen until further analyses.

The particle size of sediments was analysed using laser diffraction (LD) while the mineral composition was examined by X-ray diffraction (XRD). The content of organic matter and carbonates were determined by the sedimentary organic carbon (Rock Eval pyrolysis) and nitrogen (EA-IRMS) analyses. The stable isotope compositions of C and N of sedimentary organic matter and carbonate mineral phase were analysed by EA-IRMS and ANCA-TG coupled to IRMS systems,

respectively. The morphology of mineral particles was examined by field emission scanning electron microscope (FESEM).

The results showed that the river influence on the lake sediment is limited to occasional short-term flood events, which drain significant amount of organic and mineral detritus into the lake. Nevertheless, the authigenic formation of nanostructured calcite was found to be the most important source of sediments in the recent past. It can be produced by biomineralisation or abiotically by precipitation from supersaturated interstitial water, under prevailing physical and biogeochemical conditions. The FESEM analyses showed that calcite predominantly occurs in irregular and nanostructured forms typical for authigenically precipitated anhydrous carbonates, consisting of almost spherical nanosized subunits (Figure 1A).

Previous studies have shown that identical nanoscale morphological features of calcite can be formed in the presence of organic matter (Sondi *et al.*, 2008) and through the biological activities of bacteria that can govern initial formation and morphogenesis of carbonates on the nanoscale (Obst *et al.*, 2009). A compelling example of such precipitate is shown in Figure 1.

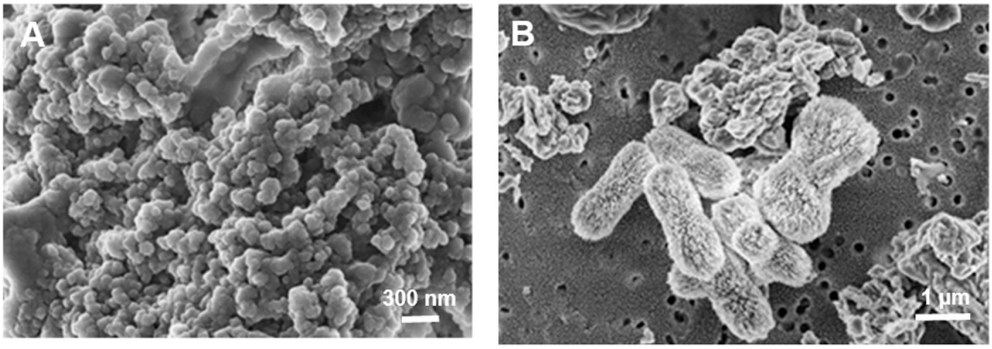

Figure 1. *The FESEM images of the authigenically precipitated calcite in the Kuti Lake sediments: the irregular shape of the early-formed nanostructured calcite precipitates (A) and calcite minerals precipitated on the bacteria cell walls (B).*

The stable isotope analysis of carbonates and sedimentary organic matter confirmed that calcites at both sampling stations were formed by active authigenic precipitation in the lake system, rather than by erosion of the surrounding carbonate rocks or terrigenous yields during the flood events. The $\delta^{13}C$ and $\delta^{18}O$ values of sedimentary carbonate (-6.2 to -0.7 and -9.5 to -2.7 ‰, respectively) were in most segments significantly lower than those determined in the surrounding carbonate rocks (in average +1.5 and -1.3 ‰, respectively), and indicate that the sedimentary carbonate is a mixture of meteogenic freshwater carbonate and detrital marine carbonates. The carbonates exhibiting high $\delta^{13}C$ values (around -1 ‰) and low $\delta^{18}O$ values are a result of calcite precipitation from interstitial water of meteogenic origin and ^{13}C-enriched dissolved inorganic carbon in methanogenic environment (Leng *et al.,* 2005; Rassmann *et al.*, 2016). This indicates intensive transfer of sedimentary carbon from the organic into the inorganic pool through

the dissolution of biogenic CO_2 and its fixation in the authigenic mineral phase, resulting in predominantly authigenic origin of calcite in the investigated lake sediments.

Keywords: karst, lake, sediment, nanostructured calcite, stable isotopes

Acknowledgment: *The study was financed by the Croatian Science Foundation (NanoMin Project No. 2504), Slovenian Research Agency (research programmes P2-0091 and P1-0143) and the EU H2020 project MASSTWIN (contract No. 692241).*

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