

# Formation of the authigenic cements in aquatic sediments through precipitation processes at the nanoscale - isotopic and FESEM study

**Sonja Lojen<sup>1</sup>, Srečo D. Škapin<sup>2</sup>, Maja Ivanić<sup>3</sup>, Tamara Troškot-Čorbić<sup>4</sup> and Ivan Sondi<sup>5</sup>**

<sup>1</sup>Jožef Stefan Institute, Department of Environmental Sciences, 1000 Ljubljana, Slovenia (sonja.lojen@ijs.si)

<sup>2</sup>Jožef Stefan Institute, Advanced Materials Department, 1000 Ljubljana, Slovenia

<sup>3</sup>Ruder Bošković Institute, Division of Marine and Environmental Research, 10000 Zagreb, Croatia

<sup>4</sup>Laboratory Department, Exploration Sector, INA-Industrija nafte d.d., Lovinčičeva 4, 10002 Zagreb, Croatia

<sup>5</sup>University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, 10000 Zagreb, Croatia

The traditional view on carbon cycle assumes that CO<sub>2</sub> is removed from the atmosphere by two major sinks, i.e. oceans and the biosphere. Terrestrial carbon sink in cements precipitated from groundwater, from interstitial water in recent sediments or from surface water (tufa) has been largely underestimated or neglected. Recent studies showed, however, that the magnitude of authigenic carbonate precipitation might be immense, so that it can be considered as the third major global C sink. Knowing this, the importance of identification and quantification of secondary carbonate becomes apparent on local, regional and global scale. While quantification of carbonate cements is rather simple in siliciclastic sediments, it remains challenging in carbonaceous environments.

Isotopic tools were proven to be efficient for differentiation between primary (marine) carbonate and authigenic cements produced in organic-rich sediments or from terrestrial groundwater. The C isotopic composition of marine carbonate (limestone, dolostone) differs significantly from that precipitated from high-alkalinity interstitial solutions where the dissolved inorganic carbon derives at least in part from the decomposition of organic matter. Namely, organic tissues are depleted in <sup>13</sup>C compared to marine and atmospheric CO<sub>2</sub> because of preferential uptake of isotopically light C from the environment and complex isotope fractionation accompanying biological processes.

Our study deals with precipitation of authigenic carbonate in recent aquatic carbonaceous sediments formed on karstic terrains in a range of environments – from freshwater (lacustrine tufa, Krka river), transitional (Neretva river delta), to marine lakes and coastal marine sediments (islands of Mljet and Dugi otok, Croatia). We analysed isotopic, geochemical and morphological characteristics of sedimentary carbonate and organic matter, and using isotopic tools, assessed the transfer of carbon between dissolved and solid pool. The CO<sub>2</sub> cycling in lakes and reservoirs, as well as organic rich marine sediments was largely dominated by biological and biogeochemical processes. Diagenetic degradation of sedimentary organic matter represents a complex suite of microbially-mediated and abiotic processes, that mineralise organic carbon to the CO<sub>2</sub> or CH<sub>4</sub>, which undergo further processing by microbial communities and provide a source of dissolved inorganic carbon for precipitation of carbonate cements. However, in organic-rich sediments with multiple C sources (soil, lithic carbonate, land vegetation, aquatic biota) and changing redox conditions, the isotopic signatures of dissolved carbonate vary not only because of different C sources, but also because of complex diagenetic processes that remove or add dissolved inorganic carbon (DIC) from/to the interstitial solution, and fractionate DIC isotopes either in same or in different directions (i.e. toward more positive or more negative  $\delta$  values). At the same time, the C isotope fractionation during precipitation of calcite remains rather stable irrespective of the temperature and precipitation rate and authigenic carbonate reflects the isotopic composition of DIC ( $\delta^{13}\text{C}$ ) within approximately  $\pm 1$  ‰. Therefore, the C isotopic composition of authigenic carbonate in organic-rich sediments is not unique or exclusive for a certain environment, but depends on the combination of processes that simultaneously or consecutively affect the concentration and  $\delta^{13}\text{C}$  of DIC. Therefore, additional identifiers of authigenic carbonate in freshwater sediments from carbonaceous settings are necessary for its unequivocal identification and quantification.

## Acknowledgments

This study was funded by the Croatian Science Foundation (project 2504 NanoMin - Nanominerals in sediments and soils: formation, properties and their role in biogeochemical processes), Slovenian Research Agency (programme P1-0143) and European Commission (Horizon 2020, project MASSTWIN - Spreading Excellence and widening participation in support of mass spectrometry and related techniques in health, the environment, and food analysis, grant agreement No. 692241).