



Geochemical indicators of authigenic calcite precipitation in carbonaceous fluvial environments

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Precipitation of fluvial carbonates follows the degassing of CO₂ at springs, rapids or waterfalls. In lentic river sections, however, the massive accumulation of clastic material may even surpass the in-situ carbonate precipitation in the water column and in the sediment. The authigenic carbonate here is mainly a product of biogeochemical processes in the interstitial water at the solid-liquid interfaces during early diagenesis. The aim of the present study was to find tools to estimate the relative proportion of authigenic and detrital carbonate in tufas and lake sediments. Therefore, we compared the elemental and isotopic characteristics of the carbonate and organic matter in the barrage tufa, stromatolite tufa and in lacustrine sediments from a tufa-precipitating Krka River, and in the groundwater-fed lake formed in a crypto-depression in the deltaic system of the Neretva River. Both environments are located close to the eastern Adriatic coast in Central Dalmatia (Croatia) with similar geological and topographical settings, surrounded by steep slopes of Cretaceous carbonaceous massifs, delivering a considerable input of terrestrial mineral and organic debris.

The grain size distribution, elemental composition and stable isotope composition of the carbonate and organic matter were analysed. The morphology of precipitates was analysed with the field emission scanning electron microscopy.

Comparison of tufa and surface sediments from lacustrine settings showed that both sediment types may contain highly variable amounts of terrigenous debris and the variations can be large even at very short distances. Lake sediments generally contain more detrital material than tufa, although tufas with dolomite content of up to 30 % were found. The main factors affecting the content of clastic material in the sediments were topography and vegetation cover. However, the self-purification mechanisms affecting the river water quality strongly affect the mineral and geochemical composition of the lacustrine sediment. The carbonate C and O isotopic compositions can vary by several per mil because of temperature variations, disequilibrium precipitation and the presence of various amounts of extraclasts of calcite and dolomite. These variations may be bigger in lacustrine sediments, where diagenetic processes can change the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of carbonates toward more positive or more negative values. Furthermore, the microbially mediated precipitation of nano-sized carbonate can be strongly reflected in isotope fingerprints of carbonate in lacustrine settings. These processes may affect the isotope fingerprints of carbonate phases in different ways; therefore, the inspection of morphological properties is needed to support their interpretation.

The content, elemental and isotopic composition of sedimentary organic matter records are much better preserved in lakes than in riverbed tufa because of erosion. Although formed in a different environment, the sediment from the karstic lake Kuti showed very similar isotopic and elemental characteristics to that from lakes on the Krka River, therefore caution is needed in palaeoenvironmental interpretation of ancient lacustrine sediments.

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