

Stable isotopes as identifiers of authigenic carbonate

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Authigenic carbonate has been recently invoked as the third mayor C sink after oceans and comparable to biological fixation. This estimation is highly uncertain and – if correct – it would completely overhaul the global C mass balance. The quantification of authigenic carbonate may be simple in siliciclastic sediments, while in carbonaceous area it remains problematic. Authigenic carbonates have distinct C isotopic compositions from that of marine carbonate because of different C sources with conspicuous ¹³C/¹²C ratios, depleted in ¹³C compared to the limestone or dolomite. However, in environments with multiple C sources and changing redox conditions, such as organic-rich sediments and aquifer in carbonate areas, the isotopic signatures of dissolved carbonate vary not only because of different C sources, but also because of several simultaneous diagenetic processes that remove or add dissolved inorganic C (DIC) from/to the interstitial solution and fractionate C isotopes in different, sometimes even opposite directions. Therefore, the $\delta^{13}\text{C}$ of authigenic carbonate in organic-rich sediments is not unique or exclusive for a certain environment, but may be variable in similar environments, or may vary seasonally even in the same environment. The isotope ratios of oxygen (¹⁸O/¹⁶O) reflect the isotopic composition of source water (continental water is depleted in ¹⁸O compared to the seawater) and the temperature of precipitation because of temperature-dependant O isotope fractionation between H₂O and CaCO₃ during precipitation of calcite.

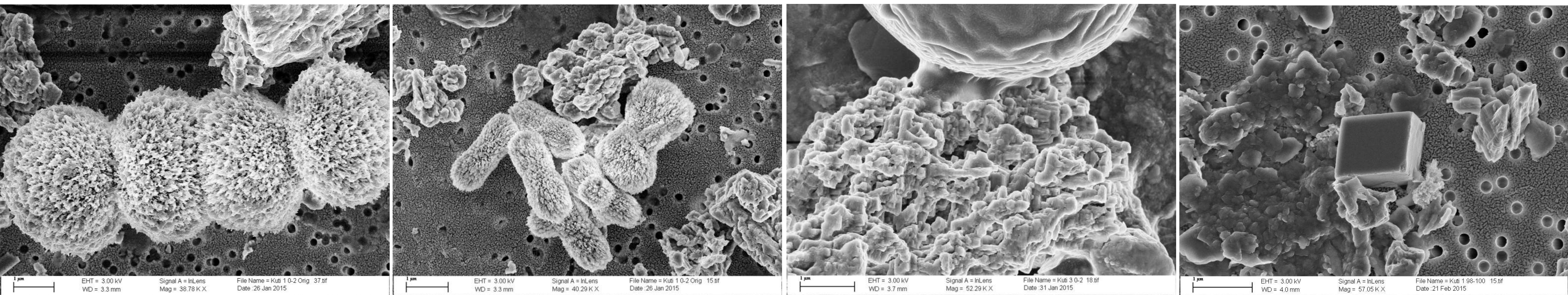
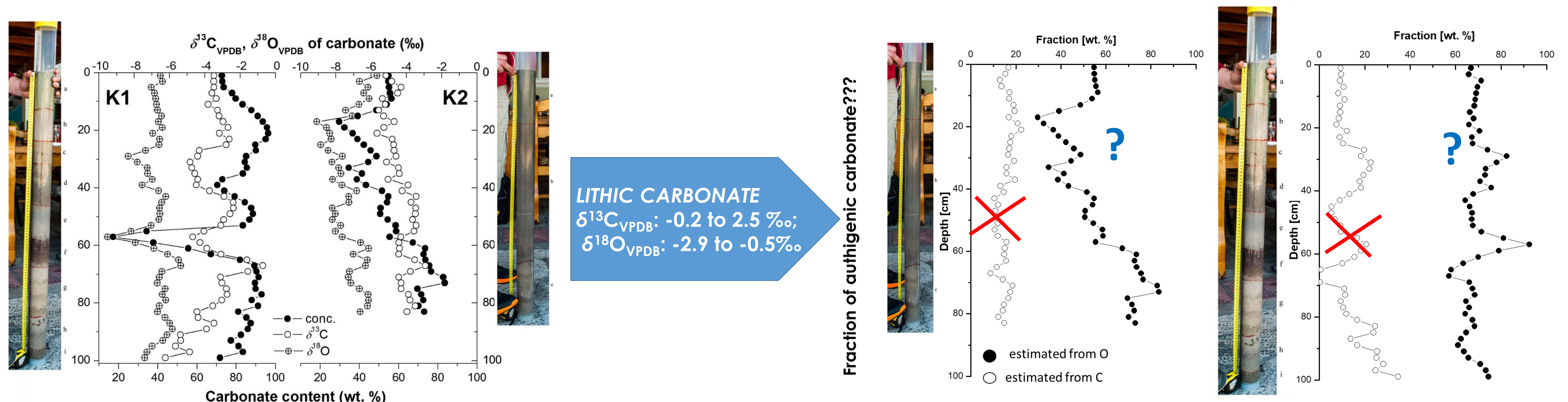
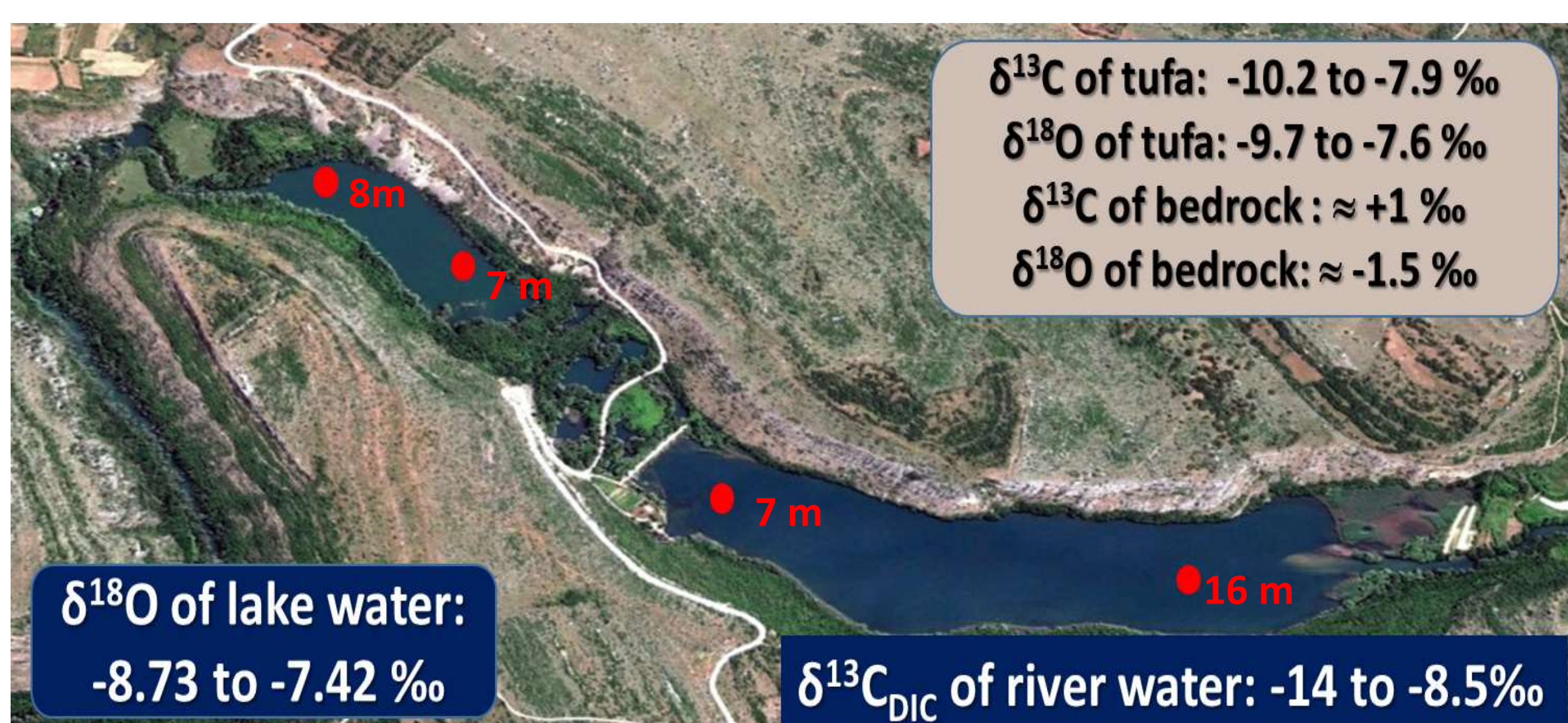
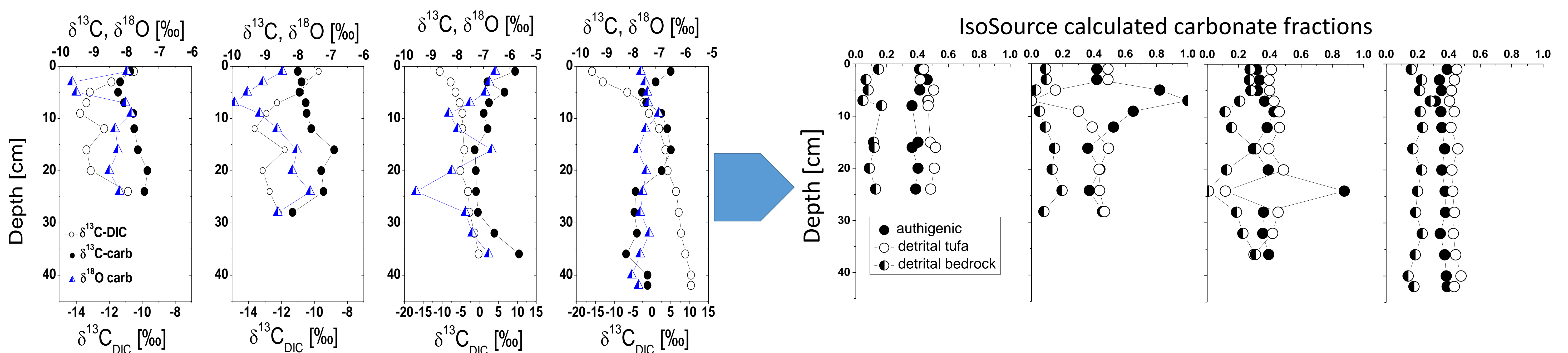


Figure 1: Field emission - SEM micrographs of authigenic carbonates from organic-rich surface sediment from a karstic lake formed in a cryptodepression in the upper Neretva River delta (Lake Kutl, Croatia).

Example from Lake Kutl – 2 sedimentary C sources (detrital bedrock, sedimentary organic C): what can we tell about authigenic carbonate fraction from organic C and carbonate C and O isotopes?



Example from Krka River – 3 sedimentary C sources (detrital bedrock, detrital tufa, sedimentary organic C): enormous uncertainties – no cross-check possible



Estimates made from oxygen isotopic composition of carbonate are reasonable (to a certain extent), but uncertainties are large because of large possible ranges of values for isotopic compositions of terrigenous carbonate debris and eroded tufa; $\delta^{18}\text{O}$ values of authigenic carbonate were assumed to be in equilibrium with interstitial water.

Conclusion

One tracer is not enough – new identifiers of authigenic carbonate are needed, e.g. non-traditional isotopes of Mg and Sr.