



Local temperature calibration of carbonate-water oxygen isotope fractionation and clumped isotopes (Δ_{47}) in a karstic freshwater limestone environment

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Oxygen isotope ratios of carbonates are widely used as palaeoclimate indicators since isotope fractionation between the carbonate and the water phase is temperature dependent. The available empirical equations are reliable for deposits which are precipitated under isotopic equilibrium. However, in many cases, precipitation of abiotic carbonate sediments (flowstones, freshwater limestones, travertines, tufas, etc.) can occur with fast CO₂ degassing, which tends to result in a kinetic fractionation of isotope compositions.

In karst environments, freshwater limestone is precipitated from cold spring waters as the creek is flowing and the dissolved CO₂ is released from the water. This process creates tufa deposits. Our aim is to investigate the suitability of the tufa deposits as a palaeoclimate archive, even if kinetic fractionation plays a significant role during carbonate formation.

In Mecsek Mts, Hungary, tufa deposits can be found in karst valleys. We have chosen a karst spring of constant annual temperature of 10.3 °C. As the water is flowing away from the spring, it is heated up or cooled down by the ambient air, so the annual temperature variation is increasing with the distance from the spring. In 2015, glass plates, as well as temperature loggers, were placed in the water downstream from the spring along with a 200 m long section, so that carbonate could be precipitated onto the glass surface. In 3-4 weeks the glass plates are replaced. Daily average temperatures of the water vary between 0 and 25.6 °C, while temperatures averaged to the sampling periods vary between 0.8 and 20.1 °C. The first $\delta^{18}\text{O}_{\text{carb}}$ and clumped isotope results show a significant temperature dependence, although the equations are shifted from those that are reliable to equilibrium circumstances. However, both $\delta^{18}\text{O}_{\text{carb}}-T$ and $\Delta_{47}-T$ relationships seem to be significant and therefore applicable to the old tufa layers for reconstructing palaeotemperatures.

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