

The ‘clumped isotope’ paleothermometer: analytical aspects and calibration

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‘Clumped isotope’ analysis of carbonates has become a new tool to reconstruct marine and terrestrial paleotemperatures (e.g., Eiler, 2011). It relies on the thermodynamic prediction that bondings between two heavy isotopes such as ^{13}C and ^{18}O are more stable than those between their lighter counterparts. The tendency to generate ^{13}C - ^{18}O clumps increases with decreasing temperature. Provided that homogeneous isotopic equilibrium is attained within the CO-bearing phase the deviation between the effective abundance of ^{13}C - ^{18}O clusters and the corresponding stochastic distribution (as computed from its bulk isotopic composition) is a function of temperature exclusively.

The abundance of ^{13}C - ^{18}O bondings inside carbonates cannot be measured directly. Fortunately, the reaction between phosphoric acid and carbonate is kinetically controlled, such that information about the original clumping of ^{13}C - ^{18}O is still preserved in the evolved CO_2 . Ghosh et al. (2006) reacted calcite that had been inorganically precipitated between 1°C and 50°C, with 103% phosphoric acid at 25°C and monitored how ^{13}C - ^{18}O clumping in the evolved CO_2 (expressed as Δ_{47}) varies with carbonate crystallization temperature. Many marine carbonates, whose growth temperatures could have been determined independently, exhibit Δ_{47} values that are in close agreement with the Ghosh calibration. However, it has to be noted that the Ghosh calibration exhibits a slope steeper than that predicted by theory (Guo et al., 2009). Dennis & Schrag (2010) performed new calcite precipitation events at Harvard but failed to reproduce the T- Δ_{47} relationship of Ghosh et al. (2006). In contrast, it closely aligned the theoretically predicted data. The observed discrepancies might be partly due to the fact that an absolute reference frame enabling interlaboratory comparison became available very recently only (Dennis et al., 2011).

We have reacted carbonates at temperatures of 25°C using McCrea reaction type vessels and at 90°C using a common acid bath. Our results imply that trace amounts of water either present in the acid or in the headspace of the reaction vessel can partly re-equilibrate with the evolved CO_2 if 103-105% H_3PO_4 is used. Re-equilibration can be overcome using the common acid bath (90°C) and phosphoric acid concentrations >105%. Using this setup, we have analyzed the clumped isotopic composition of marine carbonates (calcite), whose growth temperatures could have been constrained independently (9-38°C). The slope of our calibration is indistinguishable from that theoretically predicted, but values are roughly offset by +0.04‰. More inorganic and biogenic calibration studies are required, reporting measured Δ_{47} values on the absolute scale proposed by Dennis et al. (2010), to be able to resolve if these discrepancies are due to kinetic effects or to imprecise computation of theoretical data.

References:

Dennis Schrag (2010), GCA 74, 4110-4122

Dennis et al. (2011), GCA 75, 7117-7131

Eiler (2011), Quatern. Sci. Rev. 30, 3575-3588

Ghosh et al. (2006), GCA 70, 1439-1456

Guo et al. (2009), GCA 73, 7203-7225