Geophysical Research Abstracts
Vol. 14, EGU2012-2151, 2012
EGU General Assembly 2012

Insights into kinetic isotope fractionation in calcite using clumped isotopes in Devils Hole

T. Kluge (1), S. Zaarur (1), J. Dublyansky (2), C. Spötl (2), and H.P. Affek (1)

(1) Yale University, Department of Geology and Geophysics, New Haven, United States (tobias.kluge@yale.edu), (2) Institut für Geologie und Paläontologie, Universität Innsbruck, Innsbruck, Austria

The temperature dependence of the equilibrium fractionation of carbonate minerals can provide paleoclimatic information, provided that the fractionation factor is known. Currently, values of O'Neil (1969) and Kim and O'Neil (1997) are used for the calculation of the oxygen isotope fractionation between a super-saturated solution and precipitated calcite. These empirical relationships are consistent with theoretical considerations (Horita and Clayton, 2007) and are commonly used in a-biogenic carbonates, such as speleothems.

Mammillary calcite from Devils Hole (Nevada) should constitute an excellent natural material for testing these theoretical and laboratory-based results. This calcite grew continuously over several hundred ka at an extremely slow growth rate (about 1 μm/a, Winograd et al., 1992) and, thus, is likely to reflect formation under isotopic equilibrium conditions (Coplen, 2007). We tested this assumption using clumped isotopes.

Clumped isotopes provide a thermodynamic thermometer based on the temperature-dependent abundance of two heavy isotopes in the C-O bond of the $CaCO_3$ structure. It has been calibrated by laboratory experiments following Kim and O'Neil (1997) and confirmed using biogenic carbonate materials. An offset from the expected temperature, typically observed in speleothems, demonstrates that clumped isotopes are very sensitive to isotopic disequilibrium and are, therefore, a unique tool for the investigation of kinetic fractionation effects.

Clumped isotope results from Devils Hole calcite yield a constant paleo-water temperature that agrees with the modern-day groundwater temperature and confirms that the calcite precipitated at isotopic equilibrium. However, $\delta^{18}O$ is significantly enriched in Holocene calcite as compared to the values of Kim and O'Neil (1997). We attribute this difference to the preferential incorporation of light oxygen isotopes during fast mineral growth in laboratory experiments without affecting the ^{13}C-^{18}O distribution reflected in clumped isotopes; this effect is absent in the very slow growing Devils Hole calcite.

References:

Coplen, T.B., 2007. Calibration of the calcite-water oxygen-isotope geothermometer at Devils Hole, Nevada, a natural laboratory. Geochim. Cosmochim. Ac. 71, 3948-3957.

Horita, J., Clayton, R.N., 2007. Comment on the studies of oxygen isotope fractionation between calcium carbonates and water at low temperatures by Zhou and Zheng (2003; 2005). Geochim. Cosmochim. Ac. 71, 3131-3135.

Kim, S.T., O'Neil, J.R., 1997. Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. Geochim. Cosmochim. Ac. 61, 3461–3475.

O'Neil, J.R., Clayton, R.N., Mayeda, T.K., 1969. Oxygen isotope fractionation in divalent metal carbonates. J. Chem. Phys. 51, 5547–5558.

Winograd, I.J., Coplen, T.B., Landwehr, J.M., Riggs, A.C., Ludwig, K.R., Szabo, B.J., Kolesar, P.T., Revesz, K.M., 1992. Continuous 500,000-year climate record from vein calcite in Devils Hole, Nevada. Science 258, 255-260.