Reconstruction of isotopic compositions of mineral-forming water in calcite: direct measurements of aqueous fluid inclusions vs. equilibrium calculations

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Analysis of the oxygen isotopic composition of fluid inclusion water in calcite has long been considered not feasible (e.g., Schwarcz et al., 1976), because it was perceived that small amounts of water trapped inside calcite exchange its oxygen with the surrounding. This contention, however, has not been thoroughly tested.

Measurements of stable isotope compositions of water in fluid inclusions were performed using a dedicated line at Innsbruck University. The samples are crushed in a specially designed crushing cell with small internal volume and surface (2.8 cm^3;18 cm^2). The working zone of the crusher is kept at 130-150°C, to minimize the adsorption. The released water is transported by a He flow through a heated stainless-steel tube into the computer-controlled cryo-focusing cell (Humble, USA). The temperature and gas-flow parameters are set so that any CO_2 (and/or other poorly condensable gases) are not trapped, whereas the collection of water is quantitative. Upon completion of cryo-focusing (ca. 5 min) the cell is flash-heated to 280°C at a rate 3600°C/min, which ensures that the released water arrives into the TC/EA conversion unit (Thermo, Germany) as a concise pulse. In TC/EA the water is converted into H_2 and CO through reaction with glassy carbon at 1400°C. The evolved gases are separated in a chromatographic column and admitted, via the ConFlow III interface, into a Delta V Advantage mass-spectrometer (Thermo, Germany). Prior to crushing the line is conditioned by several injections of water with isotope compositions broadly similar (±20‰ δD) to the expected composition of the inclusion water. For samples yielding more than ca. 0.2 μl H_2O the precision is better than 1.5 ‰ for δD and ca. 0.5‰ for δ^{18}O (all uncertainties are 1σ).

Multiple isotope analyses of inclusion water were made on "pool spar" calcite collected at the bottoms of the two shallow pools in Obir cave (Carinthia, Austria). The isotope composition of the lake water (δD = -70.1±0.3‰ δ^{18}O = -10.4±0.06 ‰ V-SMOW), its temperature (5.2±0.2°C), as well as the relative humidity (97-100±3 %) at both sampling sites remained stable over the 1.5 to 4 year-long monitoring periods. The hydrogen isotope compositions measured for fluid-inclusion water in the pool spar matches the lake water (δD$_{fi}$ = -70.0±0.3 ‰ n = 3) and the oxygen isotope values agree within ca. 0.5 ‰ (δ^{18}O$_{fi}$ = -9.9±0.4 ‰ n = 2). The paired δD$_{fi}$ − δ^{18}O$_{fi}$ values plot within 1 ‰ (δ^{18}O) of the local Meteoric Water (MWL) line. This suggests that the Obir pool spar was deposited in equilibrium with the lake water and that inclusions preserved the isotope signature of this water. The equilibrium δ^{18}O$_{water}$ was calculated for the Obir samples from the δ^{18}O$_{calcite}$ and the measured water temperature using fractionation factors of Friedman & O'Neil (1977), Kim & O'Neil (1997), and Coplen (2007). The differences between the measured δ^{18}O of the lake water and the calculated equilibrium δ^{18}O were 0.3, 0.9, and -0.4 ‰ respectively. If the equations are solved for the temperature the respective errors are -1.2, -4.0, and +1.8°C.

Fluid inclusion isotope data were also obtained from low-temperature hydrothermal (40 to 50°C according to fluid inclusion microthermometry data) calcite from Yucca Mountain, Nevada, USA (sample ESF28+81). The paired δD-δ^{18}O values (δD$_{fi}$ = -101 ‰ n = 6; δ^{18}O$_{fi}$ = -14.8 ‰ n = 2) plot close to the Nevada MWL. In contrast, the equilibrium δ^{18}O$_{water}$ values (-10.3 to -7.7‰) calculated from δ^{18}O$_{calcite}$ and fluid-inclusion temperatures plot significantly (3.5 to 6.5‰) to the right of MWL. Several interpretations are possible. One is that the fluid inclusion water has re-equilibrated with the surrounding calcite upon cooling from depositional temperature (40-50°C) to modern ambient temperature (21-23°C). Isotope mass balance calculations show that this would require the W/R ratios as low as 0.1-0.4. Alternative interpretation is that the Yucca Mountain calcite was deposited in isotopic disequilibrium caused by rapid crystallization and CO_2 degassing. In such conditions the δ^{18}O of calcite could be

up to 7 ‰ more positive than expected for equilibrium (Giles & Boles, 2006).

To conclude: (1) Our results confirm the earlier findings of Dennis et al. (2001) that fluid inclusions in calcite appear to preserve the $\delta^{18}O$ compositions of parent mineral-forming waters at low temperatures characteristic of the natural cave environment. (2) The extent to which the fluid inclusion water isotopically re-equilibrates with the surrounding hydrothermal calcite upon cooling must be systematically evaluated by comparing measured $\delta^{18}O_{fi}$ and calculated $\delta^{18}O_{water}$. (3) Errors associated with equilibrium calculations vary depending on the fractionation factor used. For the Obir samples, calculations based on fractionation factors of Friedman & O'Neil (1977) and Coplen (2007) bracket the true values within ca. ± 0.4‰ $\delta^{18}O$ and $\pm 1.8°C$.

References: Coplen (2007) Geochim. Cosmochim. Acta, 71(16): 3948-3957; Dennis et al. (2001) Geochim. Cosmochim. Acta, 65(6): 871-884; Friedman & O'Neil (1977) U.S. Geol. Surv. Prof. Pap. 440-KK; Giles & Boles (2006) AGU Fall Meeting 2006, abstract #V53D-1774; Kim & O'Neil (1997) Geochim. Cosmochim. Acta, 61: 3461-3475. Schwarcz et al. (1976) Geochim. Cosmochim. Acta, 40(6): 657-665.