



Isotope equilibrium and disequilibrium effects in dissolved carbonate species and witherite in alkaline solutions: Open system experiments

M.E. Böttcher

Leibniz Institute for Baltic Sea Research, Warnemünde, Germany
(michael.boettcher@io-warnemuende.de)

The isotopic composition of solid carbonates upon precipitation from aqueous solutions is controlled by the composition of the dissolved carbonate species and the physico-chemical boundary conditions (e.g., temperature and precipitation rate). Strong depletions in C-13 and O-18 have been reported for the carbonate species in evaporating seawater, as well as in calcite precipitated from highly alkaline solutions (e.g. [1-3]). Carbonate precipitation from high-pH solutions is also found in soda lakes. The knowledge of the controlling factors for C and O isotope variations in aqueous alkaline solutions is still limited. In the present study, the absorption of gaseous carbon dioxide (atmospheric PCO₂) by alkaline solutions is investigated experimentally under open system conditions in order to determine the fractionation effects for the stable C and O isotopes as a function of time.

Due to the chemical absorption of CO₂ and water evaporation, experimental pH-values in the NaOH-experiments decreased from 12.7 (initial) by about two pH units, and DIC (dissolved inorganic carbonate) species increases up to 1M. Final PCO₂ values are limited by the equilibrium with the Earth's atmosphere. Absorption rates for carbon dioxide observed at room temperature agree with model calculations based on the film model. O-18 was always enriched in DIC compared to water and C-13 depleted compared to atmospheric CO₂. A strong depletion of DIC in O-18 and C-13 in the initial phase is due to different diffusion coefficients and hydroxylation rate constants for the isotopically different forms of CO₂(aq). In a later stage of the experiments O-18 and C-13 contents of water and DIC increase. Whereas, the O-18 content enrichment in DIC compared to water is controlled by isotope exchange equilibrium, C-13 of DIC is still far from isotope equilibrium with the atmospheric CO₂.

Upon continuous witherite precipitation in experiments using Ba(OH)₂ solutions, C-13 and O-18 were enriched by about 1.5 per mil compared to the experiments with NaOH due to pH-controlled alteration effects of the solid scums in microniches at the solution-atmosphere interface. The latter effect has to be considered in the interpretation of isotope signals in carbonates precipitating from alkaline solutions due to water-rock interactions or concrete degradation.

[1] O'Neil & Barnes (1971) *Geochim. Cosmochim. Acta* 35; [2] Macleod et al. (1991) *Chem. Geol.* 86; [3] Dietzel et al. (1992) *Appl. Geochem.* 7