

Kinetic fractionation of oxygen isotopes during CO_{2(aq)} (de)hydration and (de)hydroxylation: Revisiting theoretical and experimental data

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Recent studies indicate the difficulty, and even infeasibility, of precipitating carbonate minerals in oxygen isotopic equilibrium under laboratory conditions [1]. Non-equilibrium compositions are also widely observed in natural carbonate minerals, such as speleothems, cryogenic cave calcite, travertines, lacustrine carbonates, carbonates precipitated from alkaline solutions, some marine calcareous species and microbially-mediated carbonates [e.g., 2-5]. Clearly, isotopic equilibrium is a specific and unique state among the multiple alternatives of non-equilibrium states.

The reactions of CO_{2(aq)} (de)hydration and (de)hydroxylation play a key role in all of the environments mentioned above. However, to date, the magnitudes of the kinetic isotopic fractionations during these reactions are highly uncertain. In addition, the literature is lacking the basic theoretical framework required for any quantitative treatment of these kinetic fractionations.

Here we bridge these fundamental gaps in theory, and revisit theoretical and experimental data, in order to better constrain the kinetic isotope effects during CO_{2(aq)} (de)hydration and (de)hydroxylation. This research advances the understanding of the complex carbonate system, and is an essential step towards environmental interpretations of non-equilibrium isotopic compositions in carbonate minerals.

[1] Watkins *et al.* (2013) *EPSL* **375**, 349-360. [2] Hendy (1971) *GCA* **35**, 801-824. [3] Wefer & Berger (1991) *Mar Geol* **100**, 207-248. [4] Clark & Lauriol (1992) *Chem Geol* **102**, 217-228. [5] Clark *et al.* (1992) *GCA* **56**, 2041-2050.