Experimental investigation of kinetic isotope effects on oxygen during CO_2 hydroxylation

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CO_2 hydroxylation occurs at alkaline pH and forms HCO_3^-. The newly formed dissolved inorganic carbon (DIC) can then precipitate as solid carbonates. If hydroxylation and precipitation are rapid relative to isotopic reequilibration of oxygen isotopes between DIC and water, the kinetic isotope fractionation associated with hydroxylation may be recorded in the carbonate, thereby complicating paleoenvironmental reconstructions. The isotopic composition of HCO_3^- formed by CO_2 hydroxylation is not well known and difficult to measure and the few experiments performed so far [1,2,3] led their authors to assume that it reflects non-fractionating uptake of 2 oxygen atoms from the bulk CO_2 and 1 from the bulk OH^-. The presumed absence of kinetic fractionation seems counter–intuitive, as hydroxylation is almost instantaneous at alkaline pH.

To address this knowledge gap, we performed a series of experiments at 5 and 25°C, consisting of instantaneous and quantitative conversion of gaseous CO_2 into barium carbonates, followed by isotopic analysis of the carbonates. The results *i*) suggest that HCO_3^- formed by hydroxylation is in fact fractionated from the CO_2 and OH^- from which it formed, *ii*) place the first direct experimental constraints on the kinetic isotope fractionations due to CO_2 hydroxylation, and *iii*) provide key insight necessary for understanding out-of-equilibrium oxygen isotope compositions of carbonate minerals.

[1] Létolle *et al.* (1990b) *Compt. Rend.* **310**, 574-552 [2] Usdowski *et al.* (1991) *Z. Phys. Chem.* **170**, 237-249 [3] Clark *et al.* (1992), *Geochim. Cosmochim Acta*, **56**, 2041-2050.