Kinetic isotope effects during calcite growth: sensors of paleoenvironment and mineral surface dynamics

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Carbonate minerals rarely grow at equilibrium. Their isotopic compositions, a major source of information on paleo-environments and mineral genetic conditions, are subject to kinetic isotope fractionation effects that can be the same size as equilibrium effects. Understanding these non-equilibrium fractionation effects is critical to the interpretation of carbonate isotopic compositions. They also constitute unique probes of mineral growth mechanisms and chemical exchange fluxes at the mineral-solution interface.

Kinetic isotope effects (KIE) have not typically been used or accounted for largely because of the absence of useful models that can relate them to mineral growth conditions. In the past five years there has been considerable progress in this regard [1-4], and it is now possible to think about using KIE as paleo-environmental indicators, although the scope and reliability of such indicators is not fully defined. There are indications that Ca, O, and C KIE are dependent not only on growth rate and solution saturation state, but also on pH, solution Ca:CO_3, and equilibration rates of carbonate species in solution. There are additional interesting possibilities with Mg isotopes, Sr/Ca, and other trace element ratios.

There is still a paucity of experimental data available for testing models, but there is ample evidence that KIE and kinetic chemical effects can be valuable contributors to understanding precipitation reactions and for sensing crystal growth conditions for natural samples. KIE are so predominant at room temperature that it is difficult to establish equilibrium fractionation factors, which are needed to test models. Studies of natural systems are therefore a critical component of building better models for KIE.

[1] Nielsen *et al.* (2013) *GCA* 115, 100-114 [2] Hofmann *et al.* (2012) *PNAS* 109, 18689–18694 [3] Watkins *et al.* (2014) *EPSL* 404, 332-343 [4] Mavromatis *et al.* (2013) *GCA* 114, 188–203