

Calcium Isotopic Fractionation by Carbonate Precipitation from High pH Waters at the Cedars, CA

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The Cedars Site in the northern Coast Ranges of California consists of an ultramafic body undergoing active serpentinization at depth (1). Springs along canyon bottoms produce ultrabasic waters with high pH (~12) but negligible carbonate ion content. Water interaction with atmospheric CO₂ promotes the precipitation of Ca carbonate as rock encrustations, ephemeral thin sheets on water surfaces, and as enduring layered deposits. To evaluate inorganic Ca carbonate precipitation as natural examples of isotopic fractionation processes, we analyzed waters and Ca carbonate precipitates of various textural occurrences. Our δ¹³C and δ¹⁸O analyses of Ca-carbonates and measurements by others (2) show that water-surface precipitates are ~15‰ lighter than layered Ca-carbonates falling along an approximately 1:1 line in δ¹³C vs. δ¹⁸O, far from the expected compositions at equilibrium with atmospheric CO₂ and the spring water, indicating kinetic control on the C and O isotopic compositions of the carbonates (2). Sampled high pH (11.5-12.0) spring waters have 50ppm Ca and δ⁴⁴Ca_{BSE} of 0.17±0.09‰, while Ca-carbonate precipitates have δ⁴⁴Ca_{BSE} of -0.17‰ to -0.77‰. The lowest δ⁴⁴Ca are from thin (~100 microns) surface precipitates (-0.66±0.13‰), which float on water with 50ppm Ca and δ⁴⁴Ca of 0.16±0.06‰ suggesting fractionation of -0.82±0.18‰. For a small spring-fed pool confined by layered Ca-carbonate deposits, the contained water is depleted in Ca (12ppm) and has δ⁴⁴Ca of 1.23±0.06‰, suggesting (using a Rayleigh model, and initial δ⁴⁴Ca of 0.16‰) a fractionation of -0.74±0.08‰. The two carbonate occurrences have similar kinetic Ca isotopic fractionation factors, consistent with precipitation rates of about 3 x 10⁻⁷ mol/m²/s, but greatly different C and O isotopic fractionation. This indicates that the C, O fractionations are due to variable diffusion and/or pH effects (3) but not to differences in precipitation rate.

[1.]Barnes et al. (1967) *Science*, **156**, 830-832; Morrill et al. (2013) *GCA* **109**, 222-240. [2]. O'Neil & Barnes (1971) *GCA*, **35**, 687-697; Meister et al. (2011) in *Advances in Stromatolite Geomicrobiology*, Lect. Notes in Earth Sci. **131**, 101-121. [3]. Watkins et al. (2014) *EPSL* **404**, 332-343