Can carbonate precipitation rates be derived from dissolution rate data?

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Knowledge on precipitation rates of carbonates like magnesite, dawsonite and ankerite at various saturation states and physical conditions is vital to predict the potential of carbonate formation following CO_2 storage. Because data on precipitation rates are few compared to dissolution rates, growth rates of carbonates are commonly estimated from their dissolution rates using the Transition-State-Theory (TST).

We have compared TST-derived and experimental precipitation rates for carbonates like magnesite (Figure 1; [1, 2]) and dawsonite and find that the derived rates are orders of magnitude faster than corresponding experimental data (e.g. Figure 1).

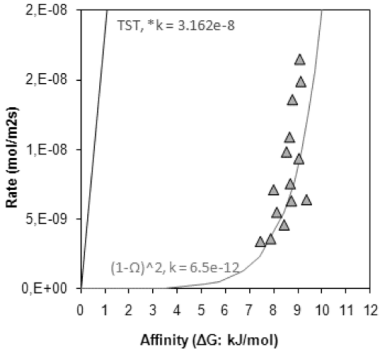

Figure 1. Comparisons of TST-derived and experimental precipitation rates of magnesite. TST-data derived from dissolution rate data from Pokrovsky *et al*. [1]. Experimental datapoints (triangles) and $f(\Delta G) = (1-\Omega)^2$ from Saldi *et al*. [2].

We conclude that precipitation rates of carbonates can generally not be derived from dissolution rates and proposes a model with distinct parameters for dissolution and precipitation reflecting the differences in mechanisms responsible for the rates.

[1] Pokrovsky *et al*. (2009) *Chem. Geol*. **265**, 20-32. [2] Saldi *et al*. (2009) *GCA* **73**, 5646-5657.

^{230}Th/U dating of pedogenic carbonate by laser ablation ICP-MS

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Dense, laminated clast-coatings of pedogenic carbonate (± silica) occur widely in semi-arid to arid regions and can be used to: (1) reconstruct paleoenvironments using trace element and isotopic proxies [1], and (2) provide reliable minimum ages for Quaternary gravels [2]. Carbonate coatings typically grow at <1 mm/ka and contain <0.2 ppb ^{230}Th, thus accurate dating requires high spatial resolution yet ^{230}Th is too low for ion microprobe analysis.

We show that ages precise to a few percent may be rapidly determined on 100-μ spots in coatings with ≥5 ppm U via laser ablation (LA) ICP-MS. Using the Melbourne 193-nm HelEx laser and Nu Plasma ICP-MS, all U-Th isotopes were measured simultaneously using known ion counter gains, ^{238}U/^{235}U to monitor mass bias, and on-peak baselines. U-Th fractionation during laser ablation was corrected using drilled samples analyzed by isotope dilution. Median $(^{230}Th/^{232}Th)_{AR} \sim 10^2$, thus corrections for initial ^{230}Th were generally minor.

LA-ICP-MS on coatings from glacio-fluvial gravels deposited during the penultimate Rocky Mountain glaciation reveal: (1) laminar sequences of carbonate that become monotonically younger away from clasts for as much as 120 ka, confirming that ages of the innermost intact laminae of such rinds most nearly approach the age of the host deposit, and (2) episodes of accelerated coating growth at ca. 80-60 and 35-15 ka, coincident with local glacial maxima, consistent with rapid onset of carbonate accumulation in syn-glacial gravels. LA-ICP-MS dating of pedogenic carbonate facilitates: (1) the construction of extended trace element and isotopic time-series, and (2) more accurate dating of host gravels.

[1] Cerling (1984) *Earth Planet Sci Lett* **71**, 229-240. [2] Ludwig & Paces (2002) *GCA* **66**, 487-506.