

Disequilibrium effects on elemental incorporation into CaCO₃

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It was shown that temperature and crystal growth environment are not the only factors affecting elemental partitioning between minerals and fluid. Growth rate of the crystal is the key parameter controlling elemental partition coefficients [1,etc.]. Different approaches were taken to explain effect of crystal growth rate on elemental uptake by calcium carbonate minerals [2,3]. Those models consider existence of diffusive boundary layer from solid or liquid side of the crystal-fluid interface. We anticipate to present simulation results on elemental uptake by CaCO₃ based on previously discussed assumptions and driving mechanisms using Unified Uptake Kinetics Model (UUKM) embedded in the GEM-Selektor code [4].

Calcite and aragonite precipitation experiments were conducted by diffusion of CO₂ into Ca-bearing fluid [5]. Crystal extension rates (*V*) were determined by marking of crystal growth layers with REE elemental spikes introduced into growth media [6]. *V* decreased with increasing crystal size. Ratios of Mg/Ca, Sr/Ca, Ba/Ca, and U/Ca were analyzed using ion microprobe instrument at UCLA. Analytical data revealed trends of elemental ratios within individual slow grown calcite crystals where Sr/Ca, Ba/Ca, and U/Ca increase but Mg/Ca decreases from crystal edge (*V*<0.01 nm/s) toward its interior (0.01<*V*<5 nm/s). In contrast, fast grown crystals (*V*>5 nm/s) demonstrated different distribution of elemental ratios: Sr/Ca, Ba/Ca, and Mg/Ca decreases but U/Ca increase from crystal edge toward its interior.

Potential explanation for these phenomena is nonlinearity of partitioning dependence on growth rate [6]. At high *V* 100% entrapment of calcite chemically distinct near-surface layer likely occurs [2]. The different distribution of U/Ca suggests that significant portion of U incorporates into calcite interstitially.

[1] Lorens, R.B. (1981) *GCA* **45**, 553-561 [2] Watson, E.B. (2004) *GCA* **68**, 1473-1488 [3] Depaolo (2011) *GCA* **75**, 1039-1056 [4] Thien *et al* (2014) *Appl. Geochem.* **41**, 135-150 [5] Gruzensky (1967) *J. Phys. Chem. Solids* **S1**, 365-367 [6] Gabitov *et al* (2014) *Chem. Geol.* **367**, 70-82