

Explaining the pH effect on strontium partitioning in calcite

QICUI JIA AND SHUO ZHANG

Tsinghua University

Presenting Author: jqc20@mails.tsinghua.edu.cn

Existing data from synthetic calcite precipitation experiments in the presence of strontium (Sr) ions suggest that the partition coefficient of strontium between calcite and solution (K_{Sr}) is strongly dependent on the precipitation rate of calcite (R_p), which can be readily explained by the surface kinetic model [1] and its extensions [2, 3]. The observed K_{Sr} - R_p relationships also change systematically with pH of the solution [4], which suggests that the speciation of aqueous carbonate species plays a role. We use an ion-by-ion calcite growth model [5] which takes into account the contribution of both HCO_3^- and CO_3^{2-} to calcite precipitation to evaluate whether the speciation between HCO_3^- and CO_3^{2-} can explain the observed pH dependence of Sr partitioning. This model is combined with another ion-by-ion model [3] which takes into account the effect of Sr impurity on the solubility of the (Sr, Ca) solid solution. We show that with one set of parameters (the detachment and attachment frequencies of Ca ions) optimized for the experimental data at pH=8.3 [6], the model can reproduce the other two sets of experimental data at pH=7.4 and 6.1 [7, 8]. In order to fit the Sr data we find that the growth of calcite in the pH=8.3 experiment [6] is driven by 2D nucleation, while in the other two sets of experiments [7, 8] the growth mechanism switches from 2D nucleation at high saturation to spiral growth at low saturation. The developed model provides a useful framework for understanding Sr partitioning in inorganic and biogenic calcite.

[1] DePaolo (2011), *Geochim. Cosmochim. Acta* 75, 1039-1056.

[2] Nielsen, DePaolo & De Yoreo (2012), *Geochim. Cosmochim. Acta* 86, 166–181.

[3] Nielsen, De Yoreo & DePaolo (2013), *Geochim. Cosmochim. Acta* 115, 100-114.

[4] Zhang & DePaolo (2020), *Geochim. Cosmochim. Acta* 289, 33-46.

[5] Wolthers, Nehrke, Gustafsson & Van Cappellen (2011), *Geochim. Cosmochim. Acta* 77, 121–134.

[6] Tang, Köhler & Dietzel (2008), *Geochim. Cosmochim. Acta* 72, 3718–3732.

[7] Lorens (1981), *Geochim. Cosmochim. Acta* 45, 553–561.

[8] Tesoriero & Pankow (1996), *Geochim. Cosmochim. Acta* 60, 1053–1063.