

## On the growth of witherite and its replacement by the Mg-bearing double carbonate norsethite: Implications for the dolomite problem

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### ABSTRACT

Witherite [BaCO<sub>3</sub>] and norsethite [BaMg(CO<sub>3</sub>)<sub>2</sub>] are perceived as chemical and structural analogs of aragonite [CaCO<sub>3</sub>] and dolomite [CaMg(CO<sub>3</sub>)<sub>2</sub>], respectively. However, norsethite, unlike dolomite, readily precipitates from aqueous solutions at ambient conditions. This is of special interest as the dehydration barrier of Mg<sup>2+</sup> may be a likely cause of the dolomite growth inhibition. The easiness of norsethite growth shows that the problem of dolomite formation is more complex. To attain a comprehensive understanding of the analog BaCO<sub>3</sub>-MgCO<sub>3</sub> system and of the formation of ordered anhydrous Mg-bearing double carbonates, we investigated the fate and behavior of aqueous magnesium during growth of witherite.

Growth experiments were conducted on witherite seeds in mixed-flow reactors at 50 °C and various Mg-concentrations (0.25–2 mM Ba<sup>2+</sup>, 0–20 mM Mg<sup>2+</sup>, pH 7.8–8.5, ionic strength 0.1 M). At Mg:Ba ratios in solution smaller than 6:1, Mg<sup>2+</sup> did not affect witherite growth kinetics. No significant amount of Mg<sup>2+</sup> was incorporated. The rate constant  $k$  and reaction order  $n$  for witherite growth were determined for the first time ( $k = 0.65 \pm 0.05 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$ ;  $n = 1.3 \pm 0.1$ ; supersaturation  $\Omega = \text{IAP}/K_s = 1\text{--}4$ , where IAP is the ionic activity product and  $K_s$  the solubility constant). The insensitivity of witherite growth kinetics to these levels of Mg is analogous to aragonite growth. The general absence of the formation of solid solutions in the entire BaCO<sub>3</sub>-MgCO<sub>3</sub> system, however, is not shared by the CaCO<sub>3</sub>-MgCO<sub>3</sub> system, for which it is well known that substitution in the sixfold-coordinated cation sites occurs extensively.

Mg:Ba ratios in solution larger than 12:1 led to a replacement of witherite by norsethite. This replacement also is in strong contrast to the CaCO<sub>3</sub>-MgCO<sub>3</sub> system, where higher temperatures and/or much longer timescales are necessary to obtain dolomite. The replacement rate of witherite at 50 °C was estimated to be ~200 times faster than the analogous replacement of aragonite by dolomite observed over 7 years at even 60 °C (Usdowski 1989).

We speculate that the preferential formation of ordered norsethite over a solid solution is facilitated by the large difference in Mg<sup>2+</sup> and Ba<sup>2+</sup> ionic radii. Due to the presumably very high free energy of formation of the solid solution, ordering into distinct Ba- and Mg-layers is the only way to combine both cations within one phase. In the CaCO<sub>3</sub>-MgCO<sub>3</sub> system, solid solution occurrence is common and effectively contributes to the inhibition of the formation of the ordered double carbonate dolomite over a wide range of conditions (cf. Arvidson and Mackenzie 1999).

**Keywords:** Carbonate growth kinetics, trace element incorporation, norsethite, barium mobility