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 [BaCO₃] and norsethite [BaMg(CO₃)₂] are perceived as chemical and structural analogs of aragonite [CaCO₃] and dolomite [CaMg(CO₃)₂], respectively. However, norsethite, unlike dolomite, readily precipitates from aqueous solutions at ambient conditions. This is of special interest as the dehydration barrier of Mg²⁺ 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 BaCO₃-MgCO₃ 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 Ba²⁺, 0–20 mM Mg²⁺, pH 7.8–8.5, ionic strength 0.1 M). At Mg:Ba ratios in solution smaller than 6:1, Mg²⁺ did not affect witherite growth kinetics. No significant amount of Mg²⁺ was incorporated. The rate constant k and reaction order n for witherite growth were determined for the first time (k = 0.65 ± 0.05 × 10⁻⁷ mol m⁻² s⁻¹; n = 1.3 ± 0.1; supersaturation Ω = IAP/K, = 1–4, where IAP is the ionic activity product and Kₘ 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 BaCO₃-MgCO₃ system, however, is not shared by the CaCO₃-MgCO₃ 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 CaCO₃-MgCO₃ 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 Mg²⁺ and Ba²⁺ 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 CaCO₃-MgCO₃ 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

INTRODUCTION

Witherite (BaCO₃) and norsethite [BaMg(CO₃)₂] (Mrose et al. 1961) have attracted much attention (Böttcher et al. 1997a, 1997b; Bucca et al. 2009; Busenberg and Plummer 1986b; De Villiers 1971; Franke et al. 1984; Hood et al. 1974; Königsberger et al. 1998; Lippmann 1968; Mavromatis et al. 2016; Pimentel and Pina 2014; Sánchez-Pastor et al. 2011; von Allmen et al. 2010) because these two minerals can be seen as analogous to aragonite (CaCO₃) and dolomite [CaMg(CO₃)₂] in the CaCO₃-MgCO₃ system. The concept of analogy is based on striking structural and chemical similarities. Witherite and aragonite are isostructural (De Villiers 1971). Dolomite and norsethite structures, in a simplified view, can be derived from the calcite structure where alternating Ca- and carbonate-layers lie perpendicular to the c-axis and every Ca²⁺ is coordinated by six equidistant oxygen ions (Lippmann 1973). In dolomite, every other Ca-layer is replaced by a Mg-layer. This replacement is accompanied by a small rotation of the carbonate groups resulting in smaller Mg-O and larger Ca-O distances. The resulting symmetry is reduced from R3c to R3 (Lippmann 1973). Norsethite can be derived from dolomite by exchanging Ca with Ba, which causes a further rotation of the carbonate groups resulting in the space group R3c (Effenberger et al. 2014). Due to this carbonate rotation, Ba is irregularly and asymmetrically coordinated by six strongly bonded O atoms (like Ca in dolomite) and by six weakly bonded O atoms with a larger Ba-O distance (Ende et al. 2017). However, there is a far more important difference between norsethite and dolomite. Norsethite, unlike dolomite, readily grows from aqueous solutions at ambient temperatures.