Synthesis of Large Norsethite Crystals in Aqueous Ammonium Nitrate Solutions

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Dolomite [$CaMg(CO_3)_2$] is a double carbonate mineral that is rare in modern sediments of Holocene (12000 years ago), but abundant in ancient carbonate of the Precambrian age (several billion years ago). This paradox, known as the “dolomite problem,” has been discussed over the past two centuries from the viewpoint of mineralogy. Norsethite [$BaMg(CO_3)_2$] garners significant research interest as a model material for elucidating the formation mechanism of double carbonates because, unlike dolomite, which is formed under hydrothermal conditions, it can be readily obtained under ambient laboratory conditions. However, intrinsic exploration of surface reactions in the solution-mediated transformation from witherite [$BaCO_3$] is restricted due to the difficulty in growing norsethite crystals. Here we demonstrate the relationship between the synthesis of norsethite via the Ostwald’s step rule and improvement in solubility by adding NH_4NO_3.

To synthesize large norsethite, 11.804 g of $BaCO_3$ powder, 0.3 M $MgCl_2$, 1 M NH_4NO_3, and 0.005 M $NaHCO_3$ were added to pure water at 90 °C in turn. The sediments obtained in one month were observed *ex-situ* by polarizing microscopy. To determine the solubility, norsethite and witherite powder were added to 0-1 M NH_4NO_3 solutions. The Ba^{2+} concentrations in the saturated solutions of norsethite and witherite were measured by inductively coupled plasma–optical emission spectroscopy. To evaluate the growth rate, 0.3 M $BaCl_2$, 0.3 M $MgCl_2$, 0–1 M NH_4NO_3, and 0.005 M $NaHCO_3$ were added to pure water at 90 °C in turn. The temporal progress of the sediments was observed *ex-situ* by polarizing microscopy.

Figure 1 shows effects of NH_4NO_3 on the solution-mediated transformation of norsethite at 90 °C. We succeeded in growing rhombohedral norsethite crystals with a size of 150 μm in a 1 M NH_4NO_3 solution at 90 °C (Figure 1A). The solubilities of norsethite and witherite in the presence of NH_4NO_3 were ~35 and ~45 times higher than those in the absence of NH_4NO_3, respectively (Figure 1B). At 90 °C, the growth rate of norsethite in NH_4NO_3 solutions was ~17 times higher than that in NH_4NO_3-free solutions (Figure 1C). These results demonstrate that especially increasing the solubility of witherite by adding NH_4NO_3 is crucial for the synthesis, namely, a high driving force of norsethite crystallization is vital for obtaining large norsethite crystals.

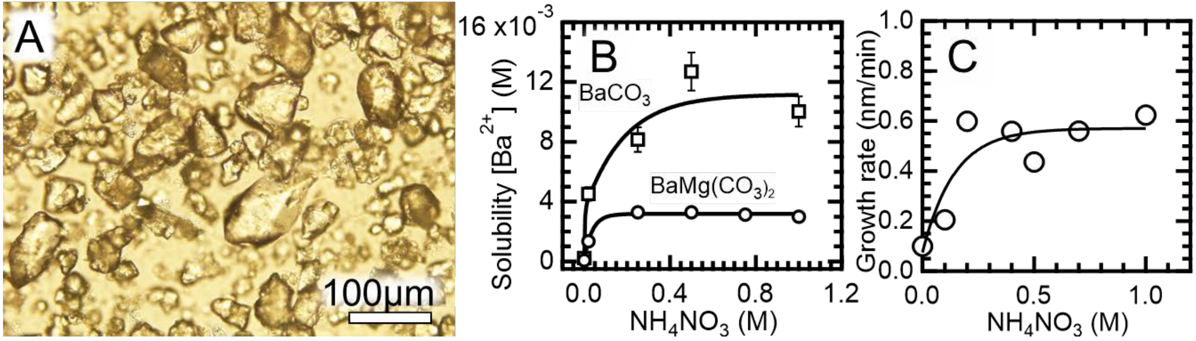

Figure 1. Effects of NH_4NO_3 on the solution-mediated transformation of norsethite at 90 °C: (A) norsethite grown in a 1 M NH_4NO_3 solution; (B) solubility of norsethite and witherite [$BaCO_3$]; (C) growth rate. In (B,C), open circles and open squares correspond to the data of norsethite and witherite, respectively.