Thermodynamic relationship between norsethite [$BaMg(CO_3)_2$] and witherite[$BaCO_3$]

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Dolomite [$CaMg(CO_3)_2$] is a double carbonate mineral that is rare in modern sediments of the Holocene starting 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 [$BaMg(CO_3)_2$] receives considerable 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. It is well-known that norsethite is formed from witherite [$BaCO_3$] by solution-mediated transformation. Therefore, to presume the ancient ambient condition, the thermodynamic relationship between norsethite and witherite is crucially important. In the present study, we investigated the energy diagram and phase diagram of norsethite, and then we demonstrated features of solution-mediated transfoamation of norsethite.

Norsethite and witherite powder were added to pure water at various temperatures. The dissolution equilibria of norsethite and witherite were confirmed by pH measurements. The barium–ion $[Ba^{2+}]_{nor}$ and magnesium–ion $[Mg^{2+}]_{nor}$ concentrations in the saturated solutions of norsethite and barium ion $[Ba^{2+}]_{wit}$ concentrations in the saturated solutions of witherite were measured by inductively coupled plasma–optical emission spectroscopy. The carbonate–ion concentrations in the saturated solution of norsethite $[CO_3^{2-}]_{nor}$ and witherite $[CO_3^{2-}]_{wit}$ were obtained from the total organic carbon measurements, respectively.

Figure 1 shows the thermodynamic relationship between norsethite and witherite at various temperatures. $[Ba^{2+}]_{nor}$ and $[Mg^{2+}]_{nor}$ were almost the same, and $[Ba^{2+}]_{wit}$ was lower than $[Ba^{2+}]_{nor}$ at a temperature of less than 60 °C. In contrast, $[Ba^{2+}]_{nor}$ was lower than $[Ba^{2+}]_{wit}$ over 60 °C (Figure 1A). $[CO_3^{2-}]_{wit}$ was also lower than $[CO_3^{2-}]_{nor}$ at less than 60 °C, and $[CO_3^{2-}]_{nor}$ was lower than $[CO_3^{2-}]_{wit}$ over 60 °C (Figure 1B). Using Figures 1A,B, the supersaturation of witherite in the saturated (equilibrium) solution of norsethite was calculated to determine the thermodynamic stability (Figure 1C). Consequently, we revealed that witherite was under supersaturation at less than 60 °C, and witherite was under undersaturation over 60 °C. In other words, the results demonstrate that over 60 °C norsethite is thermodynamically stable, and norsethite is formed by solution-mediated transformation.

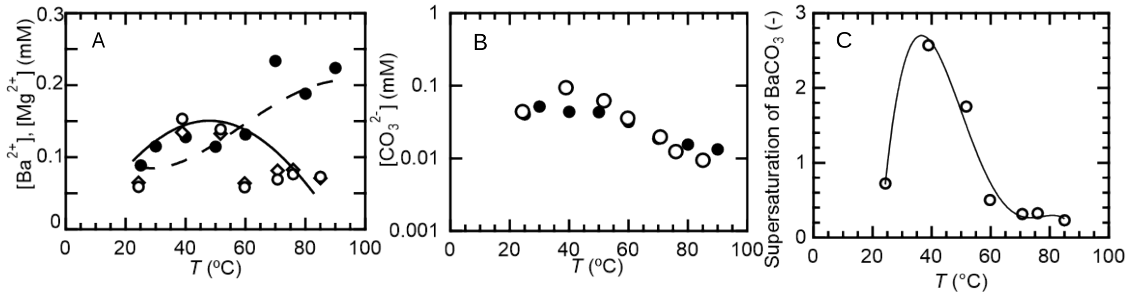

Figure 1. Thermodynamic relationship between norsethite [$BaMg(CO_3)_2$] and witherite [$BaCO_3$] at various temperatures. (A) [Ba^{2+}] and [Mg^{2+}] in saturated solution of norsethite and witherite; (B) [CO_3^{2-}] in saturated solution of norsethite and witherite; (C) supersaturation of witherite in saturated solution of norsethite. In (A), ○, ◇, and ● correspond to $[Ba^{2+}]_{nor}$, $[Mg^{2+}]_{nor}$, and $[Ba^{2+}]_{wit}$, respectively. In (C), ○ and ● depict $[CO_3^{2-}]_{nor}$, $[CO_3^{2-}]_{wit}$, respectively.