

Effects of Trace Lanthanum Ion on the Stability of Vaterite and Transformation from Vaterite to Calcite in an Aquatic System

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Introduction

Calcium carbonate, carbon dioxide and carbonic acids link to each other in aquatic environment. Calcium carbonate has three polymorphs; vaterite, aragonite and calcite, with numerous variations of morphology in the natural minerals or organisms. It is reported experimentally that that less stable polymorphs appear by addition of impurities such as some inorganic ions (e.g. Kitano, 1962) and organic substances (e.g. Falini et al., 1996) or by kinetic effects (e.g. Ogino et al., 1987). The transformation of the labile phase to the most stable calcite is also influenced by the minor or trace impurities. The presence of phosphate ions in solution stabilized the initially formed vaterite by decreasing remarkably the rate of its transformation to calcite (Katsifaras and Spanos, 1999). Akagi and Kono (1995) reported that the ion activity products (IAP) of calcium carbonate increased about 6 times when lanthanum ion was present at the molar ratio $[La]/[Ca] = 7 \times 10^{-5}$ in the parents solutions. We have investigated the mechanism of the IAP increase induced by the presence of lanthanum.

Experimental Methods

The concentration of starting solution was 15 mmol kg⁻¹ as CaCO₃. La concentration doped in the initial solutions was in the range of 0–17.3 μmol kg⁻¹. CaCO₃ was spontaneously precipitated from the initial solutions in a glass reacting vessel kept at 30 °C. The solution was stirred during the experiment. This vessel had a pH electrode and a sampling rubber-septum which enabled us to sample small aliquot of solution (about 100–300 μl) under an almost closed condition. In the case of the closed system, the total amount of carbon within the system is constant, which makes arithmetic analysis of the carbonic acid system possible. The amount of the precipitates and IAP of calcium carbonate were calculated from the pH of solutions on the assumption of chemical equilibrium among ionic species. Recovered precipitates were characterized with analyzed XRD and SEM. La concentration in the precipitates and solutions were determined by ICP-MS.

Results and Discussion

The abundance of the each polymorphs and total CaCO₃ as a function of time are shown in Figure 1. When lanthanum ion was doped in the initial supersaturated solution (B), a distinct transitional stage in the reaction was observed, whereas the transitional stage was absent without La (A). In the stage the solutions behaved like an equilibrium state and composition of polymorphs did not change. After the stage, calcium carbonate precipitated quickly to reach a new state, and the log IAP of the stage was about -7.9. This value is close to the reported log IAP value of vaterite (-7.902 at 25 °C by Plummer and Busenberg, 1982). We regarded this state as the equilibrium, as the state was maintained over a long period (more than one month). Within less than one hour from the beginning of the reaction, vaterite formation occurred quickly and calcite formation was inhibited. During the metastable state, the amounts of polymorphs were constant. After the transitional stage, the solution rapidly precipitated calcite. The amount of vaterite remained constant from the early stage of reaction. La concentrations in the solution were very low (around 1 x 10⁻⁷ mol kg⁻¹) throughout the reaction except the very early stage of reaction. On the other hand, the amounts of La in the precipitate was relatively high and stayed almost constant during the reaction. After the transitional stage, a decrease in La/Ca ratio was observed. Taking into consideration that newly precipitated polymorph was only calcite and the amount of La in the precipitate was constant, it is inferred that newly formed calcite contained only little amounts of La and La was concentrated only in vaterite. Assuming that calcite contains no La, calculated La/Ca ratio in vaterite was constant during the reaction. It can be concluded that the transformation from vaterite to calcite was heavily inhibited by the presence of La in vaterite. Or, nucleation of calcite is inhibited by the presence of La in the starting solution. The vaterite became extremely stable by concentrating La in it and stayed stable for much prolonged time.

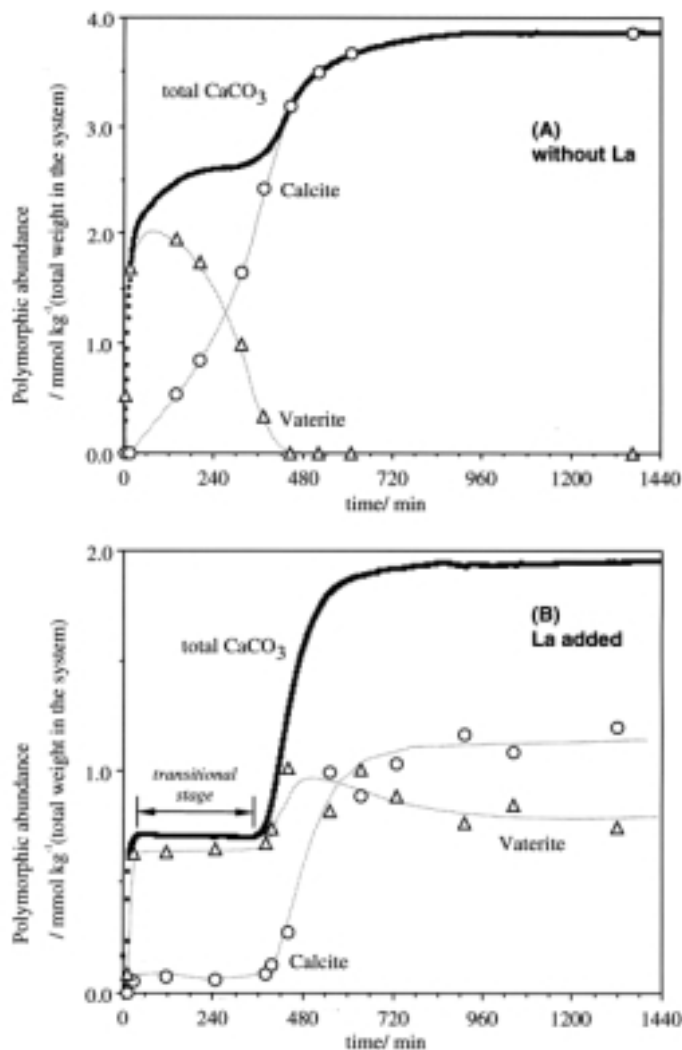


Figure 1: Plots of the abundance of each polymorph and total CaCO₃ as a function of time. Calcium carbonate precipitated from solutions without, (A) and with La (6.0 μmol kg⁻¹), (B).

Akagi T & Kono Y, *Aquatic Geochem.*, **1**, 231-239, (1995).
Falini G, Albeck S, Weiner S & Addadi L, *Science*, **271**, 67-69, (1996).
Katsifaras A & Spanos N, *J. Crystal Growth*, **204**, 183-190, (1999).

Kitano Y, *Bull. Chem. Soc. Japan*, **35**, 1973-1980, (1962).
Ogino T, Suzuki T & Sawada K, *Geochim. Cosmochim. Acta*, **51**, 2757-2767, (1987).
Plummer LN & Busenberg E, *Geochim. Cosmochim. Acta*, **46**, 1011-1040, (1982).