

含水炭酸カルシウム鉱物の変質速度と溶解度に及ぼすマグネシウムイオンの影響 Effects of magnesium ion on alteration rate and solubility of hydrated calcium carbonate

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INTRODUCTION

Calcium carbonates are abundant in nature. There are six distinct calcium carbonate species. Anhydrous polymorphs are calcite, aragonite, and vaterite, and hydrated forms are monohydrocalcite (monohydrate), ikate (hexahydrate), and amorphous calcium carbonate. Although calcite is most stable among these six phases, solutions containing Mg^{2+} , SO_4^{2-} , and organic matter, such as sea waters and brines have been known to inhibit the formation of calcite [1]. Monohydrocalcite have been found in saline and alkaline lakes and sea water environment [2]. Monohydrocalcite is metastable unlike anhydrous calcium carbonates and transformed to aragonite in aqueous solutions [3]. However there have been few studies that examine the metastability of monohydrocalcite quantitatively. In the present study, effects of magnesium ion on the alteration rate of monohydrocalcite to aragonite and on the solubility of monohydrocalcite have been examined in the laboratory experiments.

METHODS

Monohydrocalcite was synthesized by mixing solutions containing 60 mM $CaCl_2$ and 6, 30, 45, 60, and 120 mM $MgCl_2$ ($[Mg]/[Ca]$ ratio was 0.1 to 2), where Na_2CO_3 was added to yield a 80 mM CO_3^{2-} solution. The resulting suspension was collected every several hours and filtered through a 0.22 μ m membrane. Total alkalinity of filtered solutions were evaluated by acid titration and the total concentrations of Ca^{2+} and Mg^{2+} were measured with inductive coupled plasma optical emission spectrometry (ICP-OES, SII SPS7700). The filtered solid were air-dried, and analyzed by X-ray diffraction (XRD, Rigaku RINT2000). The amounts of monohydrocalcite and aragonite contained in the resulting solid were evaluated by the external standard method [4]. Solubility products of monohydrocalcite were calculated by Geochemist's Workbench [5] based on total alkalinity, total concentrations of cations, and pH.

RESULT AND DISCUSSION

Monohydrocalcite formed when mother solution contained Mg^{2+} of 30, 45, 60, and 120 mM. XRD analyses revealed that aragonite was formed 78-98, 101-126, 79-106, and 101-126 hours after beginning of the experiments of 30, 45, 60, and 120 mM of Mg^{2+} , respectively. After aragonite was formed, the peak intensity of monohydrocalcite decreased with time, while that of aragonite increased with time. Alkalinity, Mg^{2+} , and pH of the solution gradually decreased with time. Ca^{2+} increased with time until XRD peak intensity of monohydrocalcite completely disappeared. After monohydrocalcite disappeared, Ca^{2+} slightly decreased. The increment of Ca^{2+} resulted in decrement of alkalinity, because the concentrations of dissolved components must be determined by a solubility product of solid phase. The calculated solubility products of monohydrocalcite were constant in the series of Mg^{2+} concentrations, but different among experimental conditions. The solubility products of monohydrocalcite may be affected by the concentration of Mg^{2+} in solution. However, our result suggests the induction time of transformation of monohydrocalcite to aragonite were not affected macroscopically by Mg^{2+} contents in mother solutions.

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キーワード: 炭酸カルシウム鉱物, 準安定相, 変質速度, 溶解度

Keywords: calcium carbonate, metastable, alteration rate, solubility