

THE INFLUENCE OF SOME NATURALLY OCCURRING MINERALS ON THE PRECIPITATION OF CALCIUM CARBONATE POLYMORPHS

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Abstract

In this work precipitation of calcium carbonates, initiated by the addition of suspended mineral particles (quartz, kaolinite or montmorillonite) was investigated. In the precipitation system the initial concentrations of calcium and carbonate species, as well as the ionic strength, were similar to those in seawater. In the model system, in which no mineral particles were added, vaterite was the only solid phase precipitated after an induction period of approximately two minutes. Quartz had no influence on the precipitation, while the addition of kaolinite to the system partially inhibited the precipitation process; the effect could probably be attributed to the organic matter desorbed from its surface. In contrast, the addition of calcium montmorillonite caused an instantaneous precipitation of calcite thus indicating montmorillonite to be a suitable substrate for the overgrowth of this polymorph.

Key-words: calcium

Introduction

Calcium carbonate exists in three polymorphic modifications: calcite, aragonite and vaterite. Calcite is thermodynamically stable, whereas vaterite is the least stable of these polymorphs at conditions on the earth's surface. Besides the major influence of the initial concentration of constituent ions, temperature and dissolved impurities on the formation of certain modification [1, 2], suspended mineral particles may also play an important role. Namely, when crystals are formed at moderate or low supersaturation, as is the case in calcium carbonate precipitation from natural water, the mechanism of their nucleation cannot be homogeneous because the work of forming the nuclei is too large. The nucleation process may be catalyzed by the presence of any solid surface (heteronuclei); in this case the similarity of crystal lattices of a substrate and growing phase is much more important than any chemical similarity. When the lattice mismatch, δ , defined as $\delta = |a-b|/a$, is less than *ca.* 0.02, the growth of nuclei on the substrate follows a specific orientation (*a* and *b* are the stress-free lattice parameters of the substrate and the overgrowing phase respectively). This special case of heterogeneous nucleation, epitaxy, requires the initial formation of an immobile monolayer of regular atomic patterns which serves as the embryo [3, 4]. In this paper the influence of suspended mineral particles on the precipitation of calcium carbonate polymorphs was investigated. Three types of naturally occurring minerals, quartz, kaolinite and montmorillonite, were used to inoculate the solution supersaturated with respect to all calcium carbonate polymorphs. The total concentrations of calcium and carbonate species, as well as the ionic strength, were similar to those found in seawater.

Experimental

The chemicals used, CaCl_2 , Na_2CO_3 , HCl, NaOH, NaCl and MgCl_2 were all analytically pure (Merck Darmstadt, Germany) while the solutions were made from triple-distilled water. Quartz, kaolinite and montmorillonite (Aldrich, USA) were used as they were, without any purification and the specific surface area of these minerals was determined by the B.E.T. method (Micromeritics Flowsorb II 2300, USA) using nitrogen. Samples of magnesium, calcium and sodium montmorillonite were prepared by soaking the natural montmorillonite (bentonite) in a solution of respective salt ($c(\text{MgCl}_2)$, CaCl_2 or NaCl) = 1 mol dm^{-3}). These samples were occasionally shaken and after three days were separated by centrifugation and thoroughly rinsed with water.

The experiments were started by pouring 100 cm^3 of 2.10^{-2} mol dm^{-3} CaCl_2 solution into the same volume of 4.10^{-3} mol dm^{-3} freshly prepared Na_2CO_3 solution. Both solutions were preadjusted to pH = 10 by means of NaOH or HCl, while the ionic strength ($I = 0.5$ mol dm^{-3}) was adjusted by adding NaCl. The mineral particles, kaolinite, montmorillonite or quartz, were added into the sodium carbonate solution before pH adjustment. The suspension was additionally homogenized by means of an ultrasonic bath. During the experiments, the temperature was kept constant ($t = 25 \pm 1^\circ\text{C}$) and the system was continuously stirred at a constant rate by means of a teflon-coated magnetic stirring bar. The propagation of reaction was followed by measuring pH of the solution. For that purpose a combined glass-calomel electrode (GK 2401 B) connected to a digital pH meter (ION 85) and a recorder (REC 80 Servograph with a REA 160 Titrigraph Module), all Radiometer, has been used. Commercial standard buffer solutions (Radiometer) were used to adjust the pH meter (pH 7.01 and 9.18 at 25°C) prior to the start of each experiment. Composition of the precipitate was determined by using a FT-IR spectroscopy (Perkin-Elmer FT-IR spectrophotometer, Mo 2000). For this purpose, the suspensions were

filtered through 0.22 μm membrane filter, the precipitate was dried at 105°C for one hour, the KBr pellet was prepared and then analyzed. The morphology of individual particles was observed by optical (Ortoplan photographic microscope, E. Leitz, Wetzlar) and scanning electron microscopy (Hitachi S 530). Calculations of solution composition were performed by means of a BASIC program on a personal computer [5].

Treatment of data

From the recorded pH data and the initial total concentrations of calcium chloride, $[\text{Ca}]_i$, sodium carbonate, $[\text{CO}_3]_i$, and sodium chloride, the concentrations and the corresponding activities of ten ionic species assumed to exist in the solution to a considerable extent (H^+ , OH^- , CO_3^{2-} , HCO_3^- , CaCO_3^0 , CaHCO_3^+ , NaCO_3^- , Ca^{2+} , Na^+ , Cl^-) were calculated by means of a BASIC program. The equilibrium constants, determining the protolytic and other equilibria, were taken from the paper of Plummer and Busenberg [6], while the activity coefficients, γ_z , of the ionic species of the charge *z* were estimated by means of the Davies equation [7]. The amount of precipitate, [ppt], was found by subtracting the calculated total concentration of carbonate ions ($[\text{CO}_3]_{\text{tot}} = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{CaHCO}_3^+] + [\text{NaCO}_3^-]$) from the known initial total concentration of carbonate ($[\text{CO}_3]_i = 2.0 \cdot 10^{-3}$ mol dm^{-3}) – in the precipitation system described, total initial concentration of calcium species is in excess in comparison to total concentration of carbonate species ($[\text{Ca}]_i = 1.0 \cdot 10^{-2}$ mol dm^{-3} ; $[\text{CO}_3]_i = 2.0 \cdot 10^{-3}$ mol dm^{-3}); therefore, the maximum amount of calcium carbonate that could precipitate is determined by the concentration of carbonate. The program furthermore calculated the supersaturation given as saturation ratio, *S*, expressed as a square root of the activity quotient:

$$S = \sqrt{\frac{[\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}] \cdot \gamma_z^2}{K_s^0}}$$

where K_s^0 is the thermodynamic solubility product of calcite.

Results and Discussion

The initial total concentrations of calcium and carbonate species ($c(\text{CaCl}_2) = 1.0 \cdot 10^{-2}$ mol dm^{-3}) and ($c(\text{Na}_2\text{CO}_3) = 2.0 \cdot 10^{-3}$ mol dm^{-3}) in the systems investigated in this work, as well as the concentration of NaCl ($c(\text{NaCl}) = 0.5$ mol dm^{-3}), were similar to those found in seawater. The initial supersaturation has been adjusted by the addition of different amounts of NaOH or HCl to calcium or carbonate solution. The artificial seawater was not used in these experiments, since it would contain significant amount of Mg^{2+} ($c = 5.10^{-2}$ mol dm^{-3}). Namely, it is well known that, among the inorganic components dissolved in seawater, Mg^{2+} undoubtedly has a principle influence on the calcium carbonate precipitation [8]. Spontaneous precipitation of calcium carbonates from artificial seawater always results in formation of aragonite; the effect is so strong that aragonite precipitates even in the case when such solution is inoculated by vaterite or calcite [9]. By using a natural seawater, the system would become even more complex because of the presence of dissolved phosphates and organic constituents. In Figure 1 the progress curves (Fig. 1a) and the corresponding desaturation curves (Fig. 1b) for unseeded precipitation of calcium carbonates in the systems having different initial supersaturations ($5.5 \leq S_i \leq 8.5$) are shown. It can be seen that the onset of precipitation succeeded after a delay of a certain period of time (induction period) that varied between 2 and 20 minutes. In each system the final supersaturation is approximately 1.9 which corresponds to vaterite