Breakdown of the Ostwald step rule--The precipitation of calcite and dolomite from seawater at 25°C and 40°C

Introduction

Carbonate precipitation in natural waters is governed by both thermodynamic and kinetic considerations. The concentration and ionic composition of natural solutions influence not only the mineralogy of the precipitate, but also the habit of both metastable and stable phases. For example, it is difficult for dolomite to form in saline solution (i.e. seawater) due to the rapid carbonate precipitation rate of metastable phases and high hydration energy of magnesium ion. With the exception of the Arctic Ocean, surface seawater is supersaturated with respect to carbonate minerals (such as dolomite, aragonite and high-magnesian calcite), but because of the highly-ordered dolomite structure, precipitating dolomite directly from seawater below 100°C has proven to be impossible (see Land 1998).

Kinetic hindrances to dolomite precipitation from seawater

Dolomite is a highly ordered mineral, with alternating sheets of solely Ca or Mg atoms along the c axis. The kinetic inhibition of dolomite formation at low temperatures results from the fast precipitation rate of metastable carbonate minerals (e.g., vaterite, aragonite, calcite) and the strong hydration of the Mg\(^{2+}\) ion. The formation of aragonite and calcite is kinetically favoured because of their simpler structure. One of the models proposed to explain the occurrence of large, ancient dolomite deposits is the meteoric-marine mixing-zone model, which calls for the dilution of seawater with meteoric water (Land, 1973). The thermodynamic basis/working principle of this mixing model is that solutions containing more than 5% seawater are supersaturated with respect to dolomite but undersaturated with respect to calcite and aragonite. Wigley and Plummer (1976) also demonstrated that with pCO\(_2\) as high as 10\(^{-2}\) atm, dolomitization of calcite could take place in mixtures of groundwater and 35-75% seawater.

Breaking Ostwald's Rule

In 1897, Ostwald claimed as a universal principle, that a metastable solid phase will precipitate before the more stable phase (Deelman, 2001; Nordeng and Sibley, 1994). The
nucleation of a less stable phase is kinetically favoured over that of a more stable phase because the less stable phase has the lower solid-solution interfacial tension. Although dolomite can be precipitated from aqueous solutions above 100°C (Arvidson and Mackenzie, 1999), it has been impossible to synthesize dolomite at room temperatures using natural seawater (such as Land 1998)—although dolomite in the rock record has been found to form under low-temperature conditions (Alonso-Zarza and Martin-Perez, 2008). Nevertheless, by alternating between intervals of dissolution and precipitation, Deelman (1999) succeeded in synthesizing dolomite at low temperatures (between 313K and 333K). He concluded that fluctuations in solution concentration, temperature or pressure on a local scale, which are capable of breaking Ostwald's Rule, would be required to enable the low-temperature synthesis of dolomite. Deelman (1999) proposed that the natural fluctuations will result in alternating periods of dissolution and precipitation. During cycling the solution between undersaturation and supersaturation with respect to metastable phases whereas remain supersaturated with more stable phases, environmental fluctuations that result in dissolution of metastable phases will ultimately leach out all metastable phases, favouring formation of stable phases. Therefore, according to Deelman (1999), dolomite can only be synthesized in dynamic experiments in which environmental parameters are allowed to fluctuate, as is often the case in nature, but seldom applied in the laboratory. Fluctuating pH conditions are frequently observed in natural aquatic systems and occur at various frequencies (e.g., seasonal changes in water chemistry; daily changes caused by photosynthesis/respiration; temperature effect on gas solubility).

The significance of calcium carbonate and dolomite

Under Earth surface conditions, carbonate minerals are among the most chemically reactive and ubiquitous minerals in both marine and fresh water environments (Morse et al., 2007). Calcite (CaCO$_3$(s)) and dolomite (CaMg(CO$_3$)$_2$(s)) are by far the most abundant rock-forming carbonate minerals, comprising more than 90% of natural carbonates in the crust (Reeder, 1983). In modern sediments, aragonite and high-magnesian calcites dominate in shallow water environments, whereas low magnesium calcite (<4 mole% MgCO$_3$(s)) composes almost all deep-sea carbonate-rich sediments (Morse et al., 2007). These minerals largely impact the chemistry of aquatic systems by regulating pH and alkalinity through dissolution/precipitation equilibria, as well as their sorption capacity for divalent cations.
Given their environmental significance and broad industrial applications, carbonate minerals have been the subject of extensive research. The formation of low-temperature (below 100°C) dolomite is often explained by the conversion of pre-existing calcium carbonate deposits in Mg-rich solutions (e.g., seawater), but this and other "dolomitization" models fail to explain the occurrence of dolomite in soils (Sherman et al., 1962), coal (Gothan and Benade, 1932), rivers (Barnes and O'Neil, 1971), lakes (DeDecker and Last, 1988), or sea floor concretions (Brown and Farrow, 1978).

Based on results of previous experiments in various electrolyte solutions (Libermann, 1967; Deelman, 1999, 2001), cycling of the saturation state of a solution between calcite/aragonite supersaturation and undersaturation is believed to concentrate the more stable phase (i.e. dolomite). In this study, through changing pCO₂ of the solution, I propose to repeatedly cycle the ionic activity product (IAP) of a seawater solution between calcite or aragonite supersaturated and undersaturated conditions, in an attempt to nucleate and concentrate more stable phases (i.e. low magnesian calcite and/or dolomite) instead of the metastable phases (amorphous calcium carbonate, vaterite, aragonite and high-magnesian calcite) that normally precipitate from seawater.

Challenge

- There is an ongoing debate about the solubility of dolomite at 25°C (10⁻¹⁷ [Hsu, 1963] or 10⁻¹⁸.¹⁴ [Helgeson et al., 1978]), and the quantitative effects of order and stoichiometry on dolomite solubility (the most Ca-rich modern dolomite known to be ordered on the basis of TEM studies has the stoichiometry Ca₁.₂₂Mg₀.₇₈(CO₃)₂ - Mitchell et al., 1987). For the sake of our preliminary calculations, we adopted a K⁰sp₉ dolomite of 10⁻¹⁷, derived from a careful and detailed study carried out by Hsu (1963). Nevertheless, the solubility products will be more precisely determined if measurable quantities of dolomite can be synthesized at low temperature in seawater.

- Typical surface seawater has salinity 35, a specific alkalinity of 0.126 TA/Cl, and pH range between 7.5 and 8.4 on pH of 0-14 scale. Given the concentrations of Ca²⁺, Mg²⁺ and CO₃²⁻ in this surface seawater and estimates of their individual ion activity coefficients (Millero and Schreiber, 1982), the ion activity product of typical surface seawater is on the order of 10⁻¹⁵.⁰¹. Hence, modern seawater is supersaturated by two
orders of magnitude with respect to dolomite (i.e., $\Omega = \text{IAP}/\text{K}^{\circ} \text{sp} \approx 100$), yet dolomite does not precipitate readily from seawater. The most widely-accepted explanation for the lack of dolomite precipitation from seawater is that the reaction is kinetically inhibited by the fast nucleation/precipitation of metastable phases and strong hydration of $\text{Mg}^{2+}$ ion. Other kinetic inhibitors of dolomite precipitation in seawater, such as $\text{SO}_4^{2-}$ ions (Baker and Kastner, 1981) have been proposed, but the role of sulphate has been questioned (e.g. Hardie, 1987). In fact, the actual mechanism of inhibition is not clearly established.

Working hypothesis/Expected results

Although seawater is highly supersaturated with respect to dolomite, the formation of dolomite nuclei is kinetically inhibited with respect to the nucleation and growth of the less stable aragonite and calcite. The inhibition stems from its highly ordered structure (a low entropy) and the stronger hydration energy of the magnesium ion. Consequently, metastable phases, possibly a mixture of amorphous calcium carbonate (ACC), vaterite, aragonite and trace amount of nesquehonite, might precipitate out of solution during the first set of $\text{CO}_2$ cycling (first set of cycling = bubbling 5% of p$\text{CO}_2$ to equilibrium and extract $\text{CO}_2$ by ambient air bubbling ) performed at $25^\circ$C and $40^\circ$C. Deelman (1999) demonstrated that multiple cycling of a solution through between a supersaturation and undersaturation state with respect to calcite and/or aragonite would cause the metastable phases to dissolve, while preserving and concentrating more stable nuclei (i.e. dolomite and/or low-magnesian calcite). Based on the limited literature on the subject (Deelman, 1999; Liebermann, 1967), we expect that low-magnesian calcite and/or proto-dolomite (non-stoichiometric) will precipitate at $25^\circ$C, whereas a mixture of low-magnesian calcite and dolomite might precipitate at $40^\circ$C. The precipitation of more stable phases should be kinetically favoured at higher temperature due to the faster dehydration of magnesium ions adsorbed at the mineral surfaces.

Material and Methods

An initial solution will be prepared by equilibrating natural seawater with Alfa Aesar reagent grade $\text{CaCO}_3$ at a p$\text{CO}_2$ of 50000 ppm. The natural seawater was collected from station 23 (near Rimouski) at 300 m depth in the St. Lawrence Estuary. It has a salinity of 34.5 and a total alkalinity of 2290 $\mu\text{mol kg}^{-1}$ SW. The sequence of experiments described below will be carried out at $25^\circ$C and $40^\circ$C. The seawater solution will be equilibrated until a pH of ~6.63 (on
0-14 scale) is attained at 25°C. Upon equilibration with calcite ($\Omega_{\text{calcite}} = 1$; $\Omega_{\text{aragonite}} = 0.66$) at a pCO$_2$ of 5%, the total alkalinity of the solution should be ~8900 µmol kg$^{-1}$ of seawater, the calcium concentration should be 1.29*10$^{-2}$ mol kg$^{-1}$ of seawater, and the solution will be supersaturated with respect to dolomite ($\Omega_{\text{dolomite}} = 4.8$). After the solution reaches equilibrium (i.e., pH ~ 6.63 and stable), the solution will be filtered through a 0.45 µm filter to remove the calcite, and an aliquot preserved for analytical confirmation of the initial conditions of the experiments. Laboratory air (pCO$_2$ = 10$^{-3.42}$ or ~390ppm) will be bubbled through the CO$_2$-charged calcite-equilibrated seawater solution. As CO$_2$ is exsolved from the solution, the saturation state of the solution with respect to aragonite, calcite, and dolomite will dramatically increase and nucleation of carbonate minerals will likely ensue before equilibration with the gas phase is reached. At equilibrium with the gas phase and in the absence of precipitation, the solution would be highly supersaturated with all three minerals of interest ($\Omega_{\text{aragonite}} = 28$, $\Omega_{\text{calcite}} = 43$, $\Omega_{\text{dolomite}} = 8910$). I expect the first precipitate to be mixture of ACC (Amorphous Calcium Carbonate), vaterite, aragonite, with possible trace amounts of nesquehonite (Deelman, 1999). Because the kinetics of dolomite nucleation/precipitation is much slower than that of these metastable phases, it is not likely to precipitate in detectable quantities in this first precipitation. The precipitate will be filtered out of the solution and its mineralogy will be determined by X-ray powder diffraction. This first experiment will be carried out three times to demonstrate that I can reproducibly obtain the same precipitate mineralogy.

In subsequent experiments, the ambient air-equilibrated solution and the precipitate will be purged with a 10% CO$_2$:N$_2$ gas mixture. Once equilibrium is reached with respect to this pCO$_2$, the solution will be undersaturated with respect to aragonite and calcite ($\Omega_{\text{aragonite}} = 0.33$, $\Omega_{\text{calcite}} = 0.5$), but remain supersaturated with respect to dolomite ($\Omega_{\text{dolomite}} = 1.2$). Consequently, calcite crystals and metastable polymorphs should dissolve while, if present, dolomite should be preserved in solution. Once equilibrium with the gas phase is reached (pH ~ 6.34) and most of the precipitate is dissolved, ambient air will again be bubbled through the solution. As indicated above, the saturation state of the solution with respect to aragonite, calcite and dolomite will increase and nucleation of carbonate minerals will ensue before equilibration with gas phase is reached. This cycle will be run for at least 20 times. The precipitate will be filtered out of the solution after every 5 cycles and its mineralogy will be determined by X-ray powder diffraction. As the solution remains supersaturated with dolomite at all times, cycling through
undersaturation and supersaturation with respect to aragonite and calcite, dolomite nuclei should be more concentrated, and accumulate at the expense of aragonite and calcite. Nevertheless, because the lack of understanding of dolomite nucleation/precipitation mechanism, it is difficult to predict the composition of precipitate after repeated cycling. Therefore, a fallback experiment will be carried out in parallel: instead of cycling 10% CO2:N2 gas mixture, 5% CO2:N2 gas mixture will be cycled at all times to preserve calcite nuclei. According to Deelman (1999), it is highly possible that a mixture of pure calcite, low-magnesian calcite and proto-dolomite (non-stoichiometric) would precipitate when experiments are conducted at 25°C, and dolomite and low-magnesian calcite would form at 40°C in the fallback experiment.

Reference


