

# The Role of Zn, Sr, Mg and PO<sub>4</sub> in the Interaction of Carbonate-Rich Waters with Sulphate Minerals

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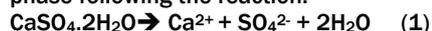
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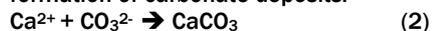
## INTRODUCTION.

The mechanism of transformation when one mineral phase reacts to form another (e.g. gypsum to calcite), in the presence of a fluid phase, is controlled by dissolution and precipitation processes (Schott et al. 2009, Putnis 2009). Sulphate deposits are abundant on Earth and even on Mars, and in many cases the interactions between sulphate minerals and carbonate-bearing groundwaters leads to the formation of carbonate deposits (Sanz-Rubio et al. 2001).

Furthermore, the potential role of gypsum (GYP, CaSO<sub>4</sub>·2H<sub>2</sub>O) in buffering CO<sub>2</sub> carbonated groundwaters stems from its relative high solubility at near neutral pHs; in natural waters gypsum dissolves easily over a wide range of pH (Arslan and Dutt 1993) and its dissolution releases calcium to the fluid phase following the reaction:



and in closed basins, the reaction with carbonate-rich waters leads to the formation of carbonate deposits:



This coupled process of dissolution/precipitation controls the formation of many carbonate deposits yet, our understanding of the reaction kinetics and mechanisms during these transformation processes is poor.

The present study aims to improve the understanding of the formation of CaCO<sub>3</sub> phases through a detailed experimental study of gypsum dissolution and CaCO<sub>3</sub> formation in the presence of Zn, Sr, Mg, or PO<sub>4</sub> at 25 °C. The purpose of this communication is to present the results of these experiments and use them to assess the role of ions in solution on the reaction kinetics of CaCO<sub>3</sub> formation.

## MATERIALS AND METHODS.

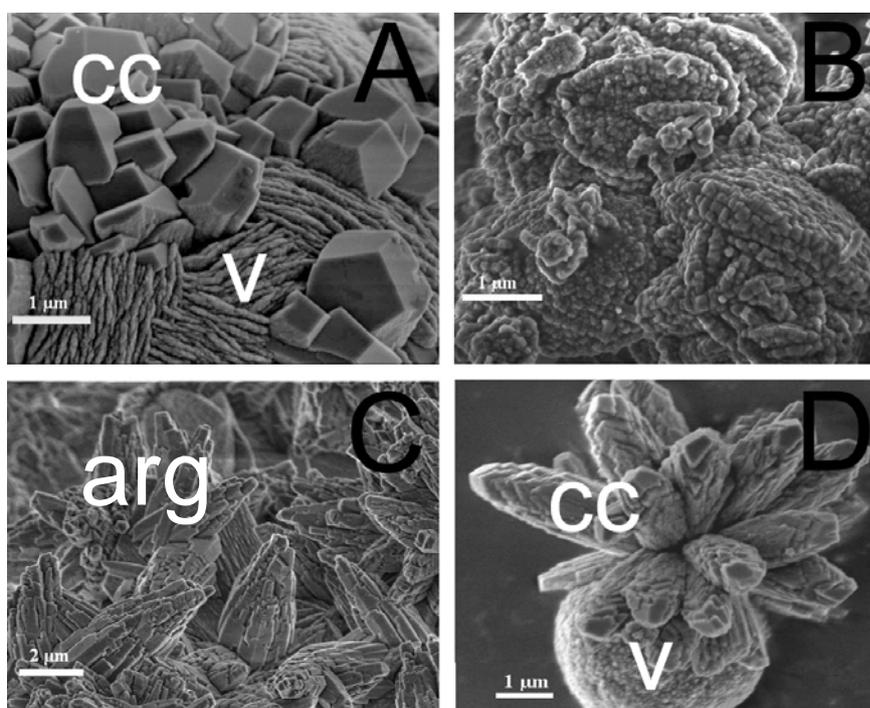
GYP was pulverized to a particle size  $\phi < 420 \mu\text{m}$ , cleaned with 18 M $\Omega$  cm<sup>-1</sup> Milli-Q grade water and air-dried. GYP powders were reacted with 50 mM Na<sub>2</sub>CO<sub>3</sub> at a GYP/liquid ratio of ~ 0.007 in stirred closed reactors. The experiments were run at two different initial pH settings (a) pH ≈ 11.4, in the presence of Na<sub>2</sub>CO<sub>3</sub> only or (b) pH ≈ 6.8, by supersaturating the mixed solutions with CO<sub>2</sub>(g). In both settings variable concentrations (1-100 mM) of Mg, Zn, Sr, or PO<sub>4</sub> were added and the reactions followed for up to 60 days.

Fluid and solid were sampled regularly from the experiments and the pH was measured during sampling. The

collected samples were filtered through 0.2  $\mu\text{m}$  acetate filters and the solution compositions analysed by ion chromatography (IC). The solid phases were washed with isopropanol and dried with a vacuum pump at 25 °C. Solids were characterized by powder X-ray diffraction (XRD) and imaged with a field emission gun scanning electron microscope (FEG-SEM) equipped with an energy dispersive X-ray spectrometer (EDX).

## RESULTS AND DISCUSSION.

The results of both pH sets showed that the dissolution of GYP lead to a relatively fast nucleation and growth of CaCO<sub>3</sub> polymorphs. As long as the solution had excess carbonate the



**Fig 1.** CaCO<sub>3</sub> polymorphs formed during experiments following approach (b at pH 6.8): (A) vaterite (V) and calcite (CC) formed in the presence of 1 mM Zn after 48 h; (B) vaterite formed in the presence of Sr after 48h; (C) aragonite (arg) formed in the presence of 100 mM Mg after 12h; (D) vaterite and calcite formed in the presence of 1 mM PO<sub>4</sub> after 48 h.

**palabras clave:** evaporitas, disolución, carbonatos, precipitación

**key words:** evaporites, dissolution, carbonate, precipitation

continuous dissolution of gypsum was mirrored by a simultaneous and continual precipitation of  $\text{CaCO}_3$ .

In all cases, the first phase nucleating on the gypsum surfaces was amorphous  $\text{CaCO}_3$  (ACC). ACC transformed gradually to crystalline  $\text{CaCO}_3$  phases with time (fig 1). The nature of the formed polymorphs depended on the experimental approach (high or low pH) or the presence and concentration of the additives.

During experiments conducted at high pH (experimental condition a) the initial pH slightly decreased (from 11.4 to 11.1) due to the precipitation of carbonate phases and all GYP completely dissolved in ~ 24 h. Concomitantly the initially precipitated ACC transformed into calcite within 2 days. This trend was also observed by Fernandez-Diaz et al. (2009), who studied the interaction between the GYP (010) surfaces and aqueous  $\text{Na}_2\text{CO}_3$ . In our experiments using 50 mM  $\text{Na}_2\text{CO}_3$  after 24 h the dominant polymorphs was calcite with only minor aragonite and vaterite present.

However, during the experiments at lower pH (experimental condition b) the process always started with a slow increase in pH due to the  $\text{CO}_2$  degassing, followed by a subsequent faster drop in pH due to the precipitation of carbonate phases. In these experiments the initial GYP took only ~ 5 h to fully dissolve and the carbonate polymorph after 30 h was solely vaterite. In this case, the lower pH and the presence of sulphate stabilized the vaterite (Bots et al. 2011, Fernandez-Diaz et al 2010).

The presence of the other additives strongly influenced both the reaction kinetics and the nature and morphologies of the crystalline end products in both experimental sets.

For example, using approach (b) and adding 1 mM Zn, lead to pure calcite with Zn being incorporated into its structure. The calcite morphology was truncated with smooth faces (fig 1 A). Interestingly, the presence of Sr in solution lead after 48 h to the formation and stabilization of vaterite with an ellipsoidal morphology with a rough surface with well defined aggregates (fig 1 B).

In contrast, if Mg was present in the initial solution, ACC transformed to

aragonite instead of vaterite, likely caused by the destabilization of vaterite by Mg (Bots et al. 2001). The presence of 5 mM Mg produced after 12 h only 32% aragonite, while with 100 mM Mg were added 95 % aragonite was produced in the same period of time with only trace amounts of calcite present (fig 1 C).

Lastly, the presence of  $\text{PO}_4$  produced spherical vaterite aggregates which after ~ 6 h started to transform into elongate calcite aggregates with the calcite crystals growing radially from the same starting point on the spherical vaterite surface (fig 1 D).

**Implications for natural systems.**

The early precipitation of calcite in saline waters determines whether the remaining solution becomes carbonate rich or poor. The first minerals to form are alkaline carbonates. Experimental data from condition b) are plotted in a Spencer Triangle – which represents the  $\text{Ca}^{2+} - \text{SO}_4^{2-} - (\text{HCO}_3^- + \text{CO}_3^{2-})$  system - (Spencer 2000) and where the line between the Calcite and the  $\text{SO}_4$  apex represent the chemical calcite divide (Hardie and Eugster, 1970) while the line from Calcite to Gypsum represents the chemical divide of gypsum (fig 2)

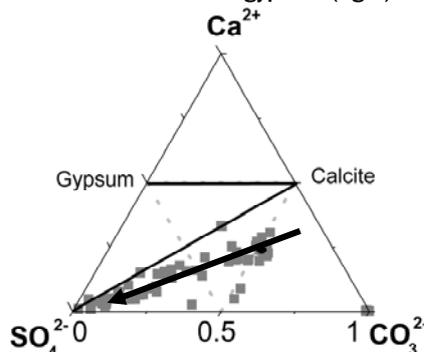


fig 2. Aqueous ratio concentration from the experiments performed at condition (b) (grey squares); The black arrow links the initial and final point of the experiments showing a depletion of  $\text{CO}_3^{2-}$  in solution due to the precipitation of  $\text{CaCO}_3$  polymorphs.

An arrow starting at the initial point and following the experimental conditions will predict the pathway, which leads to the formation of  $\text{CaCO}_3$ . The dissolution of GYP (reaction 1) released  $\text{Ca}^{2+}$  into the reacting solutions, which combined with the existing  $\text{CO}_3^{2-}$  species formed carbonate phases. Once the supersaturation with respect to carbonate was reached, ACC formed (reaction 2) and this subsequently transformed into various  $\text{CaCO}_3$

polymorphs depending on time and additives. When the fluid becomes depleted in carbonate the reaction is completed. All experiments started from the same point, but the kinetic pathways to reach the end product is different, leading to different proportions of solid  $\text{CaCO}_3$  phases. These are different not just in abundance but also in morphology that is drastically changed by the presence / concentration of ions (Zn, Sr, Mg,  $\text{PO}_4$ ) in the initial solution.

These results reveal that these additives play a fundamental role in controlling the nature and formation pathways of  $\text{CaCO}_3$  intermediate and end phases. This control of morphology and also the stabilization of for example vaterite or aragonite under conditions where in the pure system calcite is always the sole end product has major implications for biomineralization,  $\text{CO}_2$  sequestration and industrial production of  $\text{CaCO}_3$ .

**ACKNOWLEDGEMENTS:** This work was supported by the E.C. through the "MIN-GRO Research and Training Network" (MRTN-CT-2006-035488)

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