



# Dynamics of calcium carbonate formation: Geochemical modeling of a two-step mechanism

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## Abstract

A new kinetic model was developed based on a transition-state-theory (TST)/surface-complexation-model (SCM) coupling. It aims to describe the successive precipitation of amorphous calcium carbonate (ACC) and calcite, taking account of their mutual influence: ACC precipitates according to the standard TST and creates surface complexation sites from which calcite can form and create new surface complexation sites. When the kinetics of calcite precipitation are fast enough, the consumption of dissolved matter leads to the re-dissolution of ACC. This model is first compared to batch experiments (Gebauer et al., 2008) and then applied with a reactive transport calculation code to a dynamic experiment carried out on a microfluidic device composed of a single straight channel (Beuvier et al., 2015). The results show a good match between experiments and reactive transport modeling. This suggests that the combination of simple experimental microfluidic devices and reactive transport modeling could be a promising integrated methodology to study the dynamics of geochemical reactivity at the pore scale, as a first step before application to more complex and larger systems.

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## 1. INTRODUCTION

Understanding the mechanisms of calcium carbonate (CC) formation is a key issue because these minerals are quasi ubiquitous in the geosphere and are involved in a number of anthropogenic activities. A typical example concerns the geological storage of CO<sub>2</sub> in deep aquifers where the injection of this acid gas is known to induce chemical reactions involving the CaCO<sub>3</sub>-H<sub>2</sub>O chemical system, and to imply issues regarding changes in hydrodynamic proper-

ties of the rock (Gaus et al., 2005; André et al., 2010 and references therein).

### 1.1. Calcium carbonate formation mechanisms

Calcium carbonate formation has been studied for decades (e.g., Plummer and Busenberg, 1982), and it is now well accepted that it results from a multistep process. It involves nucleation (either homogeneous or heterogeneous) and crystal growth mechanisms (Morse et al., 2007).

The understanding of the process of homogeneous nucleation is still a subject under active research. It involves a number of possible mechanisms, either successive or simultaneous. They rely on several concepts/hypotheses

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including the genesis of locally dense liquid phases inside the aqueous solution, which are organized (meta)stable clusters that may act as precursors to the formation of amorphous calcium carbonate (ACC) nanocrystals (Cartwright et al., 2012). This ACC can be hydrated or anhydrous (Ihli et al., 2014). Its aging generates a calcium carbonate polymorph (vaterite, aragonite, calcite), depending on the physical and physicochemical conditions (Gebauer et al., 2008; Rodriguez-Blanco et al., 2011; Sun et al., 2015), e.g. temperature, pressure, chemical composition of the aqueous solution, including pH, salinity, Mg content, etc. (Tai and Chen, 1998; Wolthers et al., 2012; Blue et al., 2017). Dehydration of ACC provides another driving force (i.e. an energetic contribution) to orientate the crystallization process towards one particular polymorph (Ihli et al., 2014). The stable crystalline phase may also nucleate directly from the solution, without the genesis of cluster precursors (Nielsen et al., 2014). According to the classic nucleation theory, surface tension plays a key role in the evolution of a nucleus although literature data on surface energies of CC polymorphs are rather scattered and inconsistent (Aquilano et al., 1997; Spanos and Koutsoukos, 1998; Forbes et al., 2011; Manoli et al., 2002; Bruno et al., 2013; Sun et al., 2015). It is however possible to play with the shape of the CC precipitates by using organic molecules that modify surface tensions (Rudloff and Cölfen, 2004) and thus the direction of growth. Laws for calculating homogeneous nucleation rates can be found in Steefel and Van Cappellen (1990), Pokrovsky (1998), Espinosa-Marzal and Scherer (2010) and Sun et al. (2015).

Heterogeneous nucleation is often considered as a form of surface nucleation (Schott et al., 2009). It lowers the energy demand for creating a surface from a solution as for homogeneous nucleation. Thus, the induction time for nucleation is lowered when it can take place on an existing solid surface. In order to favor this type of nucleation at the expense of the homogeneous nucleation, solutions can be seeded with mineral grains that provide surfaces on which heterogeneous nucleation can take place (Nehrke et al., 2007; Noiriel et al., 2012).

Crystal growth can result from a number of mechanisms (Spanos and Koutsoukos, 1998). They include epitaxial type mechanism (Wolthers et al., 2012) according to a spiral pattern or a 2D nucleation-mediated growth, depending on the magnitude of the supersaturation of the initial solution with respect to the mineral (Teng et al., 2000). The kinetics of crystal growth can be described using a combination of a surface complexation model (SCM) and the transition state theory (TST) (Pokrovsky and Schott, 2002), especially when the reaction occurs close to equilibrium. This may particularly apply when an amorphous precursor precipitates so that the system is temporarily brought from far-from-equilibrium to conditions close to equilibrium with calcite. SCMs of calcite surface have been developed (Pokrovsky et al., 1999; Van Cappellen et al., 1993; Heberling et al., 2011; Wolthers et al., 2012) and can be used in combination with adapted kinetic laws. The role of the physicochemical conditions is also of major importance (Morse et al., 2007), including the solution stoichiometry (Zhang and Nancollas, 1998), in addition to the

saturation ratio (Schott et al., 2009). Crystal growth can also result from attachment (De Yoreo et al., 2015) and, in some instances, oriented attachment of nanoparticles (Zhang et al., 2014).

The different natural and lab conditions of occurrence of CC polymorphs have been studied (Morse et al., 2007) and main factors acting on the orientation of a system to evolve towards a given CC polymorph are identified: pH, magnitude of supersaturation, calcium vs. carbonate ratio, presence of additives (like magnesium), temperature, etc. However, the underlying mechanisms are still not well understood despite the major progress made in recent years (Van Driessche et al., 2017), which highlight the role of amorphous carbonate precursors (Ihli et al., 2014; Blue et al., 2017), of the water content in the amorphous solid (Nebel et al., 2008; Raiteri and Gale, 2010; Bushuev et al., 2015; Albéric et al., 2018), or of the incorporation of  $\text{Ca}(\text{OH})_2$  solid structure in the composition of amorphous basic calcium carbonates at high pH ( $> 11$ ) (Wang et al., 2017). There is still a matter of debate, even for the physicochemical conditions of CC polymorph occurrences, and inconsistencies can be found in the literature. For instance, Tai and Chen (1998) observed experimentally that, at 24 °C, vaterite is most abundant at  $\text{pH} < 10.5$  while aragonite is most abundant at  $10.5 < \text{pH} < 11.5$  and calcite is most abundant at  $\text{pH} > 11.5$ . On the contrary, in the pH range 8.5–10.5, Gebauer et al. (2008) observed experimentally that calcite is most abundant at  $\text{pH} < 9.5$  and vaterite is most abundant at  $\text{pH} > 9.5$ .

Of course, different natural and lab conditions have not only consequences on the nature of the stable CC, but they lead to different precipitation kinetics of CC and of calcite in particular (Spanos and Koutsoukos, 1998; Teng et al., 2000; Rodriguez-Blanco et al., 2011; Nielsen et al., 2014; Carino et al., 2017).

In this context, our study is limited to pH values ranging between 8.5 and 10.5, in the Ca-Na-Cl-CO<sub>2</sub>-H<sub>2</sub>O system, at 25 °C.

## 1.2. Towards application to porous media

Geological environments are mostly made of porous media through which fluids percolate. The porosity of rocks is largely due to small pores that are connected together and form complex frameworks (Wang, 2014; Schön, 2015). When the formation of CC takes place in the porosity, it can affect the rock hydrodynamic properties. As extensively discussed by Steefel et al. (2015), the description of these changes can nowadays benefit from numerous microscopic characterization methods as well as experimental microfluidic devices and numerical tools able to describe a number of mechanisms occurring at the pore scale.

Different modelling approaches have been developed since more than 20 years. The most popular is the Lattice-Boltzmann approach which allows a direct modelling from a particle-based technique (Blunt et al., 2013 and references therein). This approach suits well for reactive systems and fluid flows in complex geometries of pore spaces, fracture apertures and fracture networks (Meakin and Tartakovsky, 2009). These models were tested on

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