



# Influence of organic ligands on magnesite growth: A hydrothermal atomic force microscopy study

Quentin Gautier<sup>a,c,\*</sup>, Ulf-Niklas Berninger<sup>a,b</sup>, Jacques Schott<sup>a</sup>, Guntram Jordan<sup>b</sup>

<sup>a</sup> Géosciences Environnement Toulouse, Observatoire Midi-Pyrénées, CNRS, Université de Toulouse, 14, avenue Edouard Belin, 31400 Toulouse, France

<sup>b</sup> Department für Geo- und Umweltwissenschaften, Ludwig-Maximilians-Universität, Theresienstr. 41, 80333 München, Germany

<sup>c</sup> Université Paris-Est, Laboratoire Navier, 618, avenue Blaise Pascal, Champs-sur-Marne, 77455 Marne-La-Vallée, France

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## Abstract

In order to understand the effects of carboxylic ligands on magnesite growth at low hydrothermal conditions, the growth processes on the (104) surface have been investigated using hydrothermal atomic force microscopy (HAFM). Experiments were performed with various concentrations of oxalate, citrate and EDTA at  $T = 100\text{ °C}$  and a pH value of about 8.

We show that the ligands influence magnesite growth in different manners. At concentrations of 1–10 mM, citrate and oxalate both exert a significant, but different, effect on the morphology of growth islands, while EDTA has little influence. The shape modifications can be understood as a consequence of modified kink-reactivities due to ligand adsorption at particular kink-sites at the island steps, depending on the ligand conformation and chemical functionalities. However, none of the three investigated ligands significantly modifies obtuse steps velocities. On acute step velocity, HAFM resolution was unfortunately too low for a precise quantification of their influence.

Bulk crystal growth rates calculated from step generation frequencies through spiral growth are in good agreement with precipitation rates retrieved from mixed-flow reactor experiments and confirm that citrate significantly inhibits magnesite growth at concentrations higher than 1 mM. Based on these new surface scale observations, we propose that observed growth inhibition stems from a decreased rotation frequency of growth spirals, which may originate either from a decrease of the acute step velocity or from an increase of the critical step length. EDTA appears to have a negligible influence on magnesite growth kinetics at the investigated conditions. This may be due to the fact that in solution it is mostly present in form of the  $\text{MgEDTA}^{2-}$  aqueous complex, which has a low surface adsorption constant and therefore interacts little with the magnesite surface. Finally, an effect of oxalate on bulk growth rates could not be detected at the chosen conditions.

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## 1. INTRODUCTION

Mg-silicate engineered carbonation has been proposed as a means to sequester large amounts of  $\text{CO}_2$  in a stable mineral form (Seifritz, 1990; Lackner et al., 1995).

\* Corresponding author at: Ministère de l'Écologie, du Développement Durable et de l'Énergie, Tour Séquoïa, 92055 La Défense cedex, France.

E-mail address: [quentin.gautier@normalesup.org](mailto:quentin.gautier@normalesup.org) (Q. Gautier).

Mg-silicates (e.g., forsterite, serpentine) provide an abundant cation source for Mg-carbonate precipitation, among which magnesite  $\text{MgCO}_3$  is the most stable mineral in a wide temperature range (Königsberger et al., 1999; Bénézeth et al., 2011). Although thermodynamically favorable, the carbonation process is kinetically limited both by the slow dissolution of the silicate phases (Pokrovsky and Schott, 2000; Rosso and Rimstidt, 2000; Hänchen et al., 2006; Guyot et al., 2011) and the sluggish precipitation kinetics of magnesite (Saldi et al., 2009, 2012). Thermal

or mechanical pre-treatment of the silicate phase or temperatures above 100 °C are necessary to significantly accelerate the process. Alternatively, it has been suggested that organic ligands such as oxalate, citrate and EDTA, which are known to promote Mg-silicate dissolution, could be used to accelerate the whole carbonation process (Park et al., 2003; Teir et al., 2007; Krevor and Lackner, 2011; Prigiobbe and Mazzotti, 2011).

However, recent studies by our group (Gautier et al., 2011; Gautier, 2012) have shown that the polycarboxylates oxalate, citrate, and EDTA inhibit magnesite growth at  $T > 100$  °C and concentrations  $> 0.1$  mM. This effect is attributed to a combination of  $Mg^{2+}$  complexation by the ligands, which reduces solution supersaturation with respect to magnesite, and a decrease of the apparent kinetic rate constant for magnesite growth, likely stemming from ligand adsorption at the mineral surface. The strongest growth inhibition was obtained with citrate. However, the mechanisms by which these ligands inhibit magnesite growth kinetics are not understood.

Atomic force microscopy offers the possibility to probe surface processes at the nano-scale and has been used to study the effects of organic additives on mineral growth and dissolution (e.g., Gratz and Hillner, 1993; Bosbach and Hochella, 1996; Teng and Dove, 1997; Orme et al., 2001; Elhadj et al., 2005; Wu et al., 2011; Qin et al., 2013). Most of these studies, however, focused on minerals commonly forming at ambient temperature in order to better understand the mechanisms involved in biomineralization (De Yoreo et al., 2007; Qiu and Orme, 2008), or to design more efficient inhibitors for the prevention of industrial scale formation (e.g., Bosbach and Hochella, 1996; Pina et al., 2004). To our knowledge, no high resolution atomic force microscopy study has been dedicated to the interactions between organic additives and mineral growth at higher temperature.

The goal of the present study is to document at the surface scale the interactions of organic ligands with magnesite growth process and try to elucidate the mechanisms which lead to magnesite growth inhibition at 100 °C in the presence of these ligands. Toward this aim, we have used hydrothermal atomic force microscopy (HAFM) to study growth on the (104) surface under well constrained chemical conditions with varying ligand concentrations and saturation states. The extensive work that has been published on HAFM observations of magnesite dissolution (including the effects of ligands) and growth at hydrothermal conditions (Jordan et al., 2001, 2007; Higgins et al., 2002a,b; Saldi et al., 2009) provides a solid framework to which our observations can be compared. In addition, our measurements and observations will be compared to the existing models for crystal–impurity interaction, which have mostly been developed for lower temperatures.

## 2. EXPERIMENTAL METHODS

### 2.1. Hydrothermal atomic force microscopy (HAFM)

Experiments were performed with a self-constructed continuous-flow HAFM operating in contact mode. The

apparatus allows in-situ investigation of mineral surfaces at temperatures up to 150 °C under moderate pressure (c.f. Higgins et al., 1998; Aldushin et al., 2004; Jordan and Astilleros, 2006). The experiments presented here were performed at 80–100 °C with confining pressures  $< 4$  bars. Inlet solutions were placed in three containers above the HAFM cell allowing gravitational fluid feed. Flow rates were approximately 10  $\mu$ L/s allowing rapid renewal of the  $\sim 500$   $\mu$ L cell volume. Due to this rapid renewal and a mineral surface area of typically only a few  $mm^2$ , the chemical composition of the solution was negligibly affected by processes taking place within the microscope cell. The experiments were performed on the (104) cleavage surface of transparent magnesite single crystals from Brumado, Brazil. An electron microprobe analysis of the crystals revealed only minor amounts of Ca, Cu and Fe (Saldi et al., 2009). The crystals were cleaved with a scalpel immediately before fixation within the HAFM cell by a titanium wire. Then the system was pressurized and the cell heated to the desired temperature. Uncoated silicon cantilevers from Nanosensors were used.

Step velocities were obtained by measuring the step advancement perpendicular to the step orientation from images taken in the same scan direction using a fix reference point. In order to take into account the limited accuracy of instrument calibration, reported step velocities are the average of measurements taken on different islands, at different scan angles (0/90°), and different scanning directions (upward/downward and trace/retrace).

Magnesite growth rates  $R$  were derived from the layer formation frequency  $I$  measured in the accessible scan area:

$$R = I \cdot \frac{h}{V_M} \quad (1)$$

where  $h$  is the layer thickness (2.74 Å) and  $V_M$  the magnesite molar volume (28.1  $cm^3/mol$ ).  $I$  can be accessed by counting steps generated at a particular step generating point, or by counting steps passing a fixed reference point during given time (Higgins et al., 2002a).

### 2.2. Solution preparation and analysis

Solutions were prepared with high purity deionized water (resistivity 18.2  $M\Omega cm$ ), reagent grade NaCl,  $MgCl_2 \cdot 6H_2O$ ,  $NaHCO_3$ ,  $Na_2Oxalate$ ,  $Na_3Citrate \cdot 2H_2O$ ,  $Na_2H_2EDTA \cdot 2H_2O$ , and high purity 1 M HCl and NaOH solutions. Organic ligands were either used directly as salts or pre-dissolved in concentrated stock solutions from which the experimental solutions were prepared. The NaCl concentration was adjusted for a constant ionic strength of 0.1 M.

Solution pH was measured before the experiments by a standard glass electrode calibrated against NIST standard buffers with an uncertainty of 0.02 units. In all experiments, pH was kept within a range from 7.95 to 8.17 at 100 °C. This range has been chosen for consistency with the study by Saldi et al. (2009). The activity ratios  $a(Mg^{2+})/a(CO_3^{2-})$  were close to 1 in most experiments. However, solutions with high saturation states had an activity ratio of 3–5 in order to avoid significant changes of solution

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