HAFM Observations of the Growth of Calcite in the Presence of Dissolved Sulphate at 40ºC

/ NURIA SÁNCHEZ PASTOR (1), GUNTRAM JORDAN (1) LURDES FERNÁNDEZ-DÍAZ (2,*).

(1) Department für Geo und Umweltwissenschaften, Ludwig-Maximilians-Universität. 80333, Munich (Alemania)
(2) Departamento de Cristalografía y Mineralogía. Universidad Complutense de Madrid. 28040, Madrid (España)

INTRODUCTION.

Calcite and aragonite can incorporate different ions in their structure during growth. Some of these impurities have a strong influence on the formation of $CaCO_3$ polymorphs. Sulphate is common in aqueous solutions in most surface natural environments. For example, it is one of the most abundant ions in seawater. Sulphate is also present in saline ground water, rock pore water, etc. Different authors have stated that the presence of dissolved sulphate in the growth medium promotes the formation of other $CaCO_3$ polymorphs than calcite and retards or completely inhibits their transformation into this phase (Bischoff and Fyfe, 1968; Bischoff, 1968). Moreover, the morphology of growing calcite crystals is also affected by sulphate, progressively differing from the typical rhombohedron as the concentration of sulphate increases (Tracy et al., 1998). These effects have been related to the incorporation of sulphate into the structure of the $CaCO_3$ polymorphs, substituting carbonate anions. Such an incorporation mechanism has been well established in the case of calcite (Frisia et al., 2005).

A recent work by Vavouraki et al. (2008) studied the growth of calcite cleavage surfaces from sulphate-bearing solutions at the molecular scale using a conventional Atomic Force Microscope under room conditions. These authors have concluded that sulphate concentrations higher than 3 mM have an important effect on the growth of calcite $\{10\bar{1}4\}$ surfaces, affecting both the morphology of two-dimensional islands and their spread rate.

In this work we present the preliminary results of an investigation of the growth of calcite $\{10\bar{1}4\}$ surfaces from supersaturated solutions at 40 ºC in the presence of dissolved sulphate. Our results are compared to the findings by Vavouraki et al. (2008) with the aim of drawing conclusions on the combined effect of temperature and sulphate concentration on the growth of the calcite cleavage surface at the molecular scale.

METHODOLOGY.

The influence of sulphate on the growth of calcite cleavage surfaces was investigated *in situ* using a self-constructed hydrothermal atomic force microscope (HAFM). The samples used were optical clear Iceland Spar calcite crystals from Chihuahua (México). Freshly cleaved calcite $\{10\bar{1}4\}$ surfaces were mechanically affixed in the fluid cell which then was sealed, pressurized and heated. In all the experiments the temperature has been set to 40 ºC. The pressure was held between 0.9 and 1.4 bars. The flow rate was adjusted to 10 µL/s. The pH of the solutions was 10.2. Sodium sulfate was added to the growth solutions in the range 0.3 mM to 15 mM. The solutions were supersaturated with respect to calcite (Saturation Index = 0.9).

The growth rate was estimated from two types of measurements: The closure rate of etch pits and the spread rate of two-dimensional rhombohedral nuclei formed on the calcite surface. In both cases, the rate was measured along the bisector [010] (see Fig. 1).

RESULTS AND DISCUSSION.

The main crystallographic directions on calcite $(10\bar{1}4)$ surface can be established by observing the development of etch pits formed in contact with pure water (Hillner et al., 1992). The retreat of the edges of the etch pits is highly anisotropic. This anisotropy reflects the inequivalence of the two pairs of opposing straight steps parallel to the $[\bar{4}41]$ and $[48\bar{1}]$ directions. While $[\bar{4}41]_a$ and $[48\bar{1}]_a$ steps overhang the underlying layer defining an acute angle (78º) that delimits constrained kink sites, $[\bar{4}41]_o$ and $[48\bar{1}]_o$ steps define an obtuse angle (102º) and contain open kink sites (Jordan and Rammensee, 1998). The orientation of the steps is depicted in Fig. 1(a). Steps with open kinks move faster than steps with constrained kinks.

Our measurements of the rates of closure of the etch pits and the rates of spread of the two-dimensional nuclei indicate that sulphate inhibits the growth on calcite $(10\bar{1}4)$ surface. The inhibitor effect increases with the concentration of sulphate in the solution. For example, the closure rate of the etch pits decreases from 12 nm/s to 4 nm/s when the concentration of sulphate in the solution changes from 3 mM to 15 mM. These results are in agreement with the observations by Vavouraki et al. (2008), who also observed a decrease of the growth rate with the increase of the dissolved sulphate concentration. However, using solutions equally supersaturated for calcite and with identical sulfate content, we obtain higher growth rates values than reported by Vavouraki et al. (2008). Moreover, the difference between the values obtained in both works decreases as the sulfate content in the solution increases. Another interesting difference between the results reported by Vavouraki and collaborators and our measurements refers to the evolution of the growth rate for successive monolayers spreading on the calcite surface. According to Vavouraki et al. (2008), the first
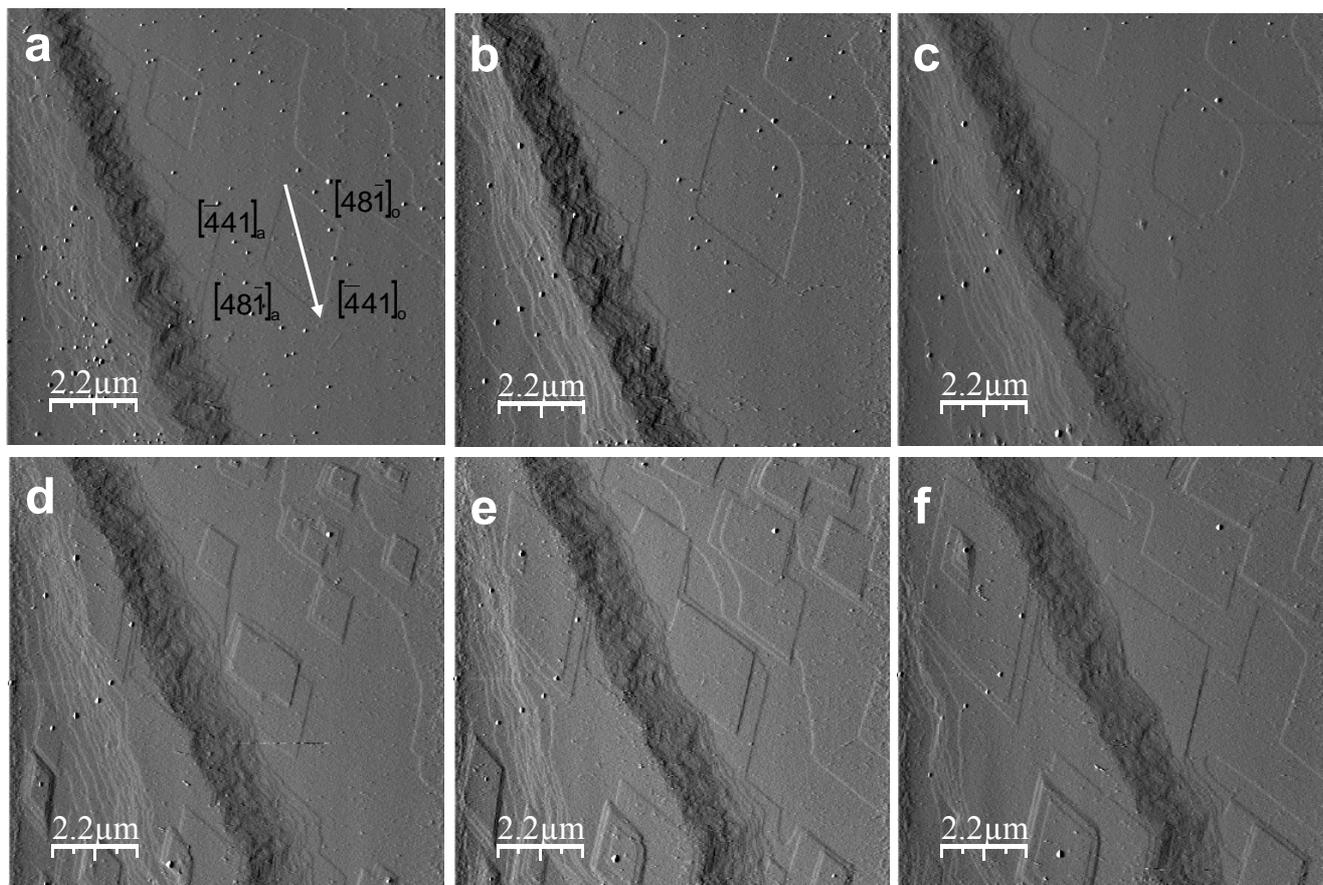
fig. 1. *Deflection images of calcite {10$\bar{1}$4} surfaces: (a) In contact with pure water at 40 °C. Crystallographic directions are depicted at one etch pit. (b) The edges of the etch pits retreat in contact with pure water. (c) After filling the fluid cell with supersaturated solution ([SO$_4^{2-}$]= 5 mmol/l) etch pits start to close. (d-f) After a short time, two-dimensional islands nucleate on the surface.*

monolayer that spreads on the calcite surface grows faster than successive monolayers. Moreover, the spread of the monolayers leads to the reproduction of the original nanotopography of the surface ("template effect, Astilleros et al., 2003). In contrast, we do not detect any change in the spread rate nor observe the reproduction of the original nanotopography, as is evidenced in figure 1. Further differences between our results and Vavouraki and coworkers' refer to the shape of the two-dimensional islands and step edges. These authors observed that the islands grown in presence of sulfate became elongated along [010] direction and the edges became jagged. In contrast, in our experiments neither a change in the island nor in the step edge shape is observed.

The important differences between the results obtained by Vavouraki et al. (2008) and our observations indicate that small changes in temperature (from 23 °C in the Vavouraki and coworker's experiments to 40 °C in our experiments) may have significant consequences on the growth mechanisms in the presence of sulphate.

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