

Molecular-scale formation of carbonate solid solutions from multicomponent aqueous solutions and other related phenomena

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Abstract

This work deals with the growth behaviour of calcite surfaces in contact with multicomponent carbonate aqueous solutions containing divalent cations (Ba^{2+} , Sr^{2+} , Mn^{2+} , Cd^{2+} or Mg^{2+}). The result of solid surface-aqueous solution interactions is the formation of solid solutions, with calcite as one of the end-members. In situ Atomic Force Microscopy and other surface techniques have revealed a wide variety of surface phenomena occurring during the formation of such solid solutions. Among them are: (1) the transition between growth mechanisms, (2) the thickening of growth steps, (3) the growth and subsequent dissolution of metastable surfaces and the formation of secondary three-dimensional nuclei, and (4) the inhibitory effect of the newly-formed surface on the subsequent growth (template effect). The last phenomenon can considerably limit coprecipitation as an effective mechanism for divalent metal uptake. All these phenomena are a consequence of the interplay between thermodynamics, supersaturation of the aqueous solution with respect to the possible solid solutions and the crystallographic control of the surfaces on the cation incorporation.

1 INTRODUCTION

The crystallisation of minerals from multicomponent aqueous solutions is one of the most ubiquitous processes occurring on the Earth's surface. Calcite (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and halite (NaCl), widely used in the industry and in our daily life, are some of the most representative examples of minerals formed in these kinds of environments.

Apart from their interest as raw materials, carbonate minerals have recently received special attention from geochemists, mineralogists and researchers who deal with the problem of environmental pollution. The first reason for this interest stems from the fact that they always contain a certain proportion of impurities in solid solution [1-3]. The knowledge of the factors that control the concentration of impurities in the "host" phase can give valuable information about the composition of paleowaters, the degree of water-rock interaction, and the pathways through which diagenesis and lithification occurs [4].

The second aspect that makes carbonates interesting arises from their ability to react with the components

present in the aqueous media. Metallic cations (Me^{2+}) and rare-earth elements, frequently present in industrial or/and nuclear wastes, but also in natural waters, can be sorbed [5] to the surface of carbonates. As a result, carbonate minerals placed in contact with solutions containing a variety of contaminating elements can sequester them or at least retard their migration [6].

Besides its importance in environmental sciences, the interactions of Me^{2+} with mineral surfaces poses a large number of fundamental questions related to different aspects of mineral crystallization. Among them, it is worth mentioning their influence in the formation of polymorphs [7], their effect as modifiers of the crystal morphology [8] and their effectiveness as inhibitors of both nucleation and growth [9].

In this paper I present some results of the investigation that I have carried out in collaboration with the Mineral Surface Groups of Münster University and Complutense University of Madrid. Our research has been focused on the acquisition of a more complete picture of the crystallisation processes occurring in solid solution-aqueous solution (SS-AS). By means of an Atomic Force Microscopy (AFM) equipped with a fluid cell it was possible to systematically investigate the surface phenomena occurring in several SS-AS systems during growth. In all experiments, calcite surfaces were used as the substrate. Our observations have revealed quite a more complicated behaviour than that shown by pure substances [10-12]. The observed growth phenomena have been interpreted as the result of the interplay of thermodynamic, kinetic, structural and microtopographic factors.

2 MATERIALS AND METHODS

Experiments were carried out at 25°C using a Digital Instruments Multimode AFM (fig. 1) equipped with a fluid cell. The AFM operates by scanning a sharp Si_3N_4 tip (fig. 2) attached to a weak spring (cantilever) across a surface. To obtain an image a piezoelectric scanner moves the sample in a raster pattern while the tip is in contact with the surface. Deflections of the cantilever (caused by surface features) are detected by a laser beam reflected off the back of the cantilever into a photodiode. A computer processes this information and determines the vertical motion of the scanner necessary to keep the beam position constant. The recorded deflection data are processed by the computer, which displays images showing the

topographic features of the surface with a sub-Angstrom resolution in the vertical direction.

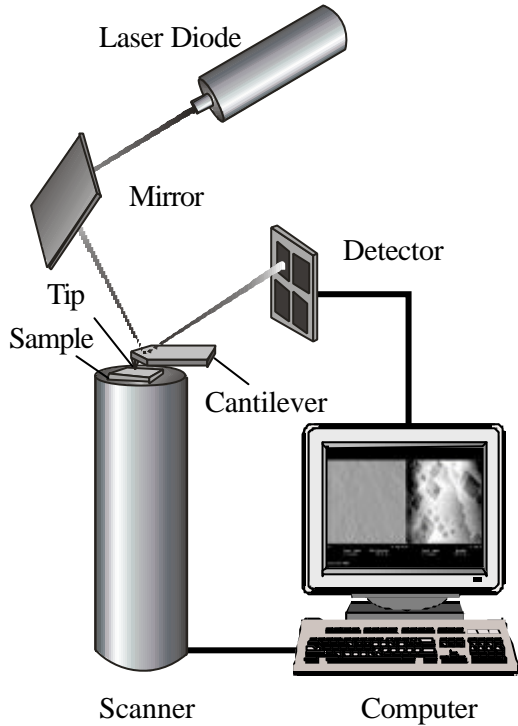


Fig. 1. Schematic drawing of an AFM showing its components.

The substrates used in the experiments were $\{10\bar{1}4\}$ cleavage surfaces of calcite natural crystals. This substrate was one of the pure end-members of the solid solutions investigated. Areas chosen for investigation were those where the cleaved surfaces showed unit-cell-high cleavage steps. Aqueous solutions supersaturated with respect to calcite and containing Ba^{2+} , Sr^{2+} , Mn^{2+} , Cd^{2+} and Mg^{2+} were passed over the substrates to promote growth by the advancement of steps.

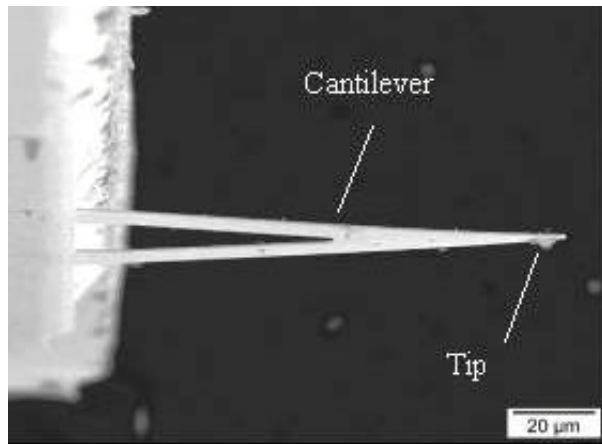


Fig. 2. Scanning Electron Microscopy image of a tip and a cantilever.

3 THE THERMODYNAMICS OF SS-AS SYSTEMS AND SUPERSATURATION EVALUATION

The growth of a solid solution is a much more complex phenomenon than the growth of an end-member both because of the nature of the crystallization process and the definition of equilibrium and supersaturation. Before describing relevant observations, the concepts of equilibrium and supersaturation in SS-AS systems will be briefly reviewed.

3.1 Equilibrium in SS-AS systems

For a pure solid, the solubility product K_{sp} is defined as the product of the activities of the relevant ionic species in solution at thermodynamic equilibrium with the solid phase; e.g. for calcite $K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 10^{-8.48}$. To describe the solubility of binary solid solutions, i.e. the thermodynamic equilibrium, the solubility concept must be extended. In the general case of an SS-AS system, $(\text{Ca},\text{Me})\text{CO}_3\text{-H}_2\text{O}$, the equilibrium conditions are:

$$[B^+][A^-] = K_{BA} a_{BA} = K_{BA} X_{BA} g_{BA} \quad (1)$$

$$[C^+][A^-] = K_{CA} a_{CA} = K_{CA} X_{CA} g_{CA} \quad (2)$$

where $[A^-]$, $[B^+]$ and $[C^+]$ are the activities of A^- , B^+ and C^+ ions in the aqueous solution; K_{BA} and K_{CA} are the solubility products of the solid solution endmembers; a_{BA} and a_{CA} are the activities of BA and CA in the solid; X_{BA} and X_{CA} are the molar fractions of BA and CA in the solid, and g_{BA} and g_{CA} are the solid phase activity coefficients. Ideal mixing occurs when both g values equal 1.0 over the whole composition range. Properties of B^+ and C^+ which are important in determining the extent of ideal mixing are the ionic radii, electronegativities of B^+ and C^+ , and the crystal structure of the mineral that the two ions tend to form. The more similar that B^+ and C^+ are, the more likely it is that the values of g will remain close to 1.0.

3.2 Supersaturation in SS-AS systems

Supersaturation is a very important parameter because it: a) exerts an influence on the partitioning of major, minor, and trace components between solid and aqueous phases, b) controls growth rates and the relative importance of the different growth mechanisms (spiral growth and two-dimensional nucleation) and c) determines the relative stabilities of the different solid phases that can occur in the system. Supersaturation in a pure one-component system can be defined by the expression $\beta = I_{AP}/K_{sp}$, where I_{AP} is the ion activity product in the solution, e.g. $[\text{Ca}^{2+}][\text{CO}_3^{2-}]$, and K_{sp} is the solubility product. When $\beta < 1$, the aqueous solution is undersaturated with respect to the pure solid. If a solid CaCO_3 is present in the aqueous solution, it will tend to dissolve. Conversely, when $\beta > 1$, a solid phase will tend to crystallise. The

saturation state is reached when $\beta=1$. The same can be applied to SS-AS systems. However, in this case, supersaturation cannot be expressed by a unique value. It is a function of the composition of both solid and aqueous phases.

On the basis of the conditions of thermodynamic equilibrium for SS-AS systems, it is possible to define an expression that allows to calculate the supersaturation, $d(x)$, of a multicomponent aqueous solutions with respect to the different compositions of a solid solutions series [13] (fig. 3).

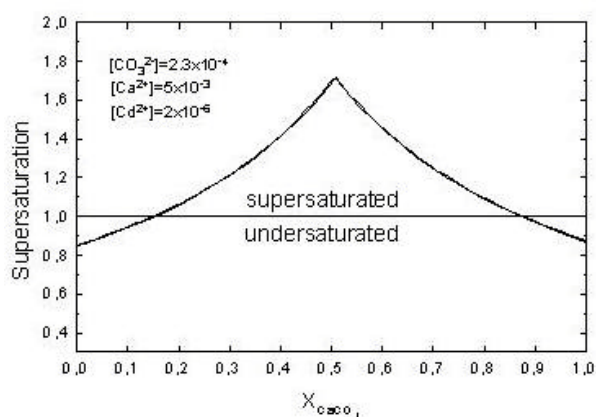


Fig. 3. Supersaturation function for the $(\text{Ca,Cd})\text{CO}_3$ solid solution, corresponding to an aqueous solution with a given composition (mol/l). The abscissa represents the molar fraction of the component CaCO_3 in the solid. As can be observed, for this particular case the aqueous solution is undersaturated with respect to the pure endmembers and supersaturated for intermediate compositions.

An important conclusion can be directly derived from supersaturation calculations: for a given aqueous solution containing A^- , B^+ and C^+ ions, the maximum of supersaturation will *never* correspond to the more insoluble pure endmember. In a solid solution, the value of both X_{BA} and X_{CA} is less than 1. According to eqs (1), and (2), this causes the concentration of BA and CA components in a stable solid solution are always lower than that of pure BA and CA solids. The formation of a solid solution is, therefore, always favoured.

A very interesting consequence is that an aqueous solution can be undersaturated with respect to both pure endmembers, but supersaturated with respect to an intermediate more-soluble solid solution (see Fig. 3). For example, CdCO_3 has not been predicted to precipitate from undersaturated solution. However, the presence of enough amounts of Ca^{2+} can cause the removal of this hazardous element from the aqueous solution due to the coprecipitation of a $\text{Cd}_x\text{Ca}_{1-x}\text{CO}_3$ solid solution. Furthermore, if calcite is previously present, precipitation of Cd^{2+} as a carbonate solid solution will always occur, even when Cd^{2+} is present at trace levels [14-15].

4 NANOSCALE PHENOMENA DURING THE GROWTH OF $\text{Me}_x\text{Ca}_{1-x}\text{CO}_3$ (Me= Ba, Sr, Mn, Cd and Mg) SOLID SOLUTIONS ON CALCITE SURFACES

In the last section we have seen that the formation of a solid solution is, from a thermodynamical point of view, always promoted. However, thermodynamics does not tell anything about how the crystallization process occurs. More important, thermodynamics and supersaturation evaluation are not sufficient themselves to predict the composition of the growing crystal. Several other factors can also play an important role. Since crystal growth takes place at the solid-aqueous interface, the substrate can play a determining role. In the next subsections I will present some surface phenomena occurring when supersaturated aqueous solutions with respect to calcite and containing Ba^{2+} , Sr^{2+} , Mn^{2+} and Mg^{2+} or Cd^{2+} were passed over a calcite surface. First, a brief description of calcite $\{10\bar{1}4\}$ cleavage surfaces is required.

4.1 Nanometric features of the calcite $\{10\bar{1}4\}$ face

Fig. 4 shows the structure and microtopography of a calcite $\{10\bar{1}4\}$ cleavage surface. The steps are 3 Å in height, the dimensions of one unit cell. Parallel steps with opposite senses of advancement are not crystallographically equivalent. Steps denoted with “-” (negative) are more constrained and smaller than “+” (positive) steps. This non-equivalence leads to: (a) differences in growth rates (positive steps migrate faster than negative steps) (b) anisotropy in the incorporation of cations (large cations will be preferentially incorporated in positive steps, whereas small cations will tend to incorporate in negative steps) [16].

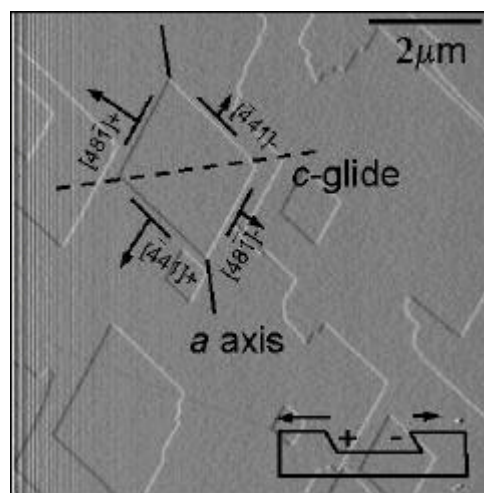


Fig. 4. Microtopography of the calcite $\{10\bar{1}4\}$ surface observed with an AFM.

4.2 Transitions between growth mechanisms

At low supersaturation crystal faces grow by spirals developed on screw dislocations or, alternatively, by lateral advancement of pre-existing steps. However, at higher supersaturation the energy barrier for the formation of two-dimensional nuclei on the crystal surface can be overcome. Consequently, the crystal grows by formation and spread of nuclei. For pure substances, the transitional supersaturation that separates these two basic growth mechanisms ($b_{calcite}^*$ and b_{rhodo}^*) strongly depends on the solubility of the compound, temperature, aqueous solution viscosity, etc. However, as we have seen in last section, the presence of additional cations causes that the supersaturation for a certain range of solid compositions will be higher than for the pure calcite end-member. This can lead to a change in the growth mechanisms. This effect has been clearly observed in the (Mn,Ca)CO₃-H₂O SS-AS system (fig. 5). When solutions supersaturated with respect to calcite ($\beta=5$) but with small amounts of Mn (solution 1 [MnCl₂]=0.01 and solution 2 [MnCl₂]=0.025 mmol/L) are used, growth on calcite surface bearing Mn takes place exclusively by step advancement. In contrast, for solution with higher amounts of Mn (sol. 3 [MnCl₂]=0.05 mmol/L) supersaturation with respect to intermediate compositions of (Mn,Ca)CO₃ solid solution increases and, hence, numerous two-dimensional nuclei rapidly appear randomly distributed on the surface.

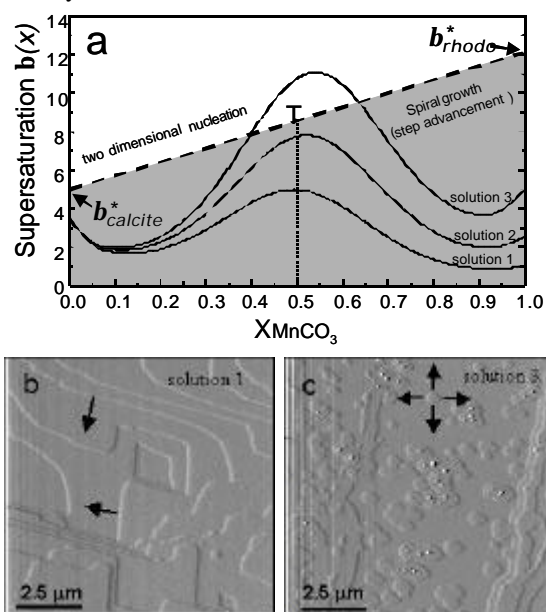


Fig. 5. (a) Stoichiometric supersaturation functions, $b(x)$, for solutions 1, 2 and 3. $b_{calcite}^*$ and b_{rhodo}^* were experimentally determined. The dotted line dividing two-dimensional and spiral growth was determined assuming a linear variation of b_{rhodo}^* with composition. (b-c) Microtopography of the {10 $\bar{1}4$ } surfaces growing from solutions 1 and 3, observed by AFM.

Diagrams similar to that shown in figure 5a can be constructed for any SS-AS system and for different surfaces. They provide a general view of the operating growth mechanisms as a function of the solid solution composition, constituting a useful tool to interpret growth behaviour in SS-AS system. However, as we will see in the next sections, frequently growth of solid solutions exhibit nanometric surface features (anomalous growth kinetics, step thickening, etc.) whose interpretation requires to consider other factors, mainly related to the surface structure of growing faces.

4.3 Anomalous thickening of growth steps

In situ AFM observations of calcite {10 $\bar{1}4$ } surfaces growing from solutions containing cations larger than Ca²⁺ (Ba²⁺, Sr²⁺) show that, when the concentration of the larger cation is high, an anomalous thickening of certain steps occurs. Fig. 6 shows an image of calcite {10 $\bar{1}4$ } surface growing from a Ba-rich solution where this microtopographic feature can be observed. In the image (Fig. 6a), those steps contrast with the rest of the scanned area. These newly formed steps, which correspond to the calcite-type structure, appear in a height image as higher areas (Fig. 6b) than the original steps. Measurements indicate that, while the initial step height are 3.0 Å, the newly grown steps are 4.6 Å. Similar microtopographic features can be observed on calcite surface growing from Sr-rich solutions.

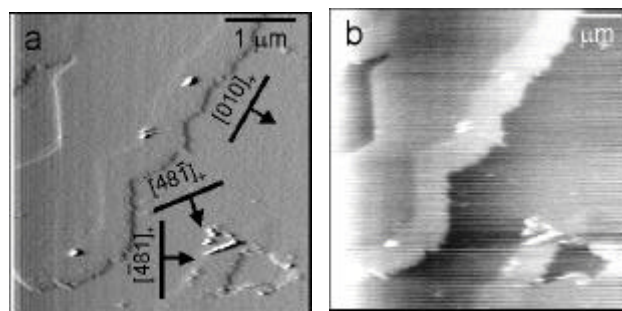


Fig. 6. Growing calcite {10 $\bar{1}4$ } surface in a supersaturated solution with respect to calcite ($\beta_{cal} = 5$) and [Ba] = 1.6 mmol/l. (a) AFM image displaying the cantilever deflection signal. Note the different contrast of the newly grown step edges. (b) Height AFM image of the same area as (a). The brighter step edges indicate that the newly grown steps are slightly thicker than the initial ones.

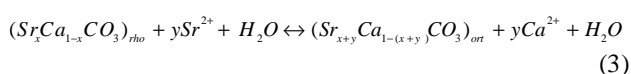
Because the ionic radii of Ba²⁺ (1.34Å) and Sr²⁺ (1.18Å) are bigger than Ca²⁺ (0.99 Å), they will incorporate preferentially in positive steps. When the incorporation is high, an increase of lattice parameters and, consequently, a thickening of those step edges will occur. This approach implicitly assumes that the incorporation of Ba²⁺ and Sr²⁺ in calcite structure occurs by substituting Ca²⁺, i.e. forming a solid solution. However, while CaCO₃ structure at 25°C and 1 atm is rhombohedral, BaCO₃ and SrCO₃ are

orthorhombic. Thus, the equilibrium solubility of either Ba^{2+} or Sr^{2+} in the calcite structure is limited. The thickness differences between “normal” calcite steps and newly formed steps are too high to be explained by a low amount of incorporation. In the experiments under consideration the solutions were either Ba-rich or Sr-rich and the supersaturation levels were relatively high. Under such non equilibrium conditions, higher incorporation of the Ba or Sr than that thermodynamically predicted, may occur. Such a situation can explain the measured step thickness differences, although additional incorporation of Ba and Sr in nonlattice sites cannot be excluded. This leads to a metastable state which can be the starting point for subsequent dissolution-recrystallisation reactions.

4.4 Metastable growth and solvent mediated transformation

When a metastable crystalline solid is in contact with an aqueous solution, the solvent can actively take part in a phase transformation process by allowing the simultaneous dissolution of the metastable phase and the crystallisation of new crystals of the stable phase. This is common in reconstructive transformations where the structures are so different that the transition between them can only occur by breaking and formation of chemical bonds. The aqueous solution acts as catalyst and such a process is called solvent-mediated transformation [17]. This process has mainly been studied for the case of polymorphic transformations of pure substances. However, solvent-mediated transformation processes can also take place in SS-AS systems. In such a case, the most important property that determines the relative solubility (and, therefore the stability and metastability) of the different phases involved in the transformation process is not the temperature but the composition of the aqueous phase.

In carbonate minerals, the structure of the single phase is determined by the size of the cation. Single carbonates with cations larger than Ca^{2+} form with the orthorhombic aragonite structure, whereas those with smaller cations form with the rhombohedral calcite structure. Both BaCO_3 (witherite) and SrCO_3 (strontianite) are orthorhombic carbonates. As was discussed in section 4.3, thick steps incorporating Sr (and Ba) can be considered as a $(\text{Sr,Ca})\text{CO}_3$,_{rhombohedral} solid solution. Such solid solutions can be metastable with respect to a certain $(\text{Sr,Ca})\text{CO}_3$,_{orthorhombic} solid solutions. In the case of Sr-carbonates, the solvent-mediated transformation process can be expressed as:



Supersaturation calculations for the Sr-rich aqueous solution ($[\text{Sr}(\text{NO}_3)_2] > 1.6 \text{ mmol/L}$) used in the experiments show that the solution is much more supersaturated with respect to a Sr-rich aragonite-type phase than with respect

to a calcite-type phase. Therefore, the formation of an aragonitic Sr-rich solid solution should be favoured.

In an initial stage, the calcite substrate allows the system to reduce its free energy by the formation of a metastable Sr-rich solid with calcite structure, causing the thickening of the steps. However, the high supersaturation with respect to the aragonite type phase leads, after an induction period, to the formation of three-dimensional orthorhombic nuclei (fig. 7). The growth of these nuclei makes the solution become undersaturated with respect to the rhombohedral phase, which begins to dissolve. Such dissolution results, in turn, in an increase of the solution supersaturation with respect to the orthorhombic phase, which will continue growing. Thus, a feed back loop results from the coupling of dissolution and growth processes.

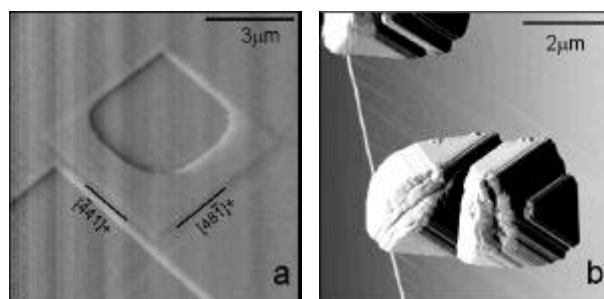


Fig. 7. AFM images of the same calcite surface obtained after injecting a solution supersaturated with respect to calcite ($\beta_{\text{cal}} = 5$) and with a concentration of strontium $[\text{Sr}] = 4.0 \text{ mmol/l}$. (a) The incorporation of Sr into the structure causes the thickening of advancing steps. After some minutes, dissolution starts and the retreat of both newly and original steps occurs. (b) Crystals of the new $(\text{Sr,Ca})\text{CO}_3$,_{orthorhombic} phase can be observed growing on the calcite surface.

4.5 The influence of newly-formed layers on subsequent growth: the template effect

The presence of ions can inhibit the normal growth of a pure crystal. Because the inhibition processes occur on mineral surfaces, the AFM seems to be the most suitable instrument to study such phenomena. However, AFM has been rarely used in this kind of experiment and, in the majority of studies, the inhibition processes are assumed to occur by: (a) adsorption and pinning of the “foreign ions” on step edges, thus hindering step advancement [18] or alternatively by (b) isomorphic incorporation of such ions into the structure of the crystal, increasing the solubility and again reducing step velocity [19].

All experiments we have carried out in the systems $(\text{Me,Ca})\text{CO}_3\text{-H}_2\text{O}$ (Me = Mn, Sr, Ba and Mg) show that the growth rate of each monolayer strongly depends on the presence of the previous layer, and that the changes in the surface properties of the crystal can retard or even completely inhibit further growth, even when the aqueous solution is still supersaturated with respect to all possible solid solution compositions. Fig. 8 illustrates this

phenomenon. The first image (a) was taken after flowing deionised water on calcite surface. The injection of a solution with very low concentration of Mn ($[\text{MnCl}_2] = 0.025 \text{ mmol/L}$) and supersaturated with respect to calcite ($\beta = 5.0$) causes the lateral advancement of growing steps (a-c). A thorough observation of the sequence shows that only the first elementary growth layer advancing on the pre-existing surface grows normally. At the beginning of the experiments the velocity advancement of step 1 and step 2 are the same. However, whereas step 1 advances without restrictions, step 2 (and subsequent ones) stops growing when it reaches the layer formed by the step 1 advancement. This leads to an almost perfect reproduction of the topography of the original surface (compare fig. 8a with 8c and schemes). We have referred this phenomenon as “template effect” because the original microtopography of the surface acts as a template that determines the subsequent growth evolution [20].

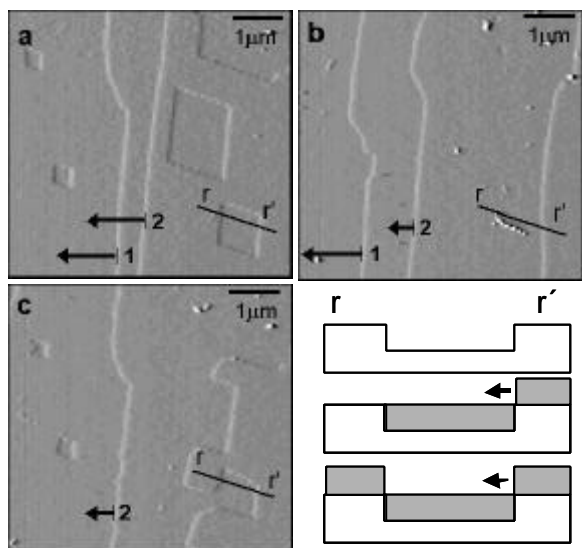


Fig. 8. Growth sequence on a calcite substrate from a solution containing Mn showing the control of the surface on the growth process. The topographic cross-section (line r-r') show the relations between original and new-formed layer.

The fact that growth eventually stops at a ‘buried’ step edge, reproducing the original topography suggests a dimensional difference, caused by changes in lattice parameters due to the formation of a mixed layer. This difference will both affect the layer-by-layer growth and the nucleation and growth of two-dimensional islands.

The factor controlling this phenomenon can be the strain normal to the growth layer, which depends on the cation size difference and the degree of substitution. These are not independent and are related through thermodynamics of the solid solution and the aqueous solutions, respectively.

5 CONCLUSIONS

In the previous sections we have illustrated the possibilities that AFM provides for the study of several crystallisation processes and phenomena that take place on calcite surfaces in presence of multicomponent aqueous solutions. Some of these phenomena can have important implications in crystal growth that have not been taken into account so far. For example, the “template effect” is a phenomenon that can occur frequently and can play a fundamental role both in the inhibition of growth and the composition of the growing phase. The generation of lattice mismatch between the growing and underlying layers due to the differences in ionic radii between the substituting ions can cause a deviation of the chemical distribution coefficient from the equilibrium value and the subsequent development of compositional zoning.

On the other hand, the fact that the newly-formed layers, with general composition $(\text{Me,Ca})\text{CO}_3$, hinder the normal crystal growth of solid solutions limits considerably coprecipitation as an effective mechanism for divalent metal uptake and can play a crucial role in the development of diagenesis, lithification and other geochemical processes.

The next step in the study of crystallisation in SS-AS systems is to check the universality of the “template effect” (it has been also observed in sulfates) and determine from experimental data the thermodynamic, kinetic and crystallographic factors involved in its development.

The metastable crystallisation processes and the development of solvent-media transformations are other aspects that deserve special attention.

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