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The effect of cation:anion ratio in solution on the mechanism of barite growth at constant supersaturation: Role of the desolvation process on the growth kinetics

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Abstract

The mechanism of barite growth has been investigated in a fluid cell of an Atomic Force Microscope by passing solutions of constant supersaturation (Ω) but variable ion activity ratio ($r = a_{\mathrm{Ba}}/a_{\mathrm{SO_4}}$) over a barite substrate.The observed dependence of step-spreading velocity on solution stoichiometry can be explained by considering non-equivalent attachment frequency factors for the cation and anion. We show that the potential for two-dimensional nucleation changes under a constant thermodynamic driving force due to the kinetics of barium integration into the surface, and that the growth mode changes from preexisting step advancement to island spreading as the cation/anion activity ratio increases. Scanning electron microscopy studies of crystals grown in bulk solutions support our findings that matching the ion ratio in the fluid to that of the crystal lattice does not result in maximum growth and nucleation rates. Significantly more rapid rates correspond to solution stoichiometries where $[\mathrm{Ba}^{2+}]$ is in excess with respect to $[\mathrm{SO_4}^{2-}]$.

Experiments performed in dilute aqueous solutions of methanol show that even 0.02 molar fraction of organic cosolvent in the growth solution significantly accelerates step growth velocity and nucleation rates (while keeping Ω the same as in the reference solution in water). Our observations suggest that the effect of methanol on barite growth results first of all from reduction of the barrier that prevents the Ba^{2+} from reaching the surface and corroborate the hypothesis that desolvation of the cation and of the surface is the rate limiting kinetic process for two-dimensional nucleation and for crystal growth.

1. INTRODUCTION

In natural systems such as seawater, pore fluids, microbial mats and body fluids, minerals precipitate from solutions which have variable ion proportions and almost pervasively in the presence of organic components. However, laboratory as well as theoretical studies more often address crystal growth from the fluids where the ion ratio matches that of the crystal lattice. Although some attempt has been made to understand the control of solution stoichiometry on the mechanism of crystal growth, there is no consistent explanation for the observations (Rashkovich et al., 2006). The issue becomes even more problematic when we consider the potential role of the organics present in the solution. The most common approach is to correlate the influence of the organic molecules on the process of the crystal growth and dissolution with specific interactions of biomolecules with the crystal surface and eventually complexation with the building ions in solution (Welch et al., 1999). Nevertheless there are very few studies attempting to investigate the effect of the biomolecules on the water structure and the resultant impact of the modified solvation environment properties on the kinetics of mineral nucleation and growth (Elhadj et al., 2006).

Crystal growth and dissolution are governed by attachment and detachment of building units to or from the crystal surface and frequencies of these elementary events are crucial terms included in crystal growth theories. For

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non-Kossel crystals that is, a crystal containing more than one growth unit per unit cell, where different types of kinks are present on the surface, there arises the question of dependence of the growth dynamics on relative incorporation rates of the non-equivalent building units and on their proportions in solution. Zhang and Nancollas (1998) first described theoretically such a system and proposed the model that predicted dependence of the step growth velocity on solution stoichiometry for binary ionic crystals, assuming independent attachment and detachment of the lattice ions at steps.

Several previous experimental studies suggested that the kinetics of incorporation of cations and anions into the crystal surface can be considerably different because of the difference in their dehydration rates and concluded that the frequency of water exchange around the cation determines the kinetics of ion integration at kink sites (Nielsen, 1984; Christoffersen et al., 1996a,b, 1998, 1999; Burke and Nancollas, 1999). For divalent metal sulfates, desolvation and solvation of the cation was suggested to be the rate-limiting process in crystal growth and dissolution, respectively (Dove and Czank, 1995). Some recent studies also attributed the kinetic barrier for attachment of building units to the growth site to hydration of the surface and of the solute (Petsev et al., 2003; Elhadj et al., 2006).

Nonetheless, it remains quite difficult to gain a deeper understanding of the influence of the solvation environment on crystal growth from experimental studies. There are recent investigations presenting the effect of different concentrations of lower alcohols on scale-forming mineral precipitation (Kan et al., 2003; Tomson et al., 2005) that show that barite nucleation rates are significantly accelerated in as little as 5 vol % of methanol. However they do not study solvent–solute-surface interactions, but propose a semiempirical approach to include the effect of cosolvent on ion activities in water/alcohol mixtures into standard pure-water thermodynamical equations. Conversely, other authors show that nucleation and growth rates of potassium chloride are hampered in the presence of ethanol (Omar and Ulrich, 2007). Recent computer simulations have brought some more insight into the atomistic details of the role of the solvent in the crystallization process (Kerisit and Parker, 2004; Kendall and Martin, 2005; Spagnoli et al., 2006). Molecular dynamics simulations performed by Piana et al. (2006) for barite growth confirmed earlier experimental observations and showed that water molecules tightly bound to the surface and surrounding the barium ion effectively prevent the latter from reaching the growth site while the barrier for the diffusion of sulfate ions to the crystal surface is much smaller. Consequently attachment of the cation is an activated and rate limiting process for two-dimensional nucleation. These findings were corroborated by crystal growth experiments performed in water–methanol solutions (25% MeOH), where observed morphological changes were attributed to a reduction of the kinetic barrier for barium ions to approach the surface. Nevertheless other workers showed experimentally that cations and anions behave similarly with respect to the growth kinetics (Rashkovich et al., 2005, 2006; Chernov et al., 2005, 2006; Nehrke et al., 2007).

The present work provides a systematic study on the dependence of barium sulfate growth rate and mechanism on varying solution stoichiometry under constant thermodynamic driving force and rationalizes the observed growth pattern by considering the role of the dehydration process on crystal growth. The effect of the solvation environment properties on the growth kinetics is addressed in this study by experiments conducted in dilute aqueous solutions of methanol.

2. EXPERIMENTAL PROCEDURE

2.1. AFM in situ experiments

Experiments were performed at room temperature in a fluid cell of Digital Instruments (Veeco Instruments, GmbH) Multimode AFM, working in contact mode. Optically clear barite single crystals were cleaved immediately before each experiment to expose an (001) surface. Growth solutions were injected at intervals of about 2 min before each AFM scan, which gives an effective flow rate of approximately 50 ml/h. This ensures that reactions will be surface controlled rather than diffusion controlled (Teng et al., 1998). Images were continuously taken and the time automatically recorded. Growth solutions were prepared by mixing Na_2SO_4 and $BaCl_2$ aqueous solutions made from solids from Merck Suprapur min. 99.995% ($BaCl_2$) and Aldrich min. 99.99% (Na_2SO_4). The saturation state was expressed as $\Omega = \mathrm{IAP}/K_{sp}$(IAP, ion activity product; K_{sp}, solubility product) and solution stoichiometry (r) defined as ratio of the activities of lattice ions in solution $r = a_{Ba}/a_{SO_4}$. The computer program PHREEQC (Parkhurst and Appelo, 1999) was used to calculate the saturation index $\mathrm{SI} = \log(\mathrm{IAP}/K_{sp})$ and ion activity in solutions. Details of the values of r and Ω investigated are given in Table 1. The step advancement rate (v) was measured as a function of r along the [100] direction, determined from the orientation of two-dimensional nucleated islands. The scanned area was (5×5) μm for measurements and (10×10) μm for verifying the possible influence of the tip or nucleation events outside the scanned area. Multiple independent experiments were performed for most of the experimental conditions (error bars indicate minimum and maximum values measured). Points on the graphs without error bars represent results from single experiments.

Methanol-containing growth solutions were prepared by simple dilution of aqueous growth solutions of a given Ω by addition of 5 ml of methanol to 100 ml of the water solution. Resulting water–methanol mixtures contained 4.8 vol % (0.02 molar fraction) of methanol. Note that Ω was always calculated for the volume of water, and methanol was added in addition to avoid solubility reduction (even though as shown by Piana et al., 2006) the solubility product of $BaSO_4$ in 5 vol % aqueous solution of methanol is virtually the same as in water). Methanol-containing growth solutions were passed either over a fresh barite surface or over a barite surface that was previously in contact with a reference barite–water solution of the same supersaturation.

Table 1
Composition of the solutions used in experiments

Ω	SI	$[Ba^{2+}]$ (μM dm^{-3})	$[SO_4{}^{2-}]$ (μM dm^{-3})	r (a_{Ba}/a_{SO_4})
12.6	1.1	2	1950	6.90E−04
		10	180	5.21E−02
		20	80	2.44E−01
		25	60	3.82E−01
		30	54	5.50E−01
		40	40	1.00E+00
		45	36	1.26E+00
		50	32	1.58E+00
		54	30	1.82E+00
		60	27	2.25E+00
		60	25	2.44E+00
		65	25	2.64E+00
		80	20	4.10E+00
		180	10	1.92E+01
		1950	2	1.48E+03
7.2	0.86	1	2750	2.25E−04
		15	61	2.41E−01
		25	36	6.92E−01
		30	30	1.00E+00
		36	25	1.45E+00
		45	20	2.28E+00
		61	15	4.15E+00
		95	10	9.84E+00
		210	5	4.54E+01
		2750	1	4.55E+03

2.2. Bulk precipitation experiments

Bulk precipitation experiments were performed for three different ion activity ratios $r = 0.24$, 1 and 4.10 at constant $\Omega = 12.6$. Solutions were prepared in 100 ml glass flasks by mixing Na_2SO_4 and $BaCl_2$ aqueous solutions. Flasks were shaken by hand and left overnight. After approximately 16 h, solutions were filtered under gentle vacuum through polycarbonate membrane filters with pore diameter 0.45 μm. Filters were dried in an oven (60 °C), carbon coated and analyzed with a JEOL 840 scanning electron microscope (SEM).

3. RESULTS

3.1. Barite growth from aqueous solutions

3.1.1. Rates of step advancement

For low ($\Omega = 7.2$) and moderate supersaturation ($\Omega = 12.6$), velocity of step advancement (v) changes with varying solution stoichiometry (r) (Fig. 1). Maximum growth rate (v_{max}) occurs at non-equimolar barium to sulfate ratio ($r \neq 1$), and corresponds to a solution composition where barium activity is in excess in relation to stoichiometric conditions ($r > 1$). Growth rates decrease non-symmetrically as r deviates from the value for which v_{max} is observed (r_{max}), but shows a tendency to diminish more sharply for $r < r_{max}$ than for $r > r_{max}$. There is some data scattering observed mainly for $1 < r < 4.10$ at $\Omega = 12.6$ when v seem to be lower than predicted by the general trend. The deviation of these values from the general trend is within the range of 10^{-2} nm/s and could lie within an experimental error.

3.1.2. Growth modes

The mechanism of barite growth also changes with varying solution stoichiometry with preexisting cleavage step advancement being mostly responsible for crystal growth for $r < 0.24$ and two dimensional island nucleation and

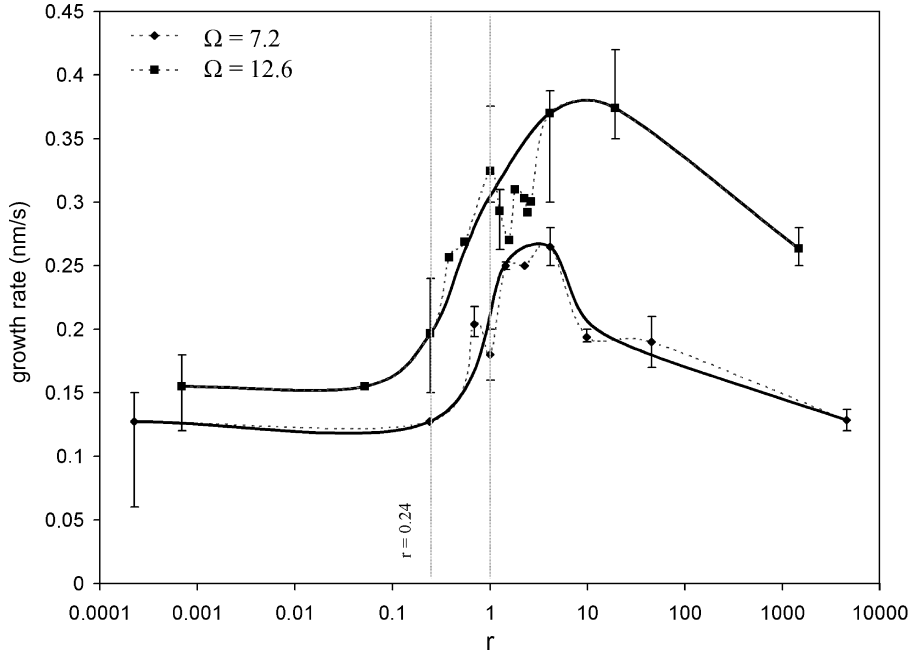

Fig. 1. Dependence of the step spreading velocity (v) on the lattice ion activity ratios in solution (r). Solid lines represent the trend in growth kinetics with varying solution stoichiometry. Dashed lines follow average values of v for given r. Vertical lines indicate the stoichiometric ion ratio and the value of r corresponding to the threshold in growth mechanism.

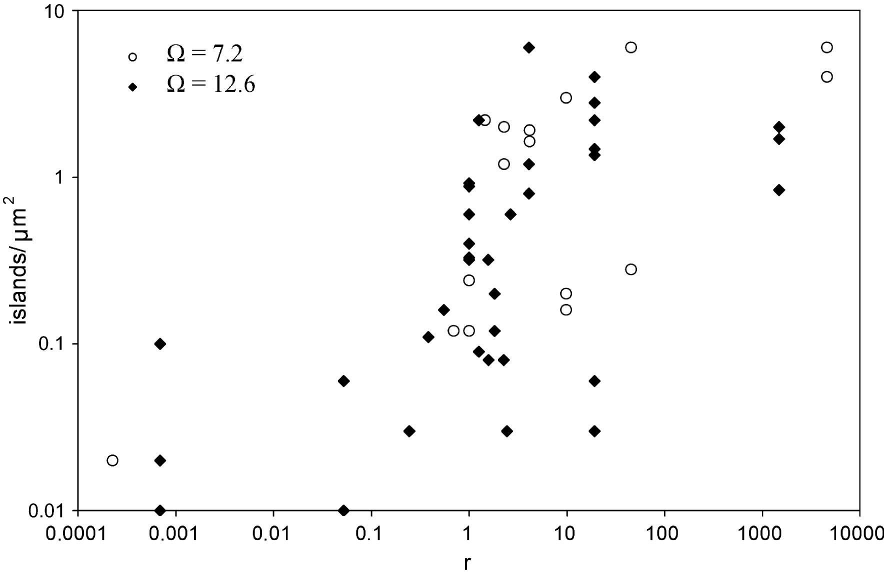

Fig. 2. Island density (number of islands per µm^2) versus solution stoichiometry (r). Surfaces that grow exclusively by preexisting cleavage step advancement are not included on the logarithmic scale of the graph.

spreading as the dominant growth mode for $r > 0.24$ (at $r = 0.24$, $a_{\text{Ba}} = (0.13$ and $0.18)$ µM for $\Omega = (7.2$ and $12.6)$, respectively). We observed a general tendency to increase island nucleation rates with increasing barium activity in solution (Fig. 2). Nevertheless we noticed that two dimensional nucleation is a very surface dependent process, as for the same r and Ω conditions we observed surfaces on which massive and continuous 2D nucleation occurred as well as surfaces on which islands were not nucleated during the time of the experiment. As growth rates measured on our (001) barite faces are quite low compared with literature data (Bosbach et al., 1998; Pina et al., 2004; Sanchez-Pastor et al., 2006) it is possible that the influence of impurities or defects which could facilitate nucleation was relatively low for crystals used in our experiments. Summarizing our observations we can conclude that for $r < 0.24$ crystal growth is controlled mainly by advancement of preexisting steps. If some islands nucleate, they are rare and spread with no new nucleation events occurring. For $r > 0.24$ island spreading is a prevailing growth mechanism and nucleation rates increase with increasing r. Finally, for $r > r_{\max}$ very high density of 2D nucleation can occur (Fig. 3).

3.2. Barite growth from dilute aqueous solutions of methanol

3.2.1. Velocity of step spreading

Fig. 4 shows that at moderate values of supersaturation ($\Omega = 12.6$) the presence of 0.02 molar fraction of methanol in the growth solution increases the growth rate for $r < r_{\max}$ and has virtually no effect on the growth rate for $r > r_{\max}$, where $r_{\max}$ denotes the lattice ion ratio corresponding to the maximum step growth velocity in pure water solutions ($v_{\max}$). The effect of growth rate enhancement expressed as a ratio of step growth velocity in a methanol-containing solution to growth velocity in a reference pure water solution (v_{met}/v) increases up to $r = 0.24$, which coincides with the lower boundary found for the growth mode dominated by 2D nucleation, and then starts to decrease. Consequently, in the presence of methanol in solution, the dependence of v on r changes such that the growth rate exhibits a maximum at stoichiometric conditions ($r = 1$) and the function of v versus r becomes more symmetrical around $r = 1$.

3.2.2. Two-dimensional nucleation

The presence of methanol in the growth solution substantially increases the potential for 2D nucleation. For $\Omega = 12.6$, islands are induced for the whole range of the solution stoichiometry investigated. The effect can be especially well observed when a methanol-containing solution is passed over a barite surface that was previously grown from solution in water (Fig. 5). New islands nucleate immediately and it is not just a single nucleation event, but new islands nucleate and spread continuously. Rates of 2D nucleation in water–methanol solutions are noticeably higher for $r > 1$ than for $r < 1$ (Fig. 6).

For a lower supersaturation ($\Omega = 7.2$) we do not have systematic data over the whole range of r. Experiments were performed for three values of $r \leqslant 1$ and the acceleration of step growth velocity and of nucleation rates was observed. Density of 2D nucleation was lower than for $\Omega = 12.6$ and for $r = 2.25 \times 10^{-4}$ the presence of methanol in a growth solution did not always result in nucleation of islands.

3.3. SEM study of barite crystals grown from pure water solutions with variable ion ratio

As can be seen in Fig. 7 barite crystals that precipitated from solutions with excess sulfate ($r = 0.24$), from stoichiometric solution ($r = 1$) and from solution with excess of barium ($r = 4.10$) have distinct morphologies and sizes. Barite crystals grown from solution with $r = 4.10$ (which approximately corresponds to the maximum growth rate

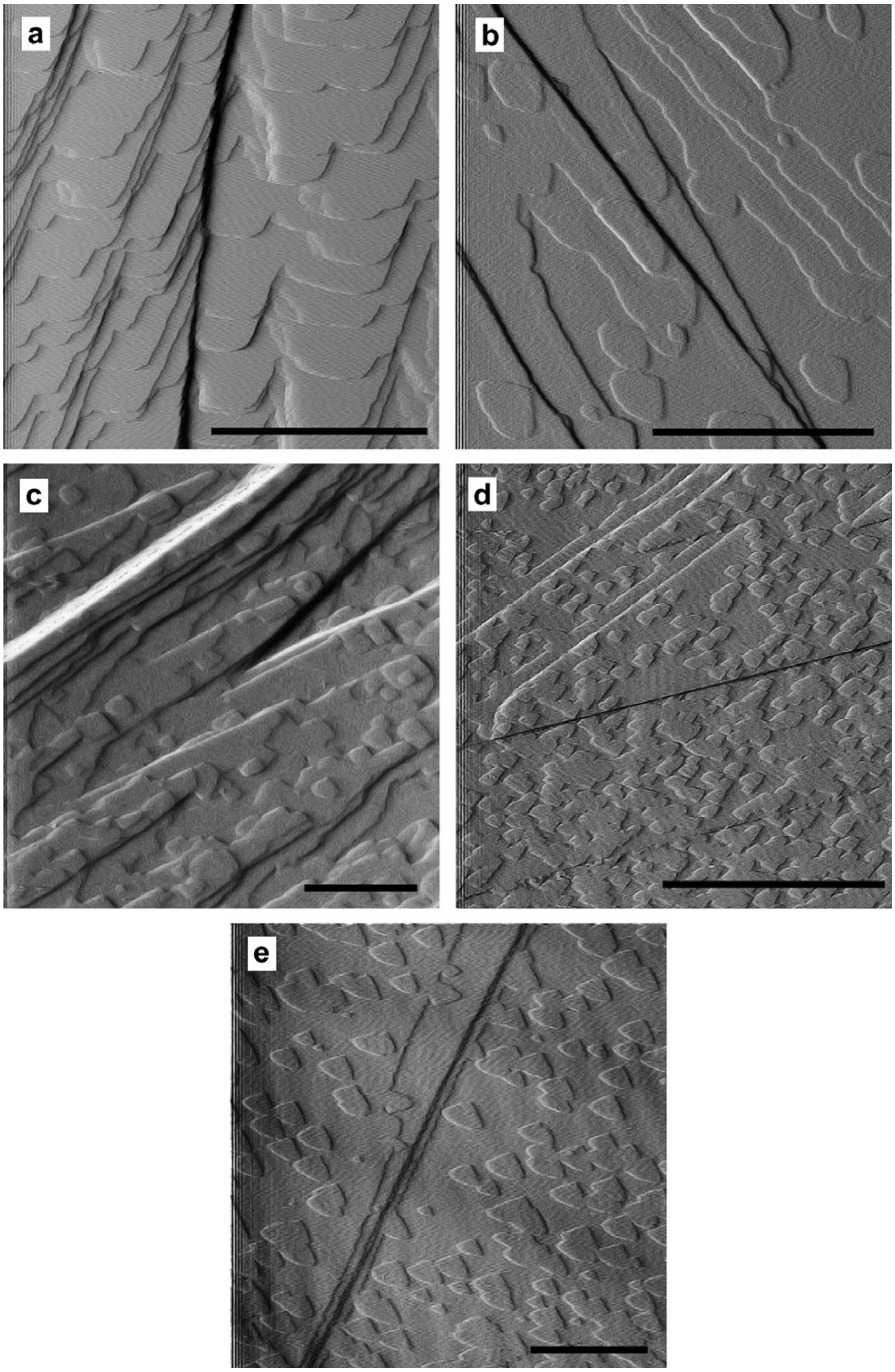

Fig. 3. AFM deflection images showing growth on barite surfaces at constant $\Omega = 12.6$ under varying solution stoichiometry: (a) $r = 0.24$, (b) $r = 1$, (c) $r = 4.10$, (d) $r = 19.2$, (e) $r = 1480$. Scale bars: 2.5 μm.

at $\Omega = 12.6$) have morphologies which suggest that they precipitated under higher supersaturation compared to those obtained at $r = 0.24$ and 1 (Li et al., 2007), even though the supersaturation was the same in each case. In accordance with our observations Kucher et al. (2006) also showed that an excess of barium ions leads to a dendritic growth mechanism. Not only are morphologies of the crystals different, but also rates of nucleation differ substantially. For a solution depleted in [Ba^{2+}] we found only very few crystals precipitating while the number of crystals in solution with excess barium was significantly higher than in the stoichiometric case.

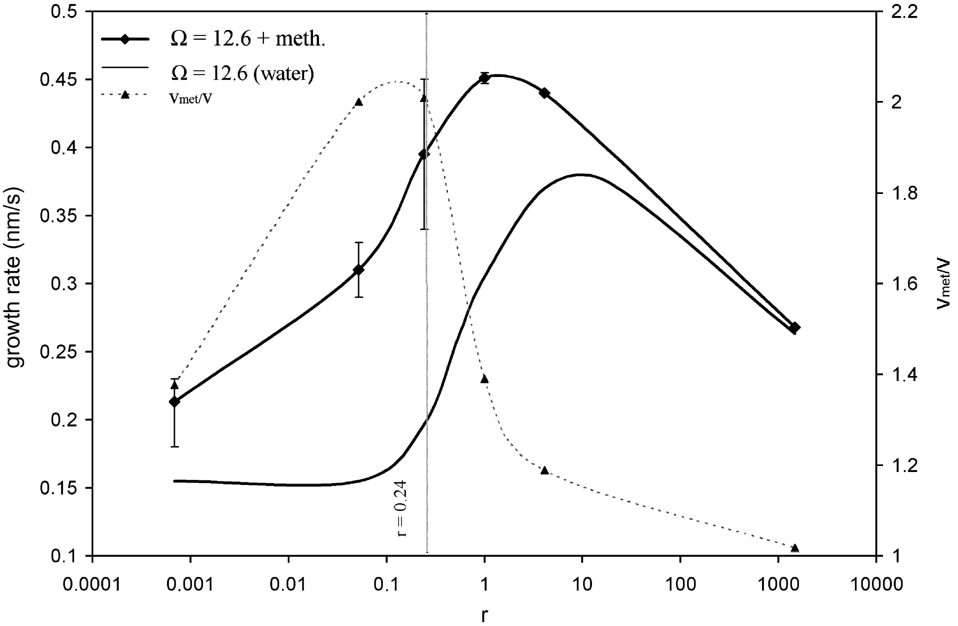

Fig. 4. Dependence of growth rate (v) on solution stoichiometry (r) in methanol-containing solutions and in reference aqueous solutions (expressed only by the trend line) under constant supersaturation ($\Omega = 12.6$) and the effect of growth enhancement in the presence of methanol (v_{met}/v).

4. DISCUSSION

4.1. Barite growth from aqueous solution

4.1.1. Kinetics of ion integration into the surface: Theoretical introduction

In our experiments the observed trend in the growth rate (v) as a function of solution stoichiometry (r) can be explained in terms of the kinetic ionic ratio model developed by Zhang and Nancollas (1998), which refers to the growth of a binary symmetric electrolyte crystal AB. In such a system two types of kinks, cation- and anion-incorporating, are present on the surface and two types of individual ions are considered as growth units. Growth and dissolution rates depend on relative frequencies of integration (k_i) and detachment (v_d) of these non-equivalent building units. Zhang and Nancollas assumed v_d to be equal for both ions as the same AB bond is broken (if the process for either ion is not affected by protonation or complexation for example), but concluded that their attachment frequencies were possibly considerably different because of the difference in cation and anion dehydration rates. To describe growth and dissolution of such system, the concept of kinetic ionic ratio was introduced and defined as

$$r_i = \frac{v_{dB} k_{iA}}{v_{dA} k_{iB}} \frac{a_A}{a_B},$$

where a_A and a_B are activities of the lattice ions in solution, k_{iA} and k_{iB} are first-order rate constants for the integration of A and B ions and v_{dA} and v_{dB} are their detachment frequencies. The expression can be reduced to

$$r_i = \frac{k_{iA}}{k_{iB}} \frac{a_A}{a_B}$$

assuming that $v_{dA} = v_{dB}$.

Maximum kink propagation rate is expected for $r_i = 1$ which means that both lattice ions are integrated into the surface with equal frequencies ($k_{iA} a_A = k_{iB} a_B$). For $r_i \neq 1$ growth is limited by the ion with the smaller overall integration rate so that A is rate limiting for $r_i < 1$ and B for $r_i > 1$. The growth rate can exhibit a maximum at the stoichiometric lattice ion ratio in solution ($r = a_A/a_B = 1$) only if attachment frequency factors for both building units are equal ($k_{iA} = k_{iB}$), which was in fact experimentally observed (Chernov et al., 2006; and Nehrke et al., 2007) although as commented by the authors "the reasons for this are still to be found" (Rashkovich et al., 2006). For $k_{iA} \neq k_{iB}$ the kinetic ionic ratio reaches unity at $a_A/a_B \neq 1$ and consequently maximum step growth velocity corresponds to solution compositions where the activity of the ion with a lower attachment frequency factor is in excess in relation to stoichiometric conditions.

4.1.2. Growth kinetics for the case of non-equivalent integration rates of lattice ions

In the light of this simplified theoretical background we can conclude that for our experimental system, where r is defined as $r = a_{Ba}/a_{SO}$, the fact that v_{max} corresponds to $r > 1$ indicates a lower attachment frequency factor for a barium than for a sulfate ion. Ba^{2+} is expected to limit the growth rate for $r < r_{max}$ ($r_i < 1$) and SO_4^{2-} for $r > r_{max}$ ($r_i > 1$), where $r_i = 1$ indicates equal integration rates for both ions.

The model also predicts that the growth rate decreases symmetrically as $\log(r_i)$ deviates from zero. However, the theory applies to rates of step movement and spiral growth and in the case of our experiments we have to consider the transition from growth driven only by step advancement, to growth influenced by induction of two-dimensional nuclei.

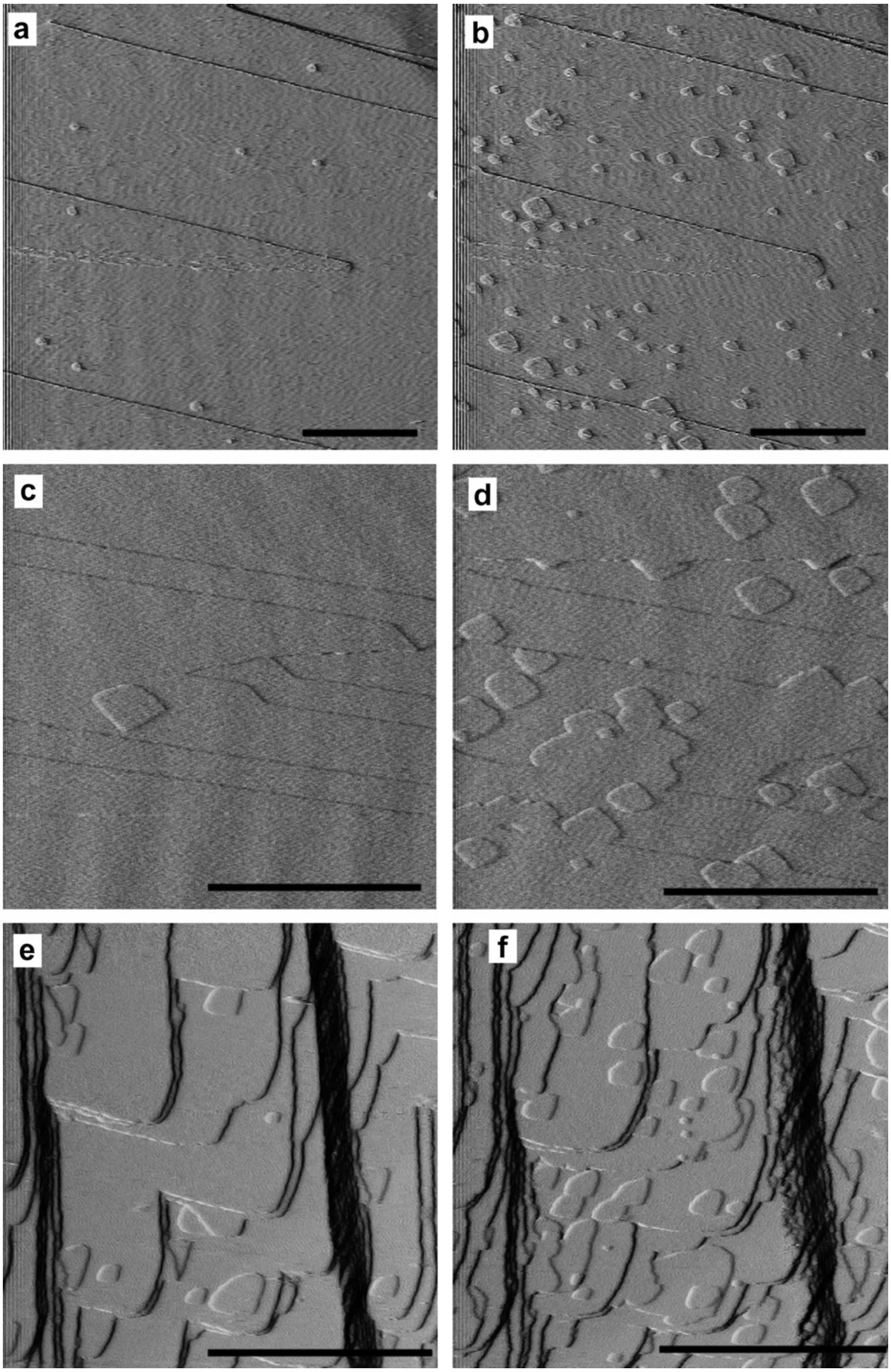

Fig. 5. AFM deflection images showing the influence of methanol on nucleation rates. Pairs of images show barite surface grown from water solution (left) and just after injection of methanol-containing solution (right) with the same supersaturation for different lattice ion ratio: (a and b) for $r = 6.90 \times 10^{-4}$, (c and d) for $r = 0.24$, (e and f) for $r = 4.10$. Scale bars: 2.5 μm.

Zhang and Nancollas (1998) address kink (1D) nucleation, but assume that kink density as a function of kinetic ionic ratio is symmetrical around $r_\mathrm{i} = 1$. We found that 2D nucleation does not depend in the same manner on r_i, but that cation excess prompts nucleation whereas anion excess does not. Consequently when we deal with the transition in the growth mechanism we should consider that kink dynamics on existing steps and kink formation via 2D nucleation could depend differently on solution stoichiometry and that in the transition region new kink creation induced by 2D

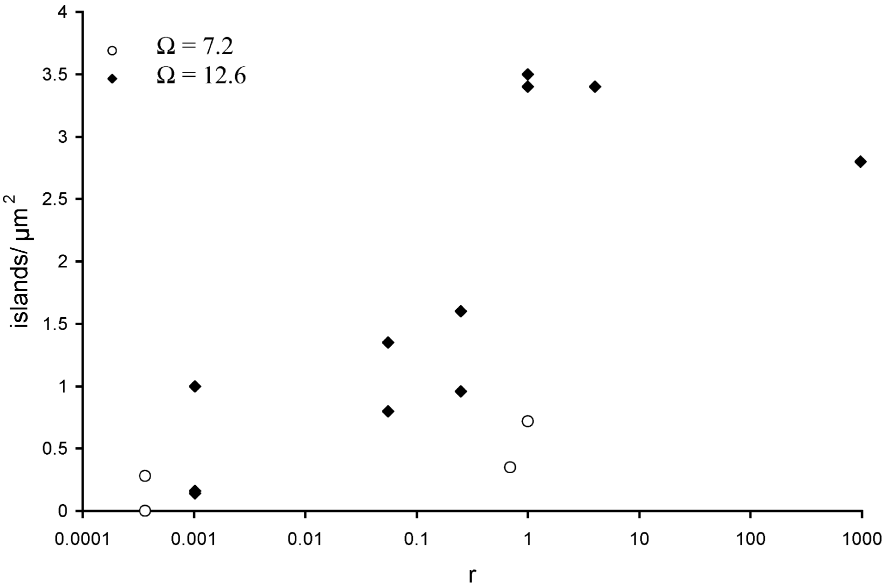

Fig. 6. Island density (number of islands per µm^2) versus lattice ion ratio (r) in methanol-containing solutions.

nucleation is probably reflected in the observed growth dynamics pattern. Of course the growth of 2D nuclei is no different than step advancement and symmetricity for cation and anion incorporation (around $r_i = 1$) can hold true in the case of 2D spreading (see Section 3.2—experiments with methanol).

4.1.3. Barium ion promotes nucleation

Although we found that two-dimensional (2D) nucleation is highly surface dependent, we observed a general trend to enhance island nucleation rates with increasing barium activity in solution. This implies that under constant supersaturation, the potential for two-dimensional nucleation is determined by Ba^{2+} incorporation.

It was previously shown that 2D nucleation rates increase not linearly, but exponentially with increasing driving force (Bosbach et al., 1998). Our observations suggest that the threshold energy barrier for 2D nucleation can be overcome not only due to the thermodynamic effect but also as a kinetic effect.

A SEM study of barite crystals precipitating from stoichiometric and non-stoichiometric solutions provides strong evidence that matching the ion ratio in solution to that of the crystal lattice does not provide the optimum conditions for barite nucleation and growth, but that the process is more effective when barium is in excess with respect to sulfate. These observations are entirely consistent with the results of our AFM experiments.

4.2. Barite growth from a dilute aqueous solution of methanol

Addition of methanol to the growth solutions results in an increased rate of 2D nucleation as well as an increase in the step advancement rate in relation to reference pure water solutions in the region where barium attachment is the rate limiting factor ($r < r_{\max}$). However there is no significant change in the rate of step advancement for $r > r_{\max}$ where [Ba^{2+}] is in excess, and sulfate integration is assumed to control growth rate. These results suggest that the effect of the methanol in solution increases the ability of Ba^{2+} to approach the barite surface.

4.2.1. Properties of the solvation environment in water–methanol solutions

Contrary to our findings, it was shown experimentally that growth and nucleation rates of KCl in water–ethanol mixtures are reduced with respect to pure water solutions (Omar and Ulrich, 2007). Enhanced induction times at equal supersaturation and temperature were explained by the fact that the cosolvent increases the solid–liquid interfacial energy, which is inversely proportional to the equilibrium solubility, and the conclusions were corroborated by calculations based on classical nucleation theory. In the following paragraph we show that this apparent discrepancy between our results and those of Omar and Ulrich (2007) can be understood by considering differences in the interactions of the respective solutes with the solvation environment.

Ion hydration in solution is the net effect of the competition between ion–water interactions, namely the tendency of the ion to orient water dipoles by electrostatic attraction and water–water interactions that tend to create a hydrogen-bonded network. Ions with high charge density (kosmotropes or structure-makers) bind the water tightly and cause strong electrostatic ordering of water molecules in their first solvation shell. Ions with relatively low charge density (chaotropes or structure-breakers) have smaller potential to attract water dipoles and the water molecules surrounding them remain largely hydrogen-bonded (Hribar et al., 2002).

Samoilov (1965) proposed that the way in which ions affect the water structure could by understood in terms of the difference (ΔE_i) between the activation energy required to transfer a water molecule from the first to the next coordi-

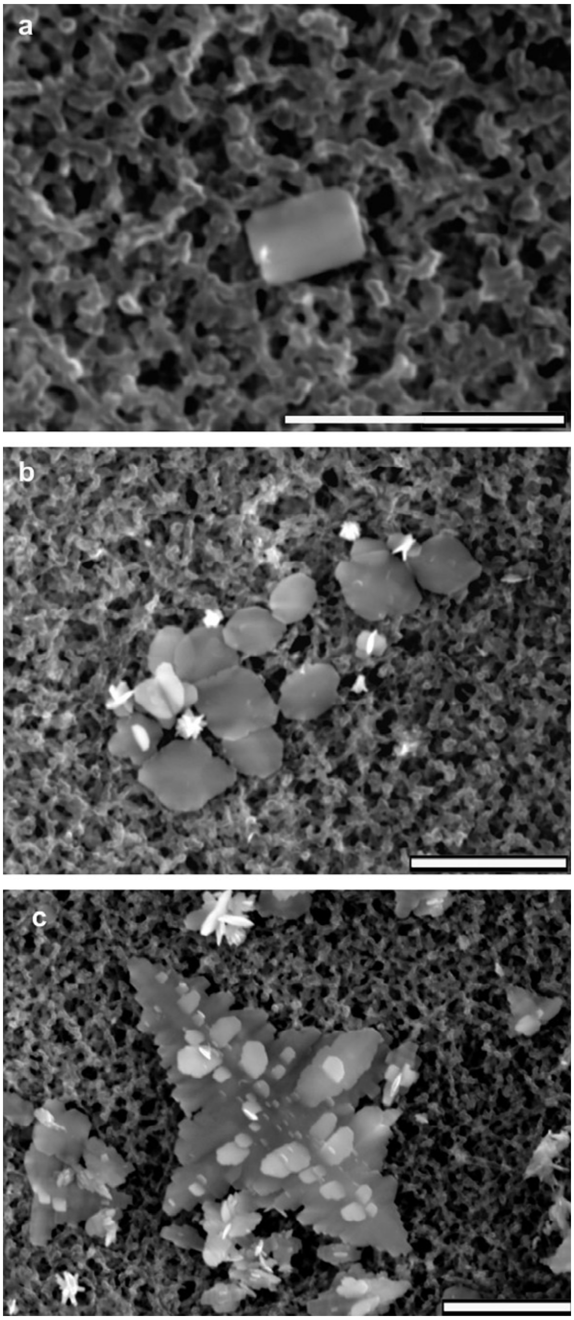

Fig. 7. SEM showing morphologies of barite crystals precipitated from solution: (a) depleted in [Ba^{2+}] in respect to SO_4^{2-} at $r = 0.24$; (b) stoichiometric ($r = 1$); (c) with excess of [Ba^{2+}] in respect to SO_4^{2-} at $r = 4.10$. Scale bars: 10 μm. Background texture is the porous filter.

nation shell of the ion (E_i) and the activation energy needed to remove a water molecule from the first coordination shell of another water molecule (E_0), i.e. $\Delta E_i = E_i - E_0$. $\Delta E_i < 0$ means that water molecules around the ions are more mobile than in the bulk solution and characterizes chaotropes, and $\Delta E_i > 0$ indicates that water exchange around ions is slower than around other water molecules in solution and corresponds to kosmotropes. Fig. 8 presents kosmotropic and chaotropic properties of some ions.

Addition of methanol to pure aqueous solutions reduces the translational motion of the water molecules (Dixit et al., 2002; Dlugoborski et al., 2000; Guo et al., 2003; Allison et al., 2005), which according to Grigorovich and Samoilov (1962) leads to decreased ion solvation in solution and consequently causes solubility reduction. Decreased ion solvation as a result of the addition of lower alcohols to water was confirmed in recent studies by Palka and Hawlicka (2005). They show that in dilute aqueous solutions of methanol (up to 0.2 molar fraction) the solvated radius of a Ca^{2+} ion is lower than in pure water. This can be considered as an effect of the competition between the ion–solvent interaction and the methanol–water hydrogen-bonding tendency. The same should be true for a barium ion and the effect of competition with methanol for water molecules could be even more pronounced as Ba^{2+} has lower charge density and attracts water molecules less strongly than Ca^{2+}.

In view of the specific interactions of the solutes with solvents, one can explain differences in the influence of the lower alcohols on nucleation and growth rates of minerals such as potassium chloride and barium sulfate. In Fig. 8 we see that K^+, with a relatively large radius and low charge, has chaotropic properties, which means that in pure aqueous solution frequency of water exchange around the cation is faster than water mobility in the bulk and its coordination shell does not retard the translational motion of the K^+. For a chloride ion it was shown that the residence time of its coordinated molecules cannot be longer than a characteristic time of Cl^- translations (Palka and Hawlicka, 2005). The logical consequence is that dehydration should not be the rate-limiting step in KCl crystal growth from water solutions. Therefore in the presence of alcohol the hampering effect of the increased fluid–solid interfacial energy on the nucleation process prevails over the effect of accelerated molecular motion in the nearest neighborhood of the ions. However for kosmotropic ions, the kinetic barrier resulting from the need to expel water molecules surrounding ions before they can attach to the surface can be a significant rate-limiting factor for crystal nucleation and growth. Our results suggest that facilitated water liberation from the ion solvation shell can have a greater effect on the growth kinetics than increased interfacial tension.

We observed that in the case of barium sulfate, lowering the solvation of the Ba^{2+} ion affects the ability of the cation to approach the growth site. This is consistent with recent molecular dynamic simulations made by Piana et al. (2006) which show that in order to reach the growth site, Ba^{2+} ions need to overcome the energy barrier provided by water molecules bound to the surface and surrounding the cation while SO_4^{2-} can much more easily diffuse to the crystal surface.

4.2.2. Response of the growth dynamics on reduced hydration

The fact that a reduced hydration barrier results in v_{max} occurring at $r = 1$, as would be expected for equal attachment frequency factors for both building units ($k_{Ba} = k_{SO_4}$, implies that differences in integration rates of the cation and anion in water solutions arise mainly from the dif-

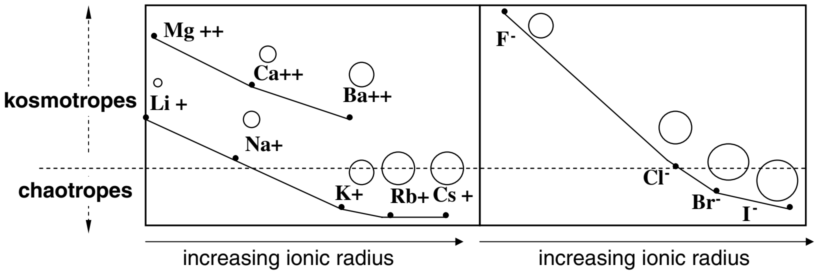

Fig. 8. Kosmotropic and chaotropic properties of the ions versus ionic radius. Circles indicate schematically the relative ion radii (after Hribar et al., 2002).

ference in their dehydration frequencies. Moreover, accelerated nucleation rates in the presence of methanol suggest that desolvation of the cation and of the surface is the rate-limiting factor for 2D nucleation, in agreement with findings of Piana et al. (2006). Enhanced potential for nucleation due to a reduced solvation barrier in methanol-containing solutions results in island spreading being the prevailing growth mechanism for the whole range of r investigated, and consequently the effect of the transition in growth mechanism on growth dynamics diminishes—v changes more symmetrically when r deviates from unity. It is possible that the threshold for island nucleation is only shifted away from our investigated range of solution stoichiometries, but is still reflected in v decreasing slightly more sharply with depletion of [Ba^{2+}] than [SO$_4^{2-}$] in relation to stoichiometry.

4.3. Kinetic effects on barite growth mechanisms at a constant thermodynamic driving force

There is a noticeable difference in density of nucleation for $r < 1$ and $r > 1$ in methanol-containing solutions, which can be understood by considering both the fact that the nucleation rate is limited by barium attachment and that step spreading is energetically more favorable than a new nucleation event. Consequently as long as the attachment of sulfate ions effectively supports growth, spreading of a fewer number of islands is preferred. When barium is in excess, the limiting effect of sulfate integration on the spreading rate is compensated by an increase in the number of nuclei. The phenomenon of an increase in number and a decrease in size of nuclei as a result of increased supersaturation due to the addition of excess [Ba^{2+}], was observed for homogenous BaSO$_4$ precipitation from bulk solution (Vicum et al., 2003). In our experiments the effect of excess barium, although not directly comparable with primary nuclei formation but the same in principle, i.e. enhanced potential for nucleation with growth hampered by the component of the lower concentration, is entirely kinetic. Note that no increase in nucleation rates is caused by excess sulfate which confirms that cations and anions behave differently with respect to crystal growth kinetics.

It can be concluded that in our methanol-containing solutions two-dimensional nucleation is the rate-limiting process for crystal growth for $r < 1$ (Ba^{2+} limits rates of growth and nucleation) while step advancement limits the growth rate for $r > 1$ (SO$_4^{2-}$ limits spreading but not nucleation rates.) The same is true for growth from pure water solutions if r is substituted by the idea of the kinetic ionic ratio (r_i) and r_max corresponds to the lattice ion ratio in solution for which attachment frequencies of cation and anion are equal ($r_\mathrm{i} = 1$). Once again it is worth pointing out that 2D nucleation was found to limit growth under lower supersaturation while diffusion of steps limits growth under higher supersaturation (Pina et al., 1998). Our findings show that the potential for 2D nucleation changes under constant thermodynamic conditions due to kinetics of barium integration, which is dominated by the process of surface and ion desolvation.

5. CONCLUSIONS

To the best of our knowledge this is the first systematic AFM study on barite growth from solutions with varying lattice ion ratio. Our investigations reveal that:

- the growth rate of steps on the (001) barite surface exhibits a maximum for a lattice ion ratio in solution where barium activity is in excess with respect to stoichiometric conditions, implying a lower attachment frequency factor for barium than for sulfate ions;
- barium ion incorporation is the rate limiting factor for two-dimensional nucleation and under constant thermodynamic driving force, the mechanism of barite growth is governed by kinetics of Ba^{2+} attachment to the surface;
- in dilute aqueous solutions of methanol, the kinetic barrier for barium ions to approach the surface is reduced, resulting in accelerated nucleation rates and enhanced step growth velocity.

In the light of the results of experiments conducted in water–methanol solutions, we conclude that the dependence of barium sulfate growth dynamics on solution stoichiometry, and the rate limiting effect of barium ion integration on 2D nucleation can be explained by considering the role of the desolvation process on the crystal growth.

Changes in crystal growth kinetics in the presence of methanol results from specific intermolecular interactions between water, methanol and solutes. Recently the effect of micromolar concentrations of peptides on the growth velocity of calcium carbonate has been reported (Elhadj et al., 2006) and the observed growth enhancement was attributed to the reduction in the diffusion barrier, mainly for the cation, caused by perturbations that displace water molecules and facilitate the release of water of solvation. This displacement was correlated to the relative hydrophilicity of peptides. Methanol, despite the simplicity of its structure, consists of both hydrophilic (hydroxyl) and hydrophobic (methyl) headgroups and changes the water structure by the same mechanism as more complex amphiphilies such as macro- and biomolecules (Dixit et al., 2002). A detailed description of water–methanol interactions is beyond the scope of this paper but we suggest that the effect of methanol and of biomolecules on crystal growth kinetics may have the same origin at the atomistic level and that lower alcohols, being much simpler to investigate, can provide a useful framework to facilitate understanding of mineral growth in biological systems.

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