The morphology of calcite crystals grown in a porous medium doped with divalent cations

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Abstract

Calcite crystals were grown in the presence of small concentrations (50, 200, and 600 ppm) of divalent cations (Ba^{2+}, Sr^{2+}, Co^{2+} and Mn^{2+}) in a silica hydrogel medium. The calcite crystals grown in the presence of cations larger than Ca^{2+} (Ba^{2+} or Sr^{2+}) developed rhombohedral habits defined by $\{10\bar{1}4\}$ form, similar to the morphology of calcite grown in a pure gel. SEM images show that growth on $\{10\bar{1}4\}$ occurs by lateral advancement of layers bounded by macroscopic dendritic or jagged steps. In the case of calcite crystals grown in a gel doped with cations smaller than Ca^{2+} (Co^{2+} or Mn^{2+}), a variety of morphologies was obtained, ranging from blocky crystals (at lower concentrations: 50 and 200 ppm) to peanut-like aggregates, spheres and spherulites (at 600 ppm). The macroscopic morphological characteristics of such doped calcite crystals reflect closely the growth behaviour of calcite $\{10\bar{1}4\}$ surface at a nanoscale, reported by previous AFM studies. Morphological features have been interpreted on the basis of the modification of growing steps characteristics as a consequence of asymmetrical cation incorporation. The use of such morphologies as a criterion of biological activity is, therefore, unreliable.

Keywords: Calcite; Crystal morphology; Gel crystal growth method; Impurities

1. Introduction

Calcite crystals grown in sedimentary environments show a wide variety of growth morphologies. Frequently, some of these morphologies have been used as a criterion to assign a biological origin to carbonates precipitates. In 1996 the finding of carbonate globules in Martian meteorite ALH84001 sparked controversy on whether those carbonates were the result of organic or inorganic processes (McKay et al., 1996). Moreover, the habit of certain calcite and other calcite type carbonates (crystals with rounded morphologies, dumbbell-like crystals, etc) have commonly been interpreted as resulting from the activity of bacteria in the crystallisation medium (Chafetz, 1986; Buczynski and Chafetz, 1991; Vasconcelos et al., 1995). Therefore, the presence in a rock of calcite crystals showing such peculiar morphologies leads researchers frequently to conclude the existence of bacteria in the medium during the growth of these crystals. However, as have been pointed out by García-Ruiz et al. (2002), using morphological criteria in order to distinguish minerals produced by living organisms can lead to erroneous conclusions. Many other factors can exert an influence on crystal morphology. Among them, the most important ones are the following: supersaturation of the medium during both nucleation and growth processes, presence of either inorganic or organic impu-

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rities, hydrodynamic factors, distribution of growth sites on the crystal surface, etc (Sunagawa, 1987). Therefore, to be able to use calcite morphology as a geological indicator it is basic to know the physic and chemical factors involved in the generation of the different morphologies.

Probably, the presence of impurities in the growth medium is the factor that most strongly affects the morphology of a crystal. When impurities incorporate into a crystal lattice defining a solid solution, they will affect the growth process by two main different mechanisms: changing the characteristics of crystal surfaces, and modifying the phase solubility. Thus, the incorporation of "foreign" ions usually occurs selectively on different crystallographic faces, changing their surface free energies and making them rougher or smoother. On the other hand, a solubility change will determine the modification of the medium supersaturation. Both aspects have a definitive influence in controlling the growth mechanisms operating on the different crystallographic faces along the growth process. Thus, those faces growing more slowly will control the final growth morphology. In this paper we study the effect that the presence of certain cations in the growth medium exerts on calcite crystals morphology. Two groups of cations have been considered: a) cations with ionic radii smaller than Ca^{2+} (Mg^{2+}, Co^{2+}, and Mn^{2+}), which can incorporate in the calcite structure forming more or less extended solid solutions, and b) cations with ionic radii larger than Ca^{2+} (Ba^{2+}, Pb^{2+}, and Sr^{2+}), which can be incorporated into calcite structure in small amounts. In this second case, there is no agreement about whether these cations substitute Ca^{2+} or they occupy nonlattice positions in calcite structure (Pingitore, 1986; Reeder et al., 1999, 2002).

The experiments of calcite crystal growth in the presence of divalent cations have been carried out by using the silica hydrogel technique. This technique has been extensively used as a method of growing crystals of sparingly soluble salts like carbonates and sulphates (Henisch, 1988; Prieto et al., 1989, 1992). Moreover, it allows reproducing most characteristics of crystallisation in sediments (García-Ruiz, 1982). Thus, in this technique, crystallization occurs from solution by chemical reaction at low temperature in a column of porous inert gel. The gel constitutes a transport medium where convection and advection are suppressed. Reactants are brought together by counter-diffusion from opposite ends of the gel.

The calcite growth morphologies obtained in the experiments are different depending on whether the gel medium was doped with a divalent cation smaller or larger than Ca^{2+}. In the case of calcite crystals grown in the presence of cations larger than Ca^{2+}, they show a rhombohedral habit, essentially defined by all the faces belonging to the form $\{10\bar{1}4\}$. However, calcite crystals grown in the presence of divalent cations smaller than Ca^{2+} show a variety of morphologies that, in all the cases considered, have common aspects: crystals are slightly elongated along the $\bar{3}$ axis and have a cleft in the equatorial region. The two types of morphologies obtained are interpreted on the basis of the geometrical characteristics of the steps operating during growth of calcite $\{10\bar{1}4\}$ and other microtopographic features.

2. Experimental

The crystallisation of calcite was carried out in a double diffusion system as shown in Fig. 1. The experimental arrangement consist in a U-tube where a column of silica hydrogel (150 mm long and 9 mm in diameter) occupies the horizontal branch, while the vertical branches (A and B) correspond to the reservoirs of the parent solutions and were filled with 8 cm^3 of $CaCl_2$ (0.5 M) and Na_2CO_3 (0.5 N), respectively. The gel was prepared by acidification with HCl (1 N) of a sodium silicate (Na_2SiO_3) solution (Merck, sp. Gr.: 1.059 g cm^{-3}, pH 11.2) to the desired initial pH (5.5) and poured in the U-tube. For the conditions established here, the silica hydrogel contains about 95.6% water filling the pores and NaCl as a soluble by-product. The solution is trapped within micron-sized pores, what makes it stagnant (Henisch, 1988). Mass transfer occurs via molecular diffusion and leads to the development of gradients of pH and concentration along the gel column. Separate experiments were carried out to study the influence of the presence of Mn^{2+}, Co^{2+}, Ba^{2+}, and Sr^{2+} in the aqueous solution on the growth of calcite. Small concentrations of these impurities (50, 200, and

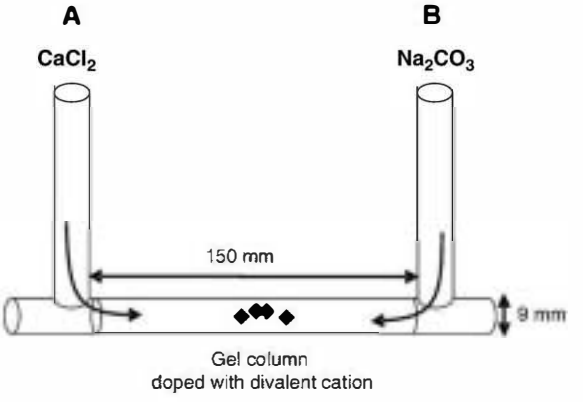

Fig. 1. Schematic representation of the experimental system (U-tube).

600 ppm) were added to the sodium silicate solution during the gel preparation. Thus, the gel column had a homogeneous concentration of additive. The experiments were carried out at 25 ± 0.1 °C. The growth evolution of the crystals was monitored by optical microscopy. The experiments were stopped a year after nucleation. Then crystals were recovered by partially dissolving the gel in a NaOH (1 M) solution. The crystals were identified as calcite by X-ray diffraction and their morphology was studied by Scanning Electron Microscopy (JEOL 8600 MXA and JEOL JSM6400).

3. Results and discussion

3.1. Growth of calcite

The morphology of calcite crystals grown from pure aqueous solutions in silica hydrogel is defined by the rhombohedron $\{10\bar{1}4\}$. During the first stages of growth process, $\{10\bar{1}4\}$ faces are essentially flat. However, as growth proceeds, the polyhedral morphology becomes disturbed as a consequence of the fact that growth occurs preferentially along certain directions. Thus, all the faces belonging to the form $\{10\bar{1}4\}$ develop large steps of which two edges are clearly defined by their intersection at the $\bar{3}$ axis. The other two edges appear diffuse and broken in steps. As a result, crystals become hopper-like, with faces that are rough and depressed in their central region. The final morphology shows only faces belonging to the form $\{10\bar{1}4\}$ restricted to those areas that are close to the two edges meeting in the $\bar{3}$ axis. Fig. 2 shows such a typical development of the edges on $\{10\bar{1}4\}$ calcite crystals. When these crystals are oriented with their $\bar{3}$ axis vertical, their equatorial region appears as a marked cleft, with peaks and troughs that alternate every 60°, reproducing the $\bar{3}$ symmetry. Such a morphology has been commonly observed in calcite-type crystals grown at high supersaturation (Franke et al., 1979; Prieto et al., 1981; Heijnen, 1985; Fernández-Díaz et al., 1996) and described in detail by Dominguez Bella and García-Ruiz (1987), Fernández-González et al. (1999) and Astilleros (2001). It is important to note that, regardless of the degree of supersaturation, the form $\{10\bar{1}4\}$ defines always the morphology of calcite crystals grown in a diffusion-reaction system. Supersaturation levels during the growth process only affect the roughness of the rhombohedral faces. When growth occurs under higher supersaturation levels, the cleft observed in the equatorial region appears more evident and the surfaces are rougher than at moderate supersaturation of the growth medium. This is a consequence of the development of supersaturation gradients around the crystal (Berg, 1938).

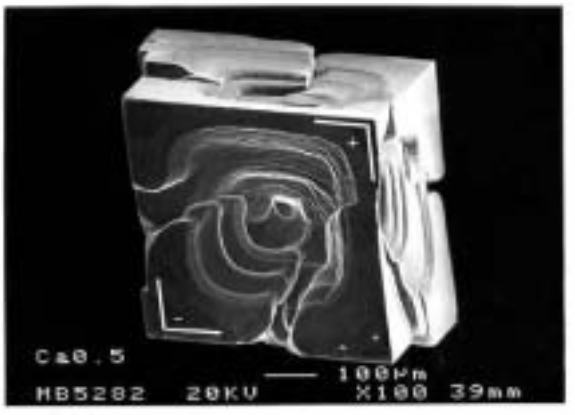

Fig. 2. Calcite crystal obtained in a gel experiment in absence of doping cations. The different development of the $(10\bar{1}4)$ face edges ("+" and "−") can be clearly observed.

The dominance of the calcite form $\{10\bar{1}4\}$ for wide supersaturation ranges reflects the strong control of the calcite structure on its crystal morphology. This is clearly evidenced by the structural analysis developed by Paquette and Reeder (1995) and Staudt et al. (1994). In the calcite structure the most stable Periodic Bond Chain (PBC) runs along $\langle\bar{4}41\rangle$ directions (Heijnen, 1985), with two different pairs of crystallographically equivalent directions being related by the c-glide: the positive directions $[\bar{4}41]_+$ and $[48\bar{1}]_+$ and the negative directions $[\bar{4}41]_-$ and $[48\bar{1}]_-$ (notation according to Staudt et al., 1994). As a consequence of the orientation of the exposed carbonate groups (Reeder and Rakovan, 1999), steps parallel to positive and negatives directions have non-equivalent step edge geometries. Positive steps contain large and open kink sites, while kink sites in negative steps have a more constrained geometry. These structural characteristics determine the growth behaviour of a calcite $\{10\bar{1}4\}$ surface, as confirmed by AFM experiments carried out by several authors (Hillner et al., 1992; Gratz et al., 1993). The growth of the faces belonging to the form $\{10\bar{1}4\}$ at a molecular scale occurs by a layer-by-layer mechanism, controlled by the advancement of steps parallel to $\langle\bar{4}41\rangle$ directions. The growth process is highly anisotropic, with a pair of steps moving rapidly, while the other pair of steps advances slowly. Those steps that advance rapidly are parallel to positive directions, i.e. they contain kink sites that are more open. Conversely, the steps that move slowly are parallel to negative directions and contain constrained kink sites. This growth behaviour at a molecular scale leads to the development of the

typical macroscopic calcite rhombohedra (Teng et al., 2000). The existence of more open and constrained kink sites in non-equivalent growth steps parallel to $\langle\bar{4}41\rangle$ directions can also explain the anisotropic development of roughness on calcite rhombohedral edges as supersaturation increases. Thus, the two well-defined edges that meet in $\bar{3}$ axis correspond to $[\bar{4}41]_+$ and $[48\bar{1}]_+$, while the two diffuse edges are parallel to $[\bar{4}41]_-$ and $[48\bar{1}]_-$. At this point it is worth mentioning that supersaturation only modifies the relative development of the non-equivalent rhombohedral edges. Therefore, any other morphological change in calcite will reflect the influence of other external factors, e.g. incorporation of impurities. In the next sections the morphology modifications due to the incorporation of cations larger and smaller than Ca^{2+} into the calcite structure will be discussed.

3.2. *Growth of calcite doped with divalent cations*

The experiments carried out using silica gel doped with different divalent cations have produced calcite crystals showing a variety of morphologies. Since calcite forms more or less restricted solid solutions with all the considered cations, the observed morphological variability can be attributed to the incorporation of these cations into the calcite lattice. Such incorporation is not isotropic as has been demonstrated by Paquette and Reeder (1990, 1995) and Hay et al. (2003).

3.2.1. *Cations larger than Ca^{2+}: Ba^{2+}, Sr^{2+}*

The morphology of calcite crystals grown in a silica hydrogel doped with Ba^{2+} or Sr^{2+} is very similar to the morphology of calcite crystals grown in a pure gel. Thus, the habit is controlled by the $\{10\bar{1}4\}$ rhombohedron form. Moreover, these faces appear to show steps with two well-defined edges, while the other two edges appear to be rough and distorted. Fig. 3a and b show calcite crystals grown in a gel doped with 200 and 600 ppm of Sr^{2+}, respectively. It is interesting to note that, as can be observed in both images, the growth of the $\{10\bar{1}4\}$ form occurs by lateral advancement of layers from the well-defined edges to the central region of the face. Macroscopic dendritic or jagged steps bounded these layers. The re-entrants of the steps lobes are especially obvious when the concentration of the doping cation in the medium is high. In such a case, several thick growth layers pile up on $\{10\bar{1}4\}$ surface. As a result, the surface develops a blocky appearance. Moreover, one pair of $\{10\bar{1}4\}$ face edges shows clear striations and the first steps of the development of a vicinal surface.

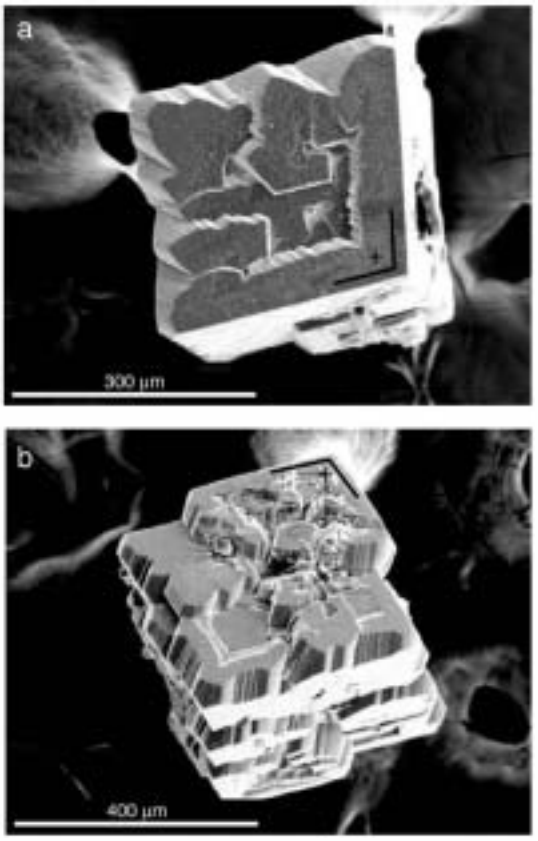

Fig. 3. Calcite crystals grown in a gel medium doped with Sr^{2+}: The amount of Sr^{2+} in the interstitial solution was (a) 200 ppm and (b) 600 ppm. The jagged appearance of positive steps can be observed.

The macroscopic characteristics of faces belonging to form $\{10\bar{1}4\}$ in calcite crystals grown in a gel medium doped with either Ba^{2+} or Sr^{2+} are a close reflection of the microscopic features observed on such surfaces during growth in the presence of any of those cations at a molecular scale. According to AFM observations carried out by Astilleros et al. (2000, 2003), the well defined pair of edges on a calcite $(10\bar{1}4)$ face must be parallel to the positive directions $[\bar{4}41]_+$ and $[48\bar{1}]_+$, while the rough pair of edges must be parallel to the negative directions $[\bar{4}41]_-$ and $[48\bar{1}]_-$. As these authors showed, the growth of calcite $\{10\bar{1}4\}$ surface in the presence of Ba^{2+} and Sr^{2+} exhibits common features at an atomic scale. In the same way as calcite growth from a pure solution, the process is controlled by the advancement of monomolecular steps parallel to $[\bar{4}41]$ and $[48\bar{1}]$ directions. However, in this case while $[\bar{4}41]_+$ and $[48\bar{1}]_+$ steps advance showing jagged edges, $[\bar{4}41]_-$ and $[48\bar{1}]_-$ remain practically immobile. Moreover, the degree of roughness of the positive steps edges increases with the concentration of "foreign" cation in the solution and, for high concentrations of Ba^{2+} or Sr^{2+}

in the solution, the newly grown positive step edges contrast with the original region, indicating that they are thicker than the initial steps (see Fig. 4). The presence of both cations in solution also reduces the velocities of the positive steps in comparison to their advancement velocity when growth occurs from a pure solution. These observations confirmed the previsions of the model by Paquette and Reeder (1995) that consider a preferential incorporation of large cations into steps with open kinks ($[\bar{4}41]_+$ and $[48\bar{1}]_+$). Such a preferential incorporation explains the roughening of these steps, their thickening and their decreasing velocity. The difficulty of large cations incorporation in steps with small kinks ($[\bar{4}41]_-$ and $[48\bar{1}]_-$) determines the blockage of these steps and explains that they remain basically straight during the growth process.

3.2.2. *Cations smaller than Ca^{2+}: Co^{2+}, Mn^{2+}*

The growth of calcite crystals in a gel doped with Co^{2+} or Mn^{2+} shows common aspects, independently of the cation considered. A variety of morphologies, ranging from blocky crystals to peanut-like aggregates, spheres and spherulites, have been obtained, depending on the concentration of each divalent cation in the gel column. Thus, when the concentration of the "foreign" cation is lower (50, 200 ppm) blocky calcite crystals are obtained. These crystals show a habit elongated along *c* axis. The habit is controlled by both $\{10\bar{1}4\}$ and $\{0221\}$ forms (see Fig. 5). Such morphology has a marked cleft

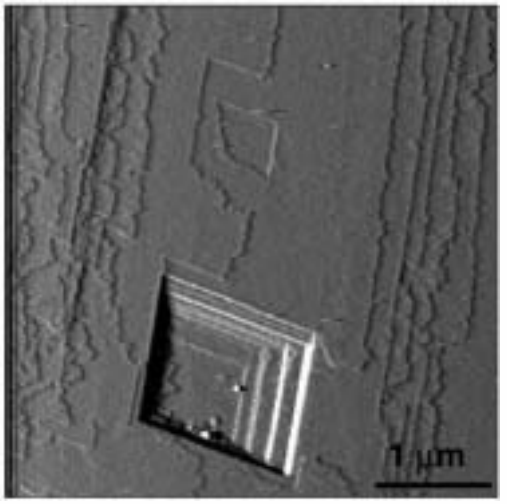

Fig. 4. AFM image showing the development of lobes in the positive steps of a calcite $(10\bar{1}4)$ surface. The composition of the grown solution was: $CaCl_2$=0.24 mmol/L, $Ba(NO_3)_2$=0.4 mmol/L and Na_2CO_3=0.3 mmol/L. The distance between lobes is approximately 80 nm. Note the contrast between the newly grown edges and the original surface, indicating the thickening of the steps as a consequence of Ba^{2+} incorporation.

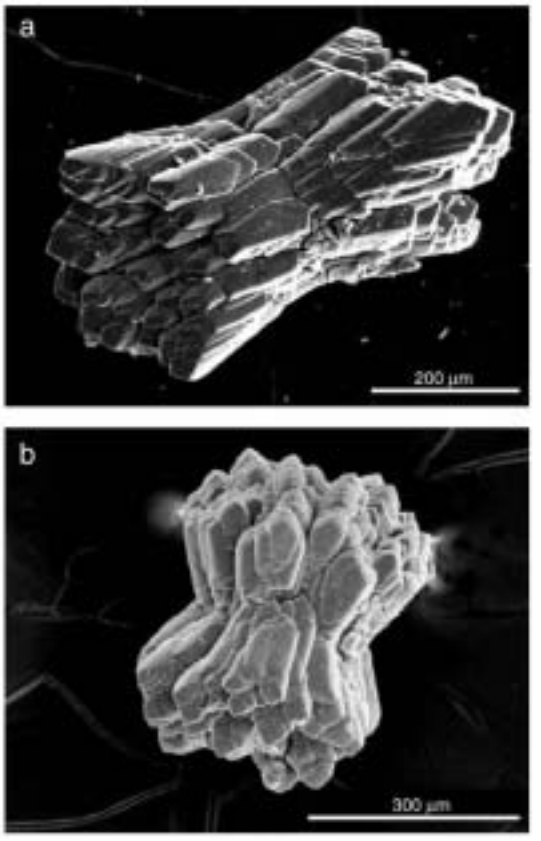

Fig. 5. Calcite crystals grown in a gel medium doped with (a) 50 ppm of Co^{2+}, and (b) 50 ppm of Mn^{2+}.

in the equatorial region as well as has been observed in calcite crystals grown both in pure gel and in gel doped with divalent cations larger than Ca. Moreover, these crystals can hardly be considered single crystals. They are constituted by numerous blocks, slightly misoriented between one to each other. In addition, these crystals show clear evidences of split growth processes, which are more intense when growth occurs in the presence of higher concentrations of foreign cations. The progress of the splitting leads to the development of aggregates with evident rounded surfaces and, in the extreme case, of sheaf-like and peanut-like morphologies (Fig. 6). A very similar morphological evolution was observed by Fernández-Díaz et al. (1996) for the growth of calcite in a silica gel medium doped with Mg^{2+}.

Astilleros et al. (2002) and Freij et al. (2004) studied the nanoscopic evolution of calcite faces belonging to the $\{10\bar{1}4\}$ form in the presence of Mn^{2+} and Co^{2+}. Only low concentrations of Mn^{2+} and Co^{2+} present in the solution are required to affect dramatically the growth of calcite $(10\bar{1}4)$ faces in contrast to the effect of Ba^{2+} and Sr^{2+}. For low supersaturated solutions, the addition of 0.01 mmol of Co^{2+} or Mn^{2+} is enough to

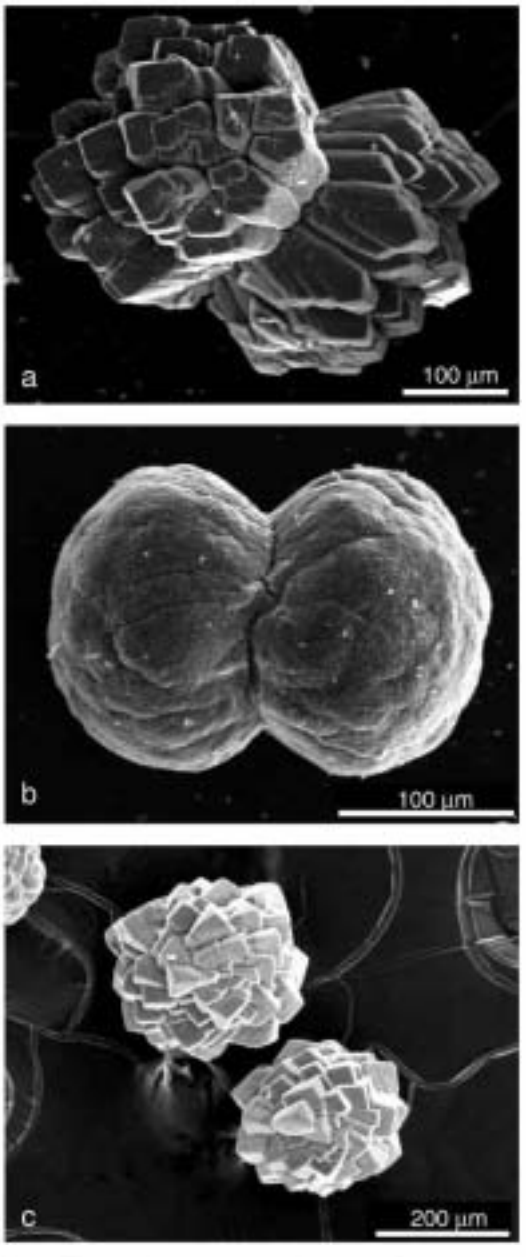

Fig. 6. Calcite crystals grown in a gel medium doped with (a) 200 ppm of Co^{2+}, (b) 600 ppm of Co^{2+}, and (c) 200 ppm of Mn^{2+}.

slow down significantly the step advancement. Higher cation concentrations ([Mn]=[Co]=0.05 mmol) almost completely stop the advancement of steps.

As has been mentioned above, the morphological variability observed in the growth of calcite in the presence of both cations basically coincides with previous observations on the influence of Mg^{2+} on calcite crystal habits (Fernández-Díaz et al., 1996). The main features of calcite $\{10\bar{1}4\}$ surface at nanoscale when growth occurs from a Mg^{2+}-bearing solution have been widely described by Davis et al. (2000, 2004). According to these authors the addition of Mg^{2+} to the growth solution exerts an inhibitory effect that causes step edges to roughen. Such roughening preferentially affects those steps parallel to the negative directions $[\bar{4}41]_-$ and $[48\bar{1}]_-$ as a result of differences in the molecular-scale structure of step edges, although at higher Mg/Ca ratios in the growth solutions roughen both types of step edges. Moreover, these authors observe that growth is preferentially inhibited in the corners between positive and negative directions, where the contact between regions with different composition should be occurring. This must also be the situation when growth occurs from solutions containing Co^{2+} or Mn^{2+}, two cations which also incorporate differently in positive and negative steps. Therefore, an especially strong inhibitory effect in the corners between positive and negative steps should be common to all divalent cations smaller than Ca^{2+} incorporating into calcite$\{10\bar{1}4\}$ surfaces. Such an effect could form the basis of the development of the marked equatorial clefts observed in all calcite crystals grown in the presence of any of these cations. The morphological changes proposed by Davis et al. (2004) basically coincide with the modifications that we have found in the habit of calcite crystals grown in the presence of divalent cations smaller than Ca^{2+}: elongation along *c* direction and emergence of rough pseudofacets that lead to the development of a new crystallographic form. Although these authors have proposed $\{01\bar{1}0\}$ as the new form, we find that the habit of calcite crystals grown in the presence of Co^{2+} or Mn^{2+} is defined by $\{10\bar{1}4\}$ and strongly pseudofaceted $\{02\bar{2}1\}$ forms.

4. Conclusions

Growth experiments presented in this paper show that the morphology of calcite is strongly affected by the incorporation of divalent cations in its structure. Depending on both the degree of cation incorporation and the relative size of each particular cation with respect to Ca^{2+}, different calcite habits have been observed. When the crystallization medium is doped with cations larger than Ca^{2+} (Ba^{2+} and Sr^{2+}) the degree of isomorphic substitution in the calcite structure is limited and crystal morphology only slightly differs from the morphology of pure calcite, i.e. the habit is dominated by the $\{10\bar{1}4\}$ rhombohedron. However, the presence of Ba and Sr in the medium leads to the development of highly stepped faces that provide the calcite crystals a blocky appearance. In contrast, when the crystallization medium is doped with cations smaller than Ca^{2+} (Co^{2+}

and Mn^{2+}) their easier incorporation into the calcite structure results in a wider variety of crystal habits as a function of the "foreign" cation concentration in the growth medium. Thus, as Co^{2+} (or Mn^{2+}) concentration increases calcite habits vary from blocky crystals to peanut-like aggregates and spherulites. Some of these calcite morphologies have been usually related to biological activity. Since our experiments are strictly "inorganic", we must conclude that the use of some peculiar morphologies of natural calcites as the only criterion to prove their biological origin is not reliable.

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