

Ontogeny of baryte crystals grown in a porous medium

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Abstract

The development of the morphology of baryte crystals grown in a silica gel medium is related to the changes in supersaturation. Nucleation occurs when the supersaturation in the system exceeds a threshold value which depends on the supersaturation rate, i.e. the rate at which the supersaturation is changing at the nucleation site. During growth the supersaturation decreases, although a high level of supersaturation is maintained throughout. These experimental results compare well with the morphological development predicted from theoretical models based on the periodic bond chain theory. The ontogeny of natural barytes corresponds, in considerable detail, to the experimental observations made here and strongly suggests that similarly high supersaturations have prevailed in nature. This correspondence indicates that the technique of crystal growth in a porous silica gel medium provides a good experimental model of studying natural growth processes.

KEYWORDS: baryte, morphology, crystal growth.

Introduction

WITH the advent of the new techniques for the study of surface structure and chemistry (see for example Hochella and White, 1990), interest has been renewed in those aspects of the crystal morphology which reflect the conditions occurring at the crystal-solution interface during growth. These internal morphologies such as sector structures and growth banding are not necessarily related to chemical variation, but may depend on the difference in surface texture or defect density induced by the growth mechanism. Even when a crystal appears, by optical microscopy, to be homogeneous this does not guarantee that it has grown under steady state conditions. Inhomogeneities may be revealed when special techniques such as cathodoluminescence, X-ray topography, and Nomarski interference microscopy are applied. By analysing morphological aspects of internal inhomogeneities, infor-

mation relating to the ontogeny of crystals can be deduced.

The effect of growth parameters on the morphology of crystals is complex in natural systems. There have been many attempts at correlating the habit of a particular mineral individual with its growth conditions (crystallisation stages, growth temperatures, composition of the growth medium, etc.). Representative works are those collected by Grigoriev (1965) and Sunagawa (1987). However, in all of these cases the observations were obviously made long after the crystal had ceased to grow, that is to say, in 'post mortem' conditions. An observation 'in vivo', by following the actual growth history under controlled conditions may therefore improve our knowledge of processes that operate in nature.

In any experiment which aims to simulate natural processes, it is necessary to establish that the growth conditions are comparable. In this paper, our aim is to demonstrate that crystal

growth of baryte in a porous silica gel medium reproduces the detailed growth features described in a natural sample.

In this experimental technique, well known to crystal growers, a column of silica gel acts as the transport medium through which the controlled double diffusion of the reacting ions (in this case Ba^{2+} and SO_4^{2-}) takes place. In a previous paper (Prieto *et al.*, 1990) we established that crystal growth in such a medium is initiated at a specific threshold supersaturation which depends on the rate at which the supersaturation changes in the system. Since the supersaturation changes continuously in space and time, the experiments must be described by specifying first the starting boundary conditions, i.e. the concentrations of the starting solutions, and second the subsequent evolution of the system, i.e. the succession in time of the physicochemical conditions everywhere in the system. The growth process must therefore be referred to in terms of the sequence of growth mechanisms and their morphogenetical influence (Garcia-Ruiz, 1986). One can expect an evolution from instability to equilibrium as growth and diffusion proceeds, during which the morphology of the crystal can be monitored because of the transparency of the gel.

This experimental technique can readily be modified to study other geologically relevant features such as compositional zoning during the growth of solid solutions, a topic discussed in a subsequent paper. In this paper we relate the ontogenetic development of synthetic baryte crystals to the interpretation of those observed in nature.

Growth of baryte crystals in a silica gel medium

Crystal growth in gels is in fact solution growth, although nucleation and growth conditions are quite different from those in conventional solution growth methods. In a gel the solution is trapped into the pores of the polymer network and remains stagnant. The gel medium allows only mass transfer by diffusion, by suppressing convection and advection.

Experiments on the growth of baryte crystals were carried out in a double diffusion system as shown in Fig. 1. This is a typical U-tube arrangement in which reservoirs of two reagents are separated by a column of polymerised silica gel. The gel behaves as a porous medium allowing counter diffusion of the reagents, which eventually meet in the gel column where precipitation occurs. The transport properties of the gel can be controlled by its method of preparation, the usual procedure involving acidification of sodium sili-

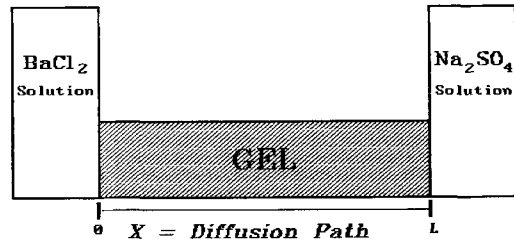


Fig. 1. Schematic representation of the experimental U-tube arrangement for crystal growth.

cate (Na_2SiO_3) solution to the desired pH, before pouring it into the U-tube where it polymerizes to a solid hydrogel (Henisch, 1989). The two reagents (BaCl_2 and Na_2SO_4 solutions in this case) are then poured into each reservoir and they begin to diffuse through the gel column. After several days, BaSO_4 precipitates in a narrow zone near the centre of the column.

Since at the start the reagent concentration throughout the gel column is always zero, the physicochemical evolution of the system may be modified by using mother solutions with different initial concentration or by using gel columns with different lengths.

Although the experimental arrangement is simple, a further analysis of the development of concentration gradients and hence the evolution of supersaturation is needed to be able to extract quantitative results. Supersaturation (β) is the parameter that reflects the deviation of a system from equilibrium. Accordingly, the first stage at studying the evolution of growth conditions is to calculate the supersaturation throughout the gel column for different diffusion times. In the case of baryte, the supersaturation can be written as follows

$$\beta = \frac{a(\text{Ba}^{2+}) \cdot a(\text{SO}_4^{2-})}{K_{\text{sp}}}$$

where $a(\text{Ba}^{2+})$ and $a(\text{SO}_4^{2-})$ are the activities of the free ions and K_{sp} is the thermodynamic solubility product. Both the experimental path to obtain concentration profiles and the procedure of calculation of β have been extensively described in previous papers (Prieto *et al.*, 1989; 1990), so they are not considered here.

The supersaturation value at a particular point of the column changes continuously with diffusion time. Consequently, one can find a fitting function $\beta(t)$ that reflects the sequence of experimental values of supersaturation. Fig. 2 shows a map of supersaturation isolines in the space $x-t$. From this map, supersaturation profiles throughout the

gel column at a particular time, may be calculated. In the same way, one can obtain supersaturation profiles as a function of time, at a particular location.

The $\beta(t)$ functions allow one to define an evolutionary parameter, the supersaturation rate ($R\beta$) that describes the speed at which the system is moving away from the equilibrium. The supersaturation rate is given by:

$$R\beta = \delta\beta/\delta t$$

Therefore, values of $R\beta$ at a particular time and location may be obtained from the derivative of the $\beta(t)$ function.

This parameter has been shown to have an important bearing on the nucleation behaviour in this kind of system (Prieto *et al.*, 1991). The supersaturation rate controls the supersaturation threshold (β_{th}) at the nucleation time and the level at which the supersaturation is maintained after nucleation, and consequently the morphological evolution of the crystals.

Table 1 shows the conditions at the moment of nucleation for the experiments reported here. The influence of the evolutionary history of the system in the nucleation event is clear from the previous paper (Prieto *et al.*, 1990). The departure from equilibrium at the nucleation time depends on $R\beta$. The results show that the metastability level as well as the nucleation density depends on supersaturation rate. At any rate the supersaturation is rather high in all cases, which is expected for media with limited particle mobility and for weakly soluble substances. Both cooperating effects help the metastability and

consequently increase the supersaturation threshold.

After nucleation the precipitation region becomes a solute sink and the supersaturation decreases locally as growth proceeds. Therefore, one can expect an evolution of the growth behaviour towards mechanisms corresponding to progressively lower supersaturations, always depending on the balance between the local consumption of solute and the supersaturation rate in the bulk. So, the supersaturation rate also controls the evolution of sizes and shapes along the growth process.

Theoretical habit and final polyhedral growth forms

One of the goals of experimental mineralogy is to describe the kinetics and mechanisms of processes with respect to the degree of departure from equilibrium. In an experiment involving precipitation, equilibrium is clearly not attained, even in the relatively slow growth conditions in a gel. In fact, the thermodynamically stable final state of precipitation reaction would be a perfect single crystal, since the free enthalpy, and in particular the surface free enthalpy, is then at a minimum. Such a single crystal would be moreover bounded by a surface which fulfills the condition that $\Sigma A_i \gamma_i$ is a minimum, where A_i and γ_i are the surface area and the interfacial free energy of the i -th facet. This condition defines therefore the equilibrium form of the crystal. It is well known however that this state is never reached in a precipitation process, the product of which is always a large number of crystals of different sizes having greater or smaller number of defects.

In natural systems growth also stops before the system reaches equilibrium and the processes of growth-redissolution that lead to a thermodynamically more stable state, i.e. to larger, less imperfect crystals, are known as Ostwald ripening (Morse and Casey, 1988). Ripening involves changes in both crystal size distribution and crystal morphology. Thus the observed habits are growth forms which represent transitional states. This is also the case in the present experiments. During the early stages the growth process occurs very far from equilibrium, in the instability region, and only after further growth polyhedra appear. The experiments were stopped before the system reached either equilibrium or homogeneity, and consequently Ostwald ripening phenomena were not allowed to occur. Therefore the so-called final polyhedral growth forms represent a transitional, yet stranded metastable state.

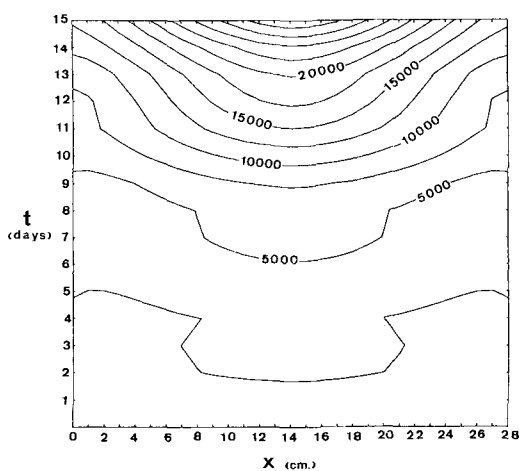


FIG. 2. Supersaturation isolines in the space $x-t$ (Location-Time). Mother solutions: BaCl_2 0.5 M and Na_2SO_4 0.5 M. Gel column length 28 cm.

TABLE 1

Supersaturation and supersaturation rate at the nucleation time.

(Experiments listed in increasing values of the supersaturation rate, $R\beta$)

$R\beta$ (l/hour)	START CONCENTRATIONS BaCl ₂ - Na ₂ SO ₄	COLUMN LENGTH (cm.)	NUCLEATION TIME (hours)	β_{th}	EVOLUTION
566	0.5 M - 0.5 M	12	55	92397	Y
153	0.3 M - 0.3 M	12	80	19729	Y
149	0.5 M - 0.5 M	20	125	16891	Y
115	0.5 M - 0.5 M	28	360	11663	Y
33	0.3 M - 0.3 M	20	220	6701	Y
22	0.1 M - 0.1 M	12	130	3808	Y
20	0.3 M - 0.3 M	28	480	5730	Y
8	0.1 M - 0.1 M	20	280	3560	N
7	0.1 M - 0.1 M	28	570	3351	N

In such a situation we must distinguish between equilibrium form and growth form. There is only one equilibrium form for a given thermodynamic condition, whereas there are many growth forms. The growth morphology of a polyhedral crystal is determined by the relative normal growth rates of faces which appear on the crystal during the growth process. The faces with slower normal rates remain on the crystal, and those with higher growth rates disappear as growth proceeds. The habit of a polyhedral crystal is therefore dependent on growth conditions, as well as on the crystal structure. Attempting to determine the influence of the internal structure on crystal morphology, neglecting growth conditions, is however useful because, if this influence is accounted for, it is possible to make inferences about the external factors which were operative during growth and determined actual morphologies.

One way of deriving the theoretical habit of a crystal is based on the PERIODIC BOND CHAIN theory (Hartman and Perdok, 1955a, b, c) and further more recent treatments (Hartman, 1987). In this approach growth rates are determined by the properties (geometry and bond strengths) of the ideal structure. Here we review these ideas and model the growth morphology of baryte crystals.

Baryte is one of the original examples given by Hartman and Perdok (1955c) for the PBC method. They identified the periodic chains of strong bonds in the baryte structure and the F (flat) faces which contain two or more PBCs. Only the F faces can grow according to a layer mechanism and therefore they have relatively small growth rates and so are habit determining. S (stepped) or K (kinked) faces containing one or

no PBCs, develop into small faces or disappear entirely. The location of the PBCs defines the surface of the F-faces and the elementary growth layers (slices). Table 2 shows the F forms of baryte as calculated in this former Hartman paper. F faces are ranked relative to each other by calculating the attachment energy (E_{att}) which is the energy per mol released when a new slice is added on the crystal face. In this case, the attachment energies were calculated using a broken bond model in which interactions of the second and higher coordination spheres were neglected. It was assumed that the sulphate ion can be represented as a point charge, and formal valences were used.

The calculation of the attachment energies leads to a theoretical habit if the growth rate of the F faces is taken to be proportional to E_{att} (Hartman and Bennema, 1980). The theoretical habit corresponding to the broken model of E_{att} is represented in Fig. 3a. The crystal drawing has been constructed using the program SHAPE (Dowty, 1980). One can observe that only {001}, {210}, {101}, {010} and {211} appear in the theoretical habit.

Although Hartmann and Perdok originally classified the form {011} as an F form, they computed the high attachment energy value 0.945, and subsequently reclassified it as a K form. However later papers (Dowty, 1976; Tassoni *et al.*, 1978) disagreed on the {011} form, which was classified as a true F form. In fact, Seager (1959) developed a method of determining the statistical morphology of natural crystals, which for the baryte group, shows that {001} is one of the dominant forms, together with {001}, {210} and {101}. The theoretical habit using Dowty's values of E_{att} are shown in Fig. 3b.

Dowty's calculations reveal that Hartman and Perdok did not compute the attachment energy of the {011} form across a 'surface of least bonding'. The attachment energy across the surface of least bonding is 0.53, which is not particularly anomalous.

Hartman and Strom (1989) reconsider the earlier work in the light of recent developments. The growth of an F face occurs in slices with thickness d_{hkl} , the interplanar spacing, taking into account submultiples due to lattice centering or to screw axes or glide planes perpendicular to the face. The application of the PBC theory often leads to an unequivocal determination of the atomic structure of such an elementary growth layer. The surface thus obtained has the lowest specific surface energy of all the conceivable surface structures. Sometimes, however, the determination of the slice structure is ambiguous, giving more than one possibility. In that case a more detailed analysis is needed to decide the growth mechanism (Hartman and Heijnen, 1983).

Following Hartman and Strom, a computerised PBC analysis of the baryte structure leads to eight F forms. Of these F forms only {002}, {210}, {211}, {020} and {201} are uniquely defined. The F forms {101} and {200} occur in two different surface configurations, while for {011} the computer program developed 33 different slices that can be classified in three kinds (a, b and c). In

this case the attachment energies and the specific surface energies were calculated in a electrostatic point charge model based on the Madelung's method. These energies depend on the charge distribution in the sulphate ion, but one can assume that q_o , the charge on the oxygen atom, has a value between -0.74 and -1.00 . Values of E_{att} and Γ as computed by Hartman and Strom for $q_o = -1$ are shown in Table 2.

The theoretical habit using these last E_{att} values is displayed in Fig. 3c. Because (011), (101) and (200) faces have more than one slice it is assumed that always the configuration with lower surface energy is present. The thermodynamic equilibrium form, determined by the minimum of the total specific surface free energies, differs from the growth form. From Γ data in Table 2 one can expect {020} and {211} to become more important in the equilibrium form, while {101} is much smaller. This is made clear in Fig. 3d where the central distance of the F faces is put proportional to Γ .

However, the theoretical habit as shown in Fig. 3c needs some discussion in relation with the growth behaviour of the non-uniquely defined F-forms:

(i) The two slices (101)a and (101)b are at different levels, creating a step of a fractional height of d_{202} that has also the character of an F face slice. The slices a and b have different surface energies and according to Hartman and Heijnen

TABLE 2
Attachment energies of F-faces

Broken bond model (Hartman & Perdok, 1955c)		Electrostatic point charge model (Hartman & Strom, 1989) ($q_o = -1$)		
Face	Attachment energy per ion in $4e^2 \cdot \text{\AA}$	Face	E_{att} (kJ/mol)	Γ (mJ/m ²)
(0 0 1)	0.388	(0 0 2)	267.4	922
(2 1 0)	0.396	(2 1 0)	298.3	964
(1 0 1)	0.435	(1 0 1) a	251.2	1297
(2 1 1)	0.472	(1 0 1) b	341.7	1777
(1 0 0)	0.521	(2 0 0) a.	379.9	1676
(0 1 0)	0.557	(2 0 0) b	385.41	164
(0 1 1) K	0.945	(2 1 1)	396.8	1083
Least bonding surface (Dowty, 1976)		(0 1 1) a	414.3	1822
(0 0 1)	0.39	(0 1 1) b	480.2	2078
(2 1 0)	0.39	(0 1 1) c	452.8	1974
(1 0 1)	0.43	(0 2 0)	516.7	1170
(2 1 1)	0.47	(2 0 1)	601.4	1947
(1 0 0)	0.51			
(0 1 1)	0.53			
(0 1 0)	0.55			

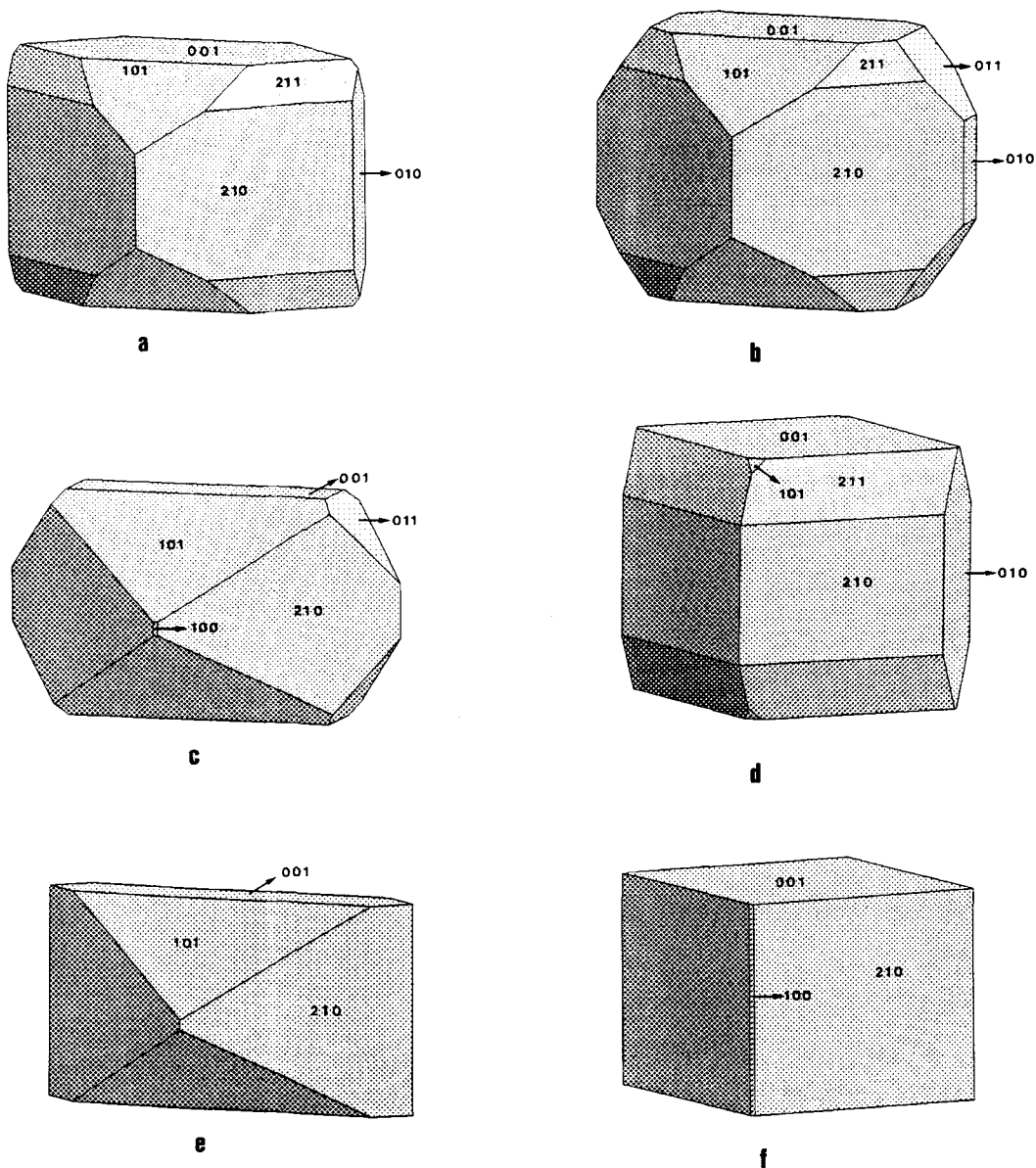


FIG. 3. Theoretical habits of baryte crystals. (a) Broken bond model (Hartman and Perdok, 1955c). (b) Dowty's calculation (1976) (Surface of least bonding). (c) Electrostatic point charge model (Hartman and Strom, 1989). (d) Plot of central distance of the F-faces proportional to G . (e, f) Hypothetical habits for low and moderately high supersaturation.

(1983), the face is expected to grow in layers d_{101} a. The (101) faces can grow by two-dimensional nucleation of d_{202} slices only when the supersaturation exceeds a critical value.

(ii) In the case of the {100} forms, the surfaces (200)a and b have about the same specific surface

energies and the fractional step d_{400} has a S character, involving the presence of a PBC in one direction only. Therefore, the layers d_{400} do not spread because lateral strong bonds are not present in two dimensions. Growth must occur in a 'domain mode', that is, by layers (200)a and

(200)b forming different domains on the face. The domain boundary is a non-moving fractional step of height d_{400} . The fractional step acts as a preferred site for two dimensional nucleation, which increases the growth rate and consequently decreases the morphological importance of this face. On final growth forms {100} faces are only expected to occur at moderately high supersaturations.

(iii) Finally, with regard to the {011} faces, because of the large number of possible configurations of these surfaces, the growth behaviour can be considered as that of a K face and it should not occur on the growth form. Only at high supersaturations or in presence of impurities a habit change might occur such that {011} becomes a major form. The form {011} becomes a major form. The form {011} is however a common form on natural baryte, and is the statistically dominant form on the isostructural celestine (Seager, 1959).

On the basis of above assumptions Fig. 3e and Fig. 3f display the hypothetical habits for low and moderately high supersaturations. At low supersaturation the growth shows {210}, {101} and {002} forms. At higher supersaturations however {101} can grow by d_{202} layers ($E_{att} = 567.7$ kJ/mol for $q_0 = -1$) and the theoretical habit becomes {210} and {002} with a minor {200} form.

The final habit of baryte single crystals grown in silica gel is a combination of {001}, {210} and {100} (Fig. 4), although this last form may be absent. In fact, the statistical importance of the {100} faces depends on the initial concentrations of the mother solutions, that is to say, on the supersaturation rate of the system. High supersaturation rates increase the importance of the {100} form. Therefore, by comparing these crystals with the theoretical habits, one can observe a complete agreement with 3f, which can

be interpreted by the maintenance of a moderately high supersaturation level during the final stage of the growth.

Form evolution during the growth of natural and gel grown baryte crystals

Crystal growth in nature is not a monotonous process. On the contrary, the external factors which influence mineral formation change during growth and therefore the chemical composition of the mineral individual or its form may evolve. For instance, during the growth, changes may occur in the relative development of the faces of various crystallographic forms, and one form may be replaced by another. The decisive reason of this evolution cannot always be attributed to one particular factor, but some general trends may be elucidated. In fact, many growth histories may be satisfactorily explained exclusively by the temporal decrease in the supersaturation of the solution in which crystallisation takes place.

This general tendency is observed in the crystallisation of baryte crystals in various environments (Grigoriev, 1965). Seager and Davidson (1952) studied the growth history of natural barytes from Westmorland and Durham by considering the internal morphologies (colour and fluorescent zoning) of the crystals. From Fig. 5 one can observe that the initial importance of the {011} form decreases during growth. A predominant development of the {210} form follows and crystals become more tabular parallel to {001}, in analogy with Fig. 4. According to the PBC analysis, this evolution may be explained by a decreasing supersaturation: the growth behaviour of the {011} faces can be considered as that of a K-Face and it should only occur on the growth form at high supersaturations. At low supersaturation {210}, {101} and {002} become the major forms.

It may be observed in Fig. 5 that fine serrations appear inside the crystal. These are bounded vertically by {210} and develop on faces and edges of the previous forms. Following Seager and Davidson, the morphological result of this kind of growth is the very rapid elimination of a particular form and the development of a new habit by further growth and coalescence of the 'teeth'. These authors also described some details about the formation of two zones, so-called 'candle flames', at the lateral [010] extremities. These morphologies are the internal 'witness' of the {210} developing and the {011} vanishing in the final growth stages.

As we discuss below, a decrease in supersaturation also explains the growth history of gel

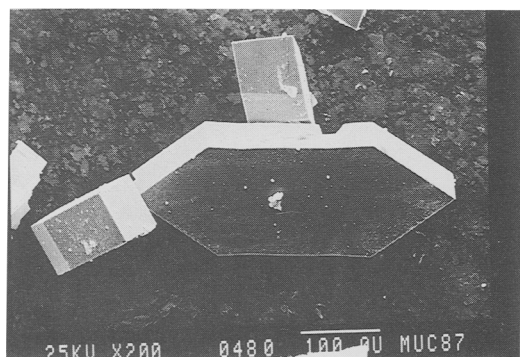


FIG. 4. Final habit of baryte single crystals grown in silica gel.

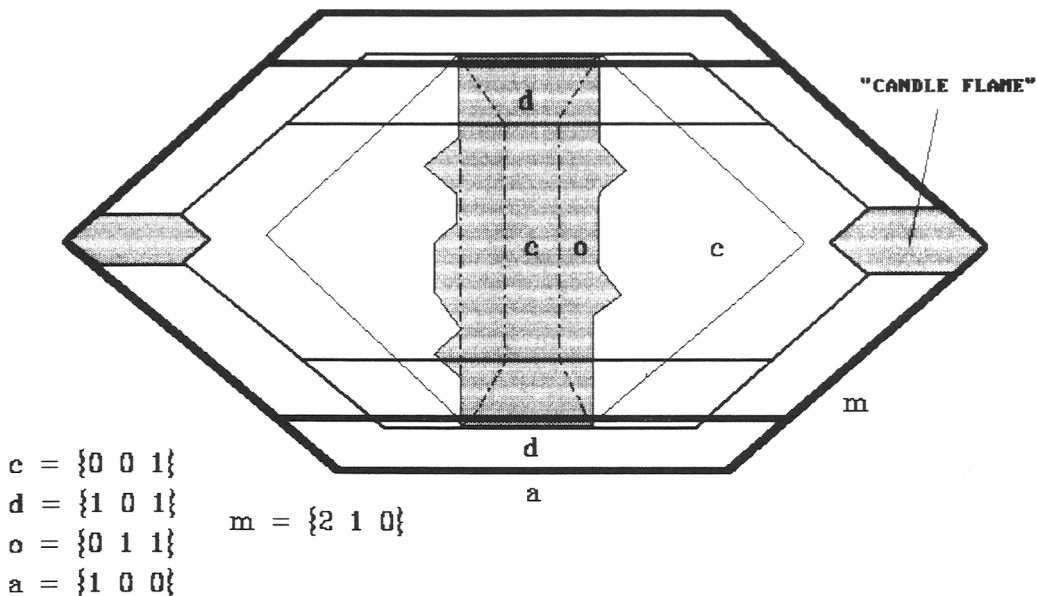


FIG. 5. Internal morphologies in baryte crystals from Westmorland (after Seager and Davidson, 1952).

grown baryte crystals. In the early stages of growth rounded and dendritic morphologies arise. Crystals develop four parallel side-branches forming 'bowtie-like somatoids' (Fig. 6a) or 'pincers-like somatoids' (Fig. 6b). From an initially more isometric and rounded shape the branches begin to grow in a poorly defined direction, around [111], but then they turn and protude along the [010] direction. The growth layers and macrosteps begin to appear.

After further growth the crystals become more faceted and they show skeletal growth as in Fig. 7. The growth continues by filling the skeletal morphologies and finally a polyhedral ($\{001\}$, $\{210\}$ and $\{100\}$) morphology develops. Fig. 9 displays this evolution. In the final stages, two re-entrant angles usually remain at the [010] extremities. These inclusions are like 'flames' in shape and are reminiscent of the 'candle flames' described by Seager and Davidson. In the same way, one can relate the side-branches along [010] with the serrations in Fig. 5.

Growth mechanisms and growth history

The observations described above can be related to changes in the growth mechanism during growth. The growth rate and the growth mechanism of a crystal interface are determined by the interface roughness. If an interface is

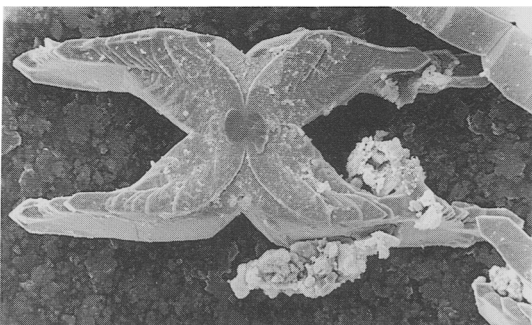
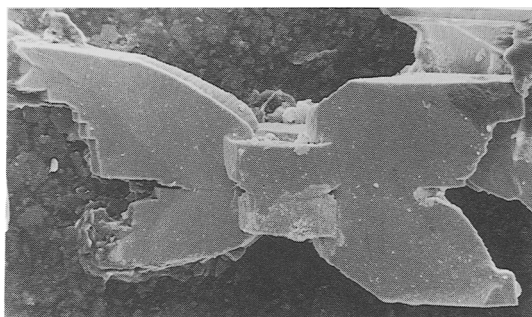


FIG. 6. (a, top) 'Bowtie-like' somatoids. (b, bottom) 'Pincer-like' somatoids. The crystals are ~0.6 mm in length.

atomically rough, the growth surface might be covered by very large numbers of steps and kinks. In this case growth occurs by direct incorporation of the growth units to the crystal surface, and one can speak of an adhesive or 'continuous growth' mechanism. However if an interface is smooth the growth occurs layer by layer, and sources of growth sites (kinks and steps) are required to maintain growth. In the case of the two-dimensional nucleation mechanism of growth, such sources are two dimensional nuclei, that form and spread on the surface. At low supersaturations the screw dislocations are an alternative source of growth steps, leading to the so-called spiral growth mechanism.

The growth by two-dimensional nucleation occurs only above a certain critical value of supersaturation, since it needs to overcome an energy barrier to form two-dimensional nuclei, whereas for the spiral mechanism there is no such energy barrier. On the other hand, at low temperatures, below the roughening thermodynamic transition temperature, a kinetically rough interface appears when one employs high supersaturations. At high supersaturations many two-dimensional or three-dimensional nuclei cover the whole growing surface, which results in the kinetic roughening of the interface. Therefore, following Sunagawa (1981) one may notice the existence of two transitional values of supersaturation β^* and β^{**} where the growth mechanism and the growth rate law change.

Above β^{**} the solid-solid interface is rough and adhesive type growth occurs. Crystals are bounded by rounded morphologies without smooth surfaces. Under these conditions the transport processes are the rate determining factor rather than the surface integration pro-

cesses: the overall growth rate is governed by the diffusion of the solute from the solution bulk to the crystal interface, through the so-called 'concentration boundary layer'. The interface becomes unstable due to preferred growth at the edges and corners and the crystal tends to protrude into the higher supersaturated region. This kind of morphological instability is due to non-uniformity of supersaturation over the interface. Therefore β^{**} is the onset of an instability of a polyhedral crystal and gives rise to a dendritic morphology at later stages. The value of β^{**} depends on the crystal size, which means that the transition from unstable to polyhedral growth may be ascribed to the decrease of the solution bulk supersaturation, but also to the increase of crystal size (Kuroda *et al.*, 1987), even though β remained constant during the growth period.

The transport properties of the medium also affect the morphological stability. The degree of supersaturation inhomogeneity on a surface is proportional to the normal gradient of concentration of growth units. As a consequence, natural convection as well as artificial stirring reduces the thickness of the concentration boundary layer, and the non-uniformity over the surface increases. Therefore, flow in the ambient phase tends to make polyhedral growth unstable.

When gel growth is compared with solution growth from free solutions one of the main differences is caused by the degree of supersaturation. In a previous work (Prieto *et al.*, 1990) we have reported the high metastability level before the nucleation begins. Table 1 shows the supersaturation threshold after which the nucleation begins. Such a supersaturation level in a free

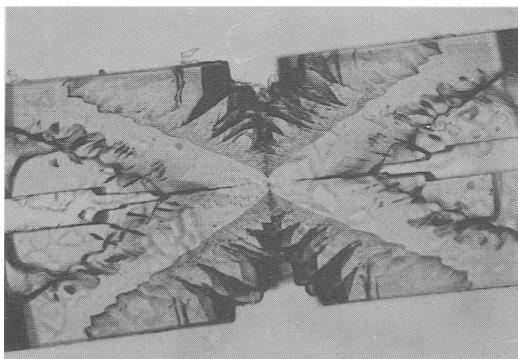


FIG. 7. Skeletal growth. The crystal is ~ 0.6 mm in length.

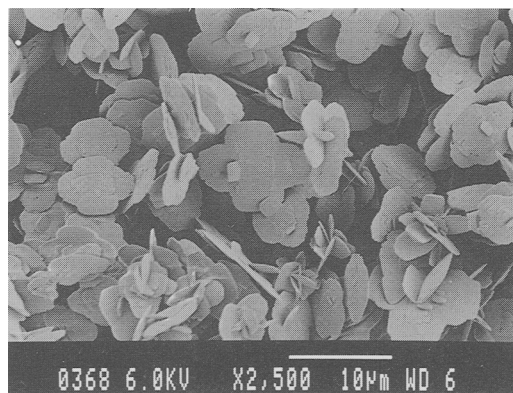


FIG. 8. Growth morphology of baryte crystals from a free solution. Mother solutions: BaCl_2 0.3 M and Na_2SO_4 0.3 M.

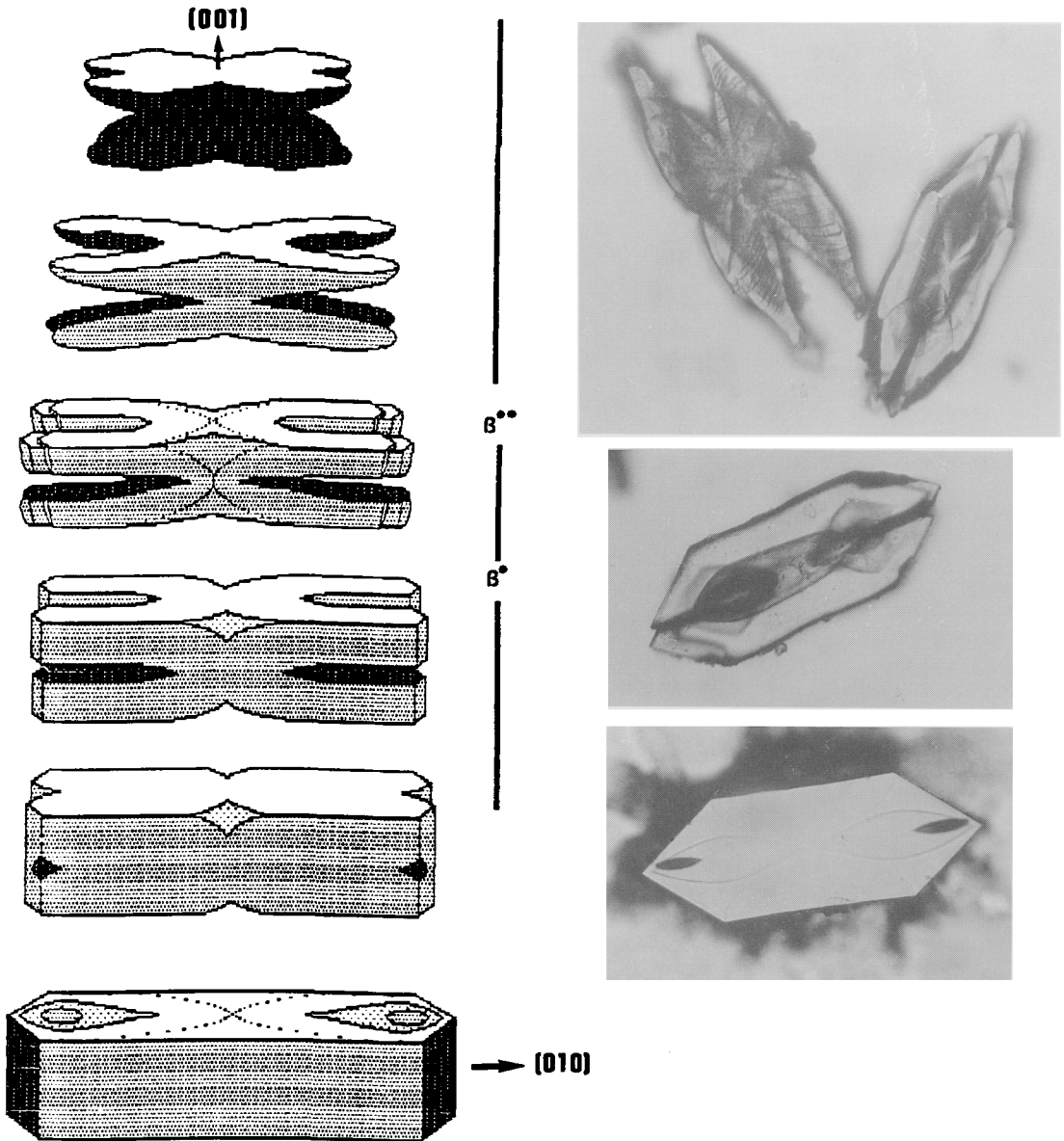


FIG. 9. Morphological evolution of baryte crystals from unstable to stable growth.

solution involves a catastrophic nucleation and consequently a high density of crystalline individuals. These crystals never become larger because the supersaturation quickly diminishes as soon as the nucleation occurs. The fact that larger crystals are grown in a gel proves that the supersaturation near the surface of these crystals remains high because the gel is very effective at suppressing nucleation.

As a consequence of the high supersaturation

level at the nucleation time, the early growth stages of the baryte crystals take place in the instability region, and a dendritic array would be expected to arise. In this way we can interpret the 'somatoid' morphologies as described above. It is likely that the formation of serrations in Seager and Davidson's specimens may be attributed to unstable growth. The growth in the instability region continues until both the decrease of the supersaturation and the increase of the crystal

size, moves the crystal beyond the instability limit. The final size when this transition occurs depends on the supersaturation rate and hence on the start boundary conditions. In fact for low values of the supersaturation rate the crystal growth begins as polyhedra. This is shown in Table 1, where the experiments in which morphological evolution from unstable to polyhedral growth occurs are labelled Y, and those in which growth begins as polyhedra are labelled N.

At this point, let us make some comparisons with growth from free solutions. Unlike the above, growth of baryte crystals by direct mixing of mother solutions leads to unstable morphologies, even at lower supersaturations than that of Table 1 (Fig. 8). The explanation is the smaller size of individuals and the much smaller thickness of concentration boundary layer in a free solution. In this case the system is closed and no new reactant quantities arrive to it. So, the growth stops soon after nucleation. Even if new quantities of reagents are added to the solution, the earlier crystals do not grow, but new nuclei are formed.

After further growth the supersaturation decreases as a consequence of both the growth of the crystals and the decrease of the supersaturation rates as the diffusion time. So, below β^{**} the crystals show skeletal growth with flat facets. The growth continues by filling the skeletal crystal until the final polyhedral growth form is attained, below β^* . This evolution from unstable to stable growth as supersaturation decreases is displayed in Fig. 9, which also shows the hypothetical position of β^* and β^{**} in relation to the morphological sequence.

Conclusion

In this paper we have established that the ontogeny of experimentally grown baryte crystals is consistent with predicted growth in a system with decreasing supersaturation. Even though a final polyhedral growth form is achieved, it does not correspond to an equilibrium state but can be related to a theoretically determined habit associated with the maintenance of a moderately high supersaturation level, even in the final stages. The high levels of initial supersaturation required to grow the 'bow-tie' morphology have been quantified. The correspondence, in considerable detail, of the experimental ontogeny with that described in natural baryte strongly suggests that this experimental technique may be able to reproduce natural growth processes. Furthermore, the implication is that the natural barytes have grown at high to moderate supersaturations. A conse-

quence of this is that any attempt to relate growth features of natural baryte-celestine, such as compositional zoning, etc. to equilibrium phenomena such as miscibility gaps is unlikely to be justifiable.

References

- Dowty, E. (1976) Crystal structure and crystal growth: I. The influence of internal structure on morphology. *Amer. Mineral.*, **61**, 448–59.
- (1980). Computing and drawing crystal shapes. *Ibid.*, **65**, 465–71.
- Garcia-Ruiz, J. M. (1986) Growth history of PbS single crystals at room temperature. *J. Crystal Growth*, **75**, 441–53.
- Grigoriev, D. P. (1965) *Ontogeny of Minerals*. Israel Program for Scientific Translations, Jerusalem.
- Hartman, P. (1987). Modern PBC theory. In *Morphology of crystals* (I. Sunagawa ed.). Terra Scientific Publishing Company, Tokyo, 269–319.
- and Bennema, P. (1980). The attachment energy as habit controlling factor. *J. Crystal Growth*, **49**, 145–56.
- and Heijnen, W. M. M. (1983). Growth mechanism of a crystal face for which more than one surface structure is possible. *Ibid.*, **63**, 261–4.
- and Perdok, W. G. (1955a). On the relations between structure and morphology of crystals. I. *Acta Cryst.*, **8**, 49–52.
- (1955b). On the relations between structure and morphology of crystals. II. *Ibid.*, **8**, 521–524.
- (1955c) On the relations between structure and morphology of crystals. III. *Ibid.*, **8**, 525–9.
- and Strom, C. S. (1989) Structural morphology of crystals with the baryte (BaSO_4) structure: a revision and extension. *J. Crystal Growth*, **97**, 502–12.
- Henisch, H. K. (1989) *Crystals in gels and Liesegang's rings*. Cambridge University Press.
- Hochella, M. F. and White, A. F. (eds.) (1990) Mineral-water interface geochemistry. *Reviews in Mineralogy*, **23**. Mineralogical Society of America.
- Kuroda, J. W., Irisawa, T. and Ookawa, P. (1987) Transition from polyhedral to dendritic morphology. In *Morphology of crystals* (I. Sunagawa, ed.). Terra Scientific Publishing Company, Tokyo, 269–319.
- Morse, J. W. and Casey, W. H. (1988) Ostwald processes and mineral paragenesis in sediments. *Amer. J. Sci.*, **288**, 537–60.
- Prieto, M., Fernandez-Diaz, L., and Lopez-Andres, S. (1989) Supersaturation evolution and first precipitate location in crystal growth in gels: application to barium and strontium carbonates. *J. Crystal Growth*, **98**, 447–60.
- Putnis, A., and Fernandez-Diaz, L. (1990) Factors controlling the kinetics of crystallisation: Supersaturation evolution in a porous medium. Application to baryte crystallisation. *Geol. Mag.*, **127**, 485–95.
- Fernandez-Diaz, L., and Lopez-Andres, S. (1991) Spatial and evolutionary aspects of nucleation in diffusing-reacting systems. *J. Crystal Growth*, **108**, 770–8.

- Seager, A. F. (1959) The morphology of the baryte group. *Mineral. Mag.*, **32**, 63–86.
- and Davidson, W. F. (1952). Changes in habit during the growth of baryte crystals from the north of England. *Ibid.*, **29**, 885–94.
- Sunagawa, I. (1981) Characteristics of crystal growth in nature as seen from the morphology of mineral crystals. *Bull. Mineral.*, **104**, 81–7.
- (1987) Morphology of minerals. In *Morphology of crystals* (I. Sunagawa, ed.). Terra Scientific Publishing Company, Tokyo, 507–87.
- Tassoni, D., Riquet, J. P., and Durand, F. (1978) Recherche des chaines periodiques de liaisons par ordinateur. *Acta Cryst.*, **A34**, 55–60.

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