Journal of Crystal Growth 73 (1985) 251–262
North-Holland, Amsterdam

ON THE FORMATION OF INDUCED MORPHOLOGY CRYSTAL AGGREGATES

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Received 29 March 1985

A general explanation of induced morphology crystal aggregates of $BaCO_3$, $SrCO_3$ and $CaCO_3$ grown in silica gel is described. The matrix surrounding the crystallites is shown to be formed by a metal carbonate silicate membrane, with diverse degree of two-dimensional order. The existence of co-orientation between the three-dimensional crystallites forming the aggregate has been demonstrated, suggesting that epitaxial relations exist between them and the surrounding membrane which acts as a template. The degree of order of the particles forming the membrane is a result of the local supersaturation, and is identified as the main origin of the morphological evolution in space and in time. Some mechanisms which may be active in morphogenesis are suggested.

1. Introduction

In previous papers [1–4], we described the growth and morphological properties of a new kind of composite which we call "induced morphology crystal aggregates" (IMCA). Like other types of crystal aggregates, they are composed of an ill-defined number of three-dimensional (3D) crystallites, but in IMCA, by way of contrast, the growth and morphological properties as a whole are not governed by crystal to crystal relationships. These properties are controlled by an external substrate, usually a two-dimensional (2D) membrane, which acts as the site for progressive 3D growth of the crystals which form the aggregate. This morphology presents in most cases a well-defined non-crystallographic symmetry. For instance, typical induced morphology crystal aggregates constitute the hard parts of living organisms. If we observe the ultrastructure of an invertebrate shell, it consists of a great number of 3D crystallites which are separated from each other by a thin layer of an organic matrix. At lower magnification we can observe that the crystallites are arranged in a non-random way. An ordered pattern exists and certain geometrical laws control the position of the crystals in such a way that a non-crystallographic symmetry is obtained in most cases [5]. Laboratory reproduction of such structure can shed light on biomineralization mechanisms, and could also be developed as a means of preparing appropriate materials for orthopaedic implants. Such aggregates are also of interest in conection with cement. Shell from living organisms has in fact been proposed (for instance, see ref. [6]) as a model for making stiff and tough structures in man-made sticky solids.

A laboratory procedure for obtaining such composites (specifically alkaline-earth carbonate crystals versus silicate matrix) is described below. Judged by the great variety of events observed in the precipitation of IMCA and by the complex phenomenology associated with its morphological evolution, this procedure cannot be analyzed in terms of classical crystal growth problems: it is a complicated phenomenon in which several process act together. The main purpose of this paper is to discuss the nature of the IMCA phenomenon in general by analysing the experimental results obtained to date. It is shown that this kind of IMCA is formed by a catalytic effect of the carbonate groups on the hydration of metal silicate, giving a membraneous material, with composition and order evolving as the growth progresses. Some morphogenetical mechanism which could be involved are also discussed.

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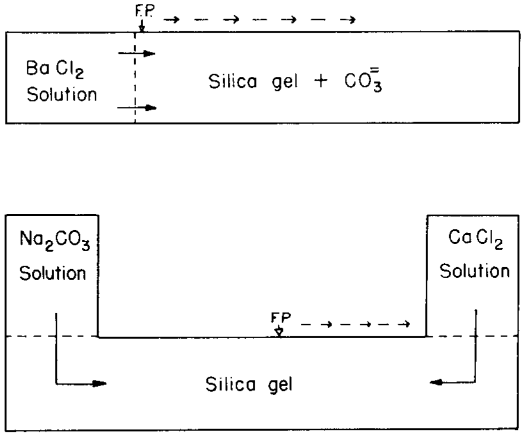

Fig. 1. Two different arrangements for the growth of induced morphology crystal aggregates. FP stands for the position of the first precipitate. Arrows indicate the advance of the precipitation front.

2. Growth procedures and characterization of IMCA

The experimental procedures used for the growth and characterization of induced morphology crystal aggregate has been described elsewhere [1–4] and therefore only the general method will be reported below.

Induced morphology crystal aggregates of alkaline-earth (Ca, Ba or Sr) carbonates can be obtained by a double decomposition reaction between two appropriate solutions counter-diffusing through a silica gel of pH between 8.5 and 10.5. The use of other gels (such as polyacrylamide, agar-agar, tetramethoxysilane, or gelatine) has been found unsuccessful [7] and the phenomenon is thus, as far as we know, closely related to the chemistry of silica gels. The gels were prepared

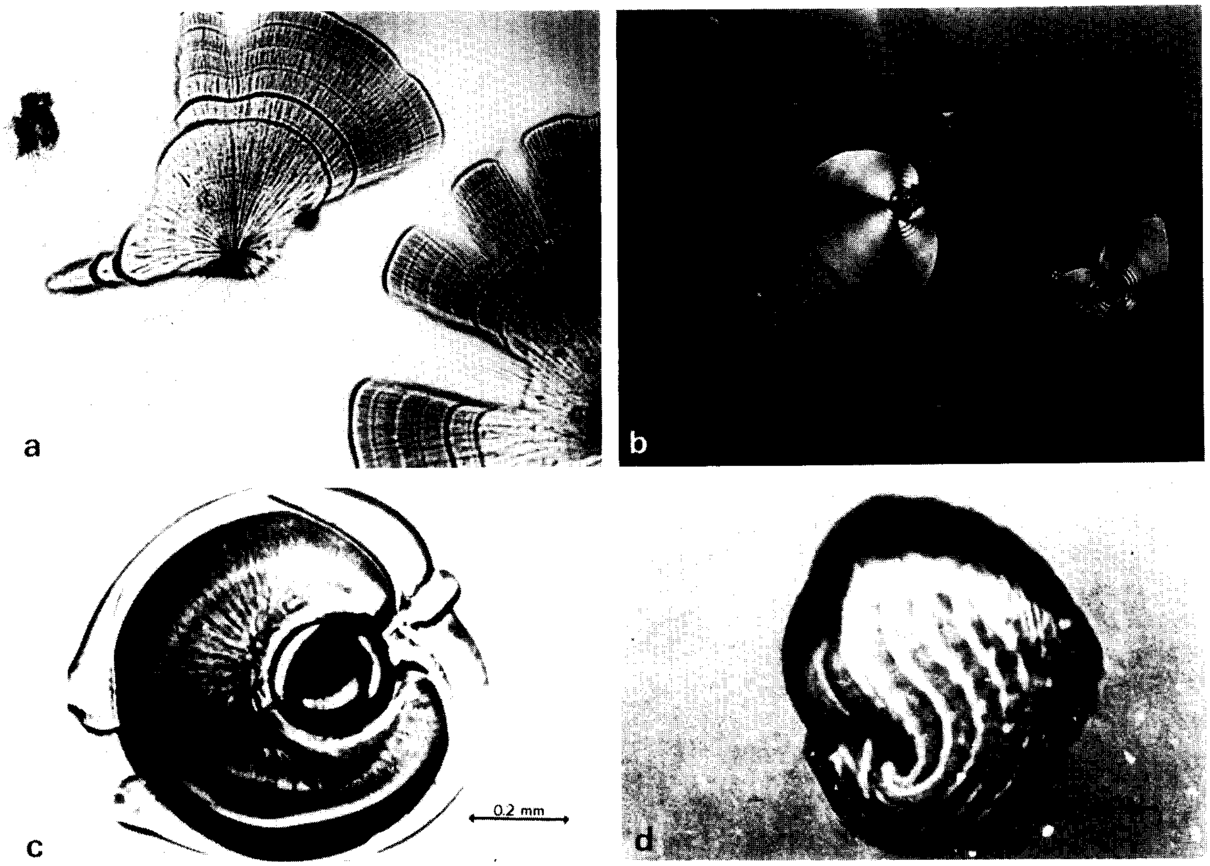

Fig. 2. Optical micrographics of some IMCA: (a) $CaCO_3$ showing growth bands; (b) foil-like $BaCO_3$ with crossed polarizers; (c) $SrCO_3$ with cycloidal pattern, (d) spiral pattern in $SrCO_3$; (a), (b) and (c) at same magnification.

by acidifying (to the desired pH) a solution of Na_2SiO_3 with a density of 1.059 g/cm^3 and initial pH = 11.2. Before gelling, the sol is placed in the horizontal part of a U-tube (fig 1a). After gelling, the two reactant solutions (the carbonate-donor and the cation-donor) are placed in the vertical branches of the U-tube, in such a way that counter-diffusion of the carbonate groups and alkaline-earth ions occurs. In another variant, a simple test tube arrangement can be used as shown in fig. 1b. In this case, the carbonate-donor salt is mixed with the sodium silicate solution before gelling. Once the gel is formed, the other reactant solution is poured on.

Depending on the specific conditions, a number of astonishing morphologies appear in the silica gel after several hours (fig. 2). A morphological evolution from the position of the first precipitate

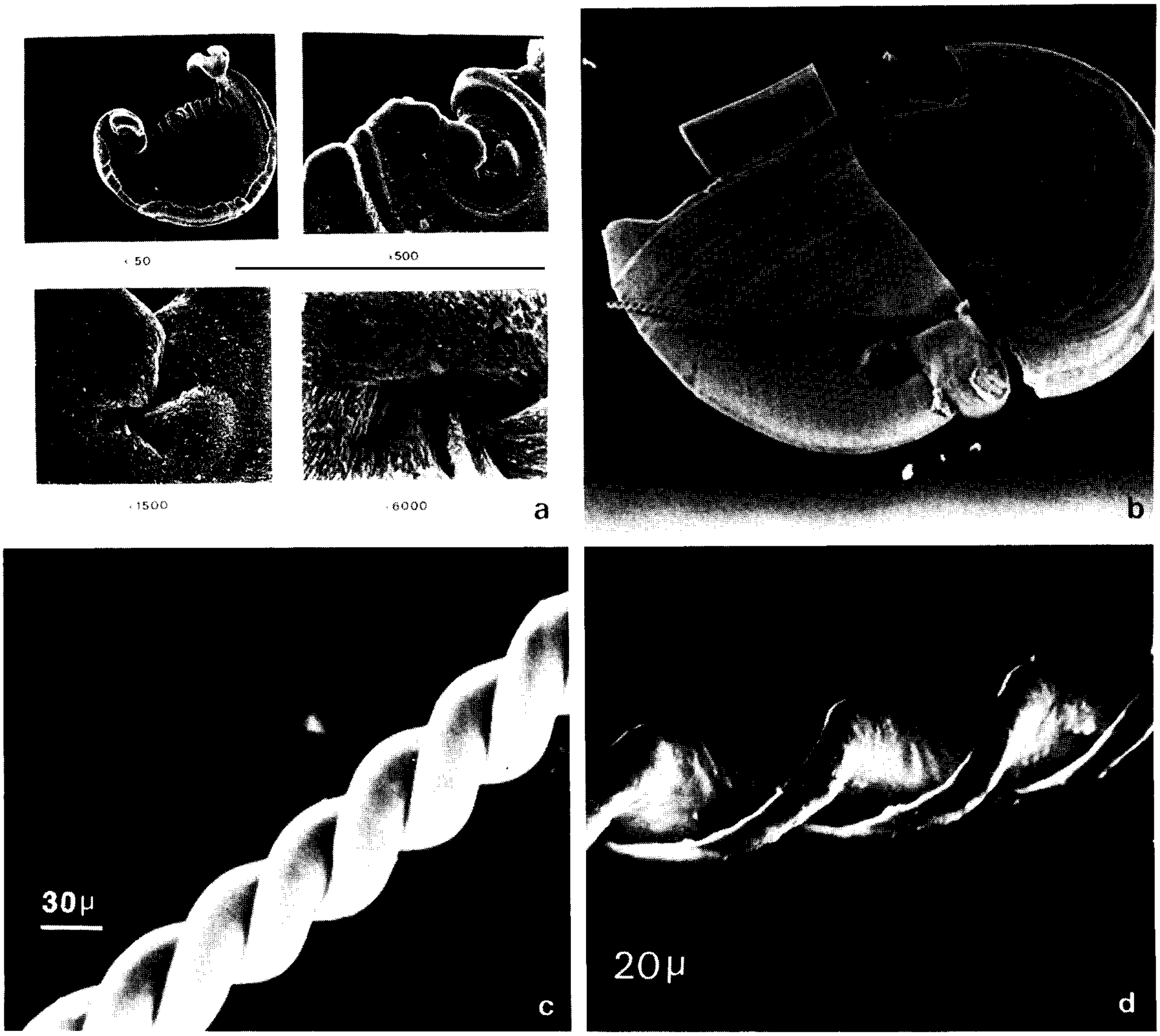

Fig. 3. SEM views of some IMCA morphologies: (a) planar aggregate with banding, showing a morphogenetical point; (b) idem with two morphogenetical points – the twisted ribbon on it does not belong to this aggregate; (c) twisted ribbon with ∞4:2 symmetry; (d) twisted ribbon with ∞2:2 symmetry.

to the last can be observed, without a solution of continuity (see fig. 8 below, and fig. 3 in ref. [4]). Moreover, each one of these morphologies evolves with time according to different patterns [8]. A distinctive and very important characteristic of these morphologies is that they present non-crystallographic symmetry. Thus, stars with a 5-fold symmetry axis, spirals and cycloidal arrangements, twisted ribbons with $\infty 2:2$ and $\infty 4:2$ symmetry, etc. can be observed under an optical microscope (fig. 3 and ref. [2]). Under crossed nicols, they present a pseudo-uniaxial dark cross, which implies the existence of an ordered arrangement of material (fig. 2b). These growths were recovered by dissolving the gel with NaOH solution. X-ray diffraction (powder method) diagrams show typical peaks belonging to $CaCO_3$ (calcite), $BaCO_3$ or $SrCO_3$, and also several broad bands, the positions of which are related to the cation used for the carbonate precipitation. A high voltage electron diffraction pattern of one of these aggregates shows typical spots of carbonate crystals, misoriented as in a polymeric pattern [3]. Thus, the coexistence of an ordered arrangement of crystallites with a non-crystallographic overall morphology allows us to infer that there is a substrate which controls the texture of the carbonate crystals, and therefore the morphology of the crystal agregate. The presence of this support was confirmed by a simple experiment. A cleaned and non-cracked aggregate was placed on a glass slide, and a drop of a HCl (0.5 N) solution was placed on it under a microscope. No modification is observed in this case. However, if the aggregate has a micro-crack the acid penetrates and the carbonate crystals are dissolved. A sequence of the carbonate dissolution stages by time laps photography is shown in refs. [1-3]. Once the carbonate is completely dissolved, a substrate of the same shape as that of the whole aggregate remains. This confirms the usefulness and validity of the induced morphology concept.

3. Discussion

3.1. On the nature of the phenomenon

The formation of IMCA can be explained on the basis of two simultaneous processes:

(a) the nucleation and growth of alkaline-earth carbonate crystals;
(b) the formation of a silicate matrix, as a result of the hydration of silicic acid (with different degrees of condensation) and metal ions.

As judged from the electron diffraction pattern, from the pseudo-uniaxial figure under crossed nicols, and from the observed morphologies, it is clear that an effective interaction between (a) and (b) must be postulated. In addition to their coincidence in time and space, there must also be some crystallographic relation between the products of (a) and (b). Unfortunately, the ultrastructure of the metal polysilicate hydrate forming the membrane is unknown at this time, and no quantitative epitaxial relations can therefore be established between the carbonate crystals and the silicate membrane. Nevertheless, the existence of such epitaxial relations can be indirectly infered. On the one hand, several investigators have observed the existence of epitaxial growth of calcium hydroxide on the surface of calcite crystals [9,10]. On the other hand, it is also well-known that, as a result of the hydration at basic pH of β-$2CaO \cdot SiO_2$ (C_2S) and $3CaO \cdot SiO_2$ (C_3S), calcium silicate hydrate (CSH) is formed [11-13]. CSH has been described as a $Ca(OH)_2$-like lamellar region with silicate material on its surfaces [14]. It follows that epitaxial relations must also exist between the carbonate crystals and the silicate membrane. The existence of this structural relation is experimentally observed by analyzing the textures (i.e., the geometrical relations between the crystals forming the aggregate) appearing in IMCA. Some textures have already been described [1,4,8], and a more comprehensive treatment of them will be published elsewhere [15].

Fig. 4 shows an induced morphology crystal aggregate of $CaCO_3$ with a sheaf-of-wheat morphology. As in all the cases studied, secondary interference figures (maltese crosses) are observed with crossed polarizers. Since the silicate matrix is optically isotropic [14], such figures mean that optical continuity between the carbonate crystals which form the aggregate exist. In fact, when the outer parts of the aggregate are observed by scanning electron microscopy (SEM), they show a number of calcite crystals with equilibrium mor-

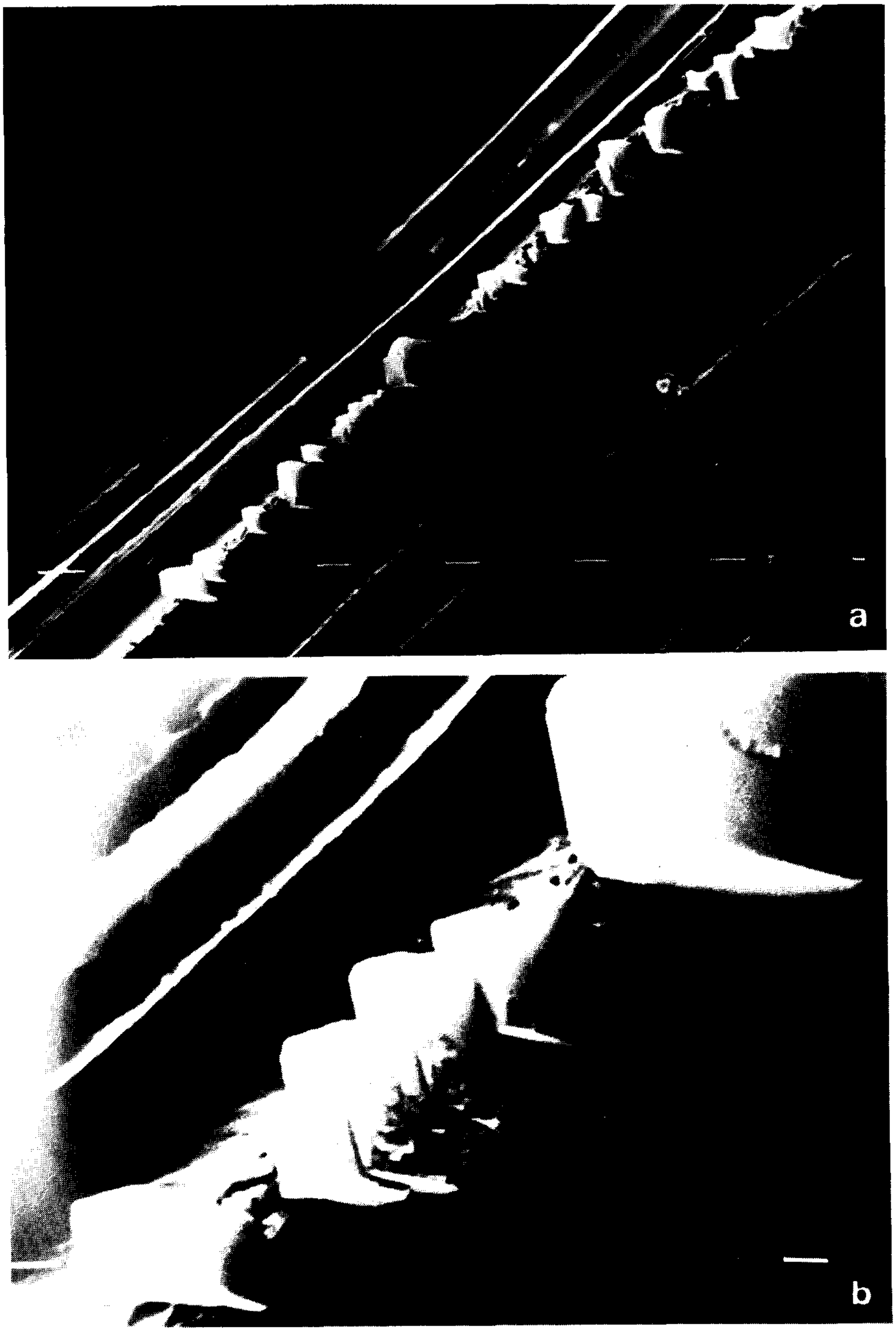

Fig. 4. Calcite rhombohedral crystals forming the outer part of an IMCA with a whole morphology as in fig. 2a: (a) scale bar 5 μm; (b) enlarged view of (a); scale bar 0.5 μm.

phology (i.e., rhombohedral F-faces). All crystals are arranged with the same orientation, parallel to the [0001] *c*-axis, even when no physical contact between them exists. A co-orientation of the crystals in this way cannot be explained without postulating the existence of not only a substrate but an epitaxial one. Unlike fig. 4, fig. 5a refers to an IMCA of $SrCO_3$. At the front of the aggregate, parallel to the growth direction, polysynthetic twinned crystals can be observed. They are typical

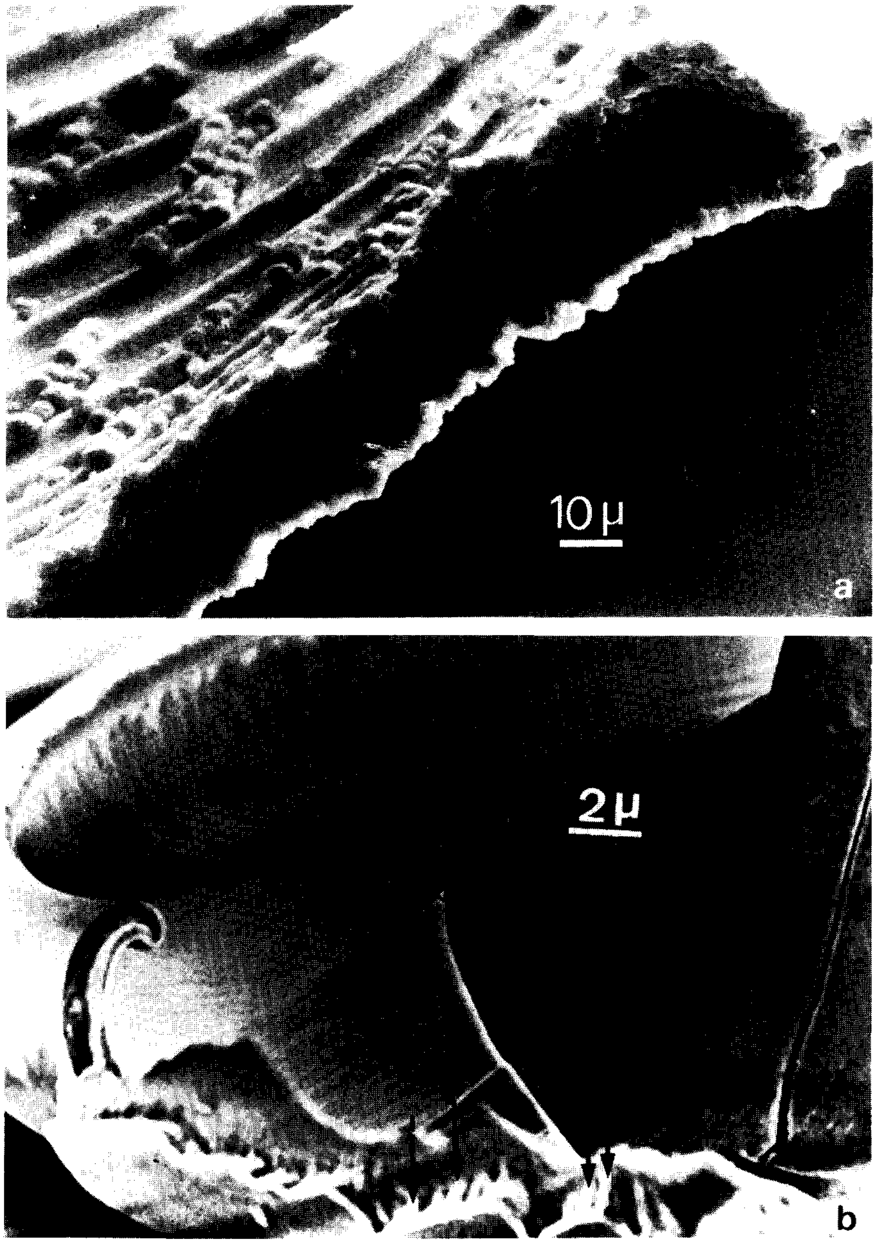

Fig. 5. (a) Pseudohexagonal prismatic twinned crystals forming an IMCA of $SrCO_3$. (b) A cracked IMCA of $BaCO_3$ showing the inner texture. Arrow shows $BaCO_3$ crystals.

of the aragonite-type carbonate structure. The carbonate crystals are ordered, and are here arranged along the [0001] direction of the pseudo-hexagonal prism. Fig. 5b refers to a $BaCO_3$ crystal aggregate which has been previously cracked in order to study the inner crystal texture. Arrows show carbonate crystals parallel and clearly independent of each other between two silicate membranes in a sandwich-like structure. The observations and arguments here discussed, demonstrate not only the existence of a matrix but its role as an effective template controlling the orientation and geometrical relations between the crystals which form the aggregate.

3.2. On the nature of the IMCA membrane

As seen from the above experimental conditions for the growth of IMCA, a close relation could be postulated between them and the so-called silicate garden, a chemical curiosity known from the earlier years of this century [16–19]. Such gardens are formed by the reaction of a soluble salt of di- or trivalent cations with alkali silicate solutions. In recent years, as a result of the work of Double et al. [20–23] and Birchall et al. [24,25], interest in silicate gardens, mainly in the so called reverse silicate garden, has increased because of its importance for the understanding of the hydration behaviour of cement. That is why such silicate precipitates are now better known. Recently, Birchall, Howard and Double [26] have summarized their view on silicate garden information in a phenomenological model. Two steps are clearly distinguished in this model which has been applied – in view of the analogy with cement hydration – specifically to the case of the calcium silicate garden. The first step is the formation of a calcium silicate hydrate (CSH) membrane. According to these authors, calcium silicate hydrate is formed by the reaction between a basic (pH = 12.6) sodium silicate bulk solution with an acid (pH = 6) calcium solution arising from the surface dissolution of the calcium containing crystal (fig. 6). At the interface of the two solutions, a narrow zone is formed in which the pH will change to intermediate values, at which calcium ions and silicate groups become rapidly hydrolyzed. As a result, nucleation takes place at very high supersaturation, and heterocoagulation of $Ca(OH)_2$ and polysilicic acid occurs, leading to a combined precipitate in the form of a membrane (see Sears [27] and Stoyanov [28]).

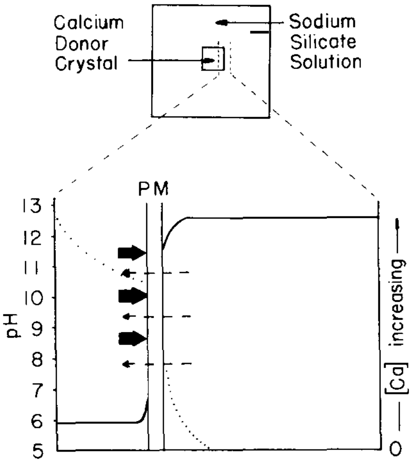

Fig. 6. The formation of silicate garden after the membrane-osmosis model. PM: precipitating-membrane. Dotted line: calcium concentration; full line: pH change. Dashed arrows show the influx of water; full arrows represent the osmotic forces.

Some important differences between silicate gardens and IMCA formation should be pointed out. In the experimental procedures for the formation of IMCA, the metal chloride solution diffuses through a silicate gel at a pH of < 10 in which Ca^{2+} exists as the main calcium species. The low concentration of hydrolyzed calcium ions explain the fact that $Ca(OH)_2$ (portlandite) crystals are not found in the gel, neither by optical microscopy nor by X-ray examination. Therefore, we cannot expect the IMCA-forming membranes to be of a calcium silicate hydrate nature as in the cases of the silicate garden and the hydration of cement, i.e., to have a non-stoichiometric structure, built up with $Ca(OH)_2$-like lamellar regions and silicate material on the surfaces. In fact, the X-ray diffraction diagram of CSH usually shows three broad peaks corresponding to spacing 12.5 Å (which is reduced to 9.8 Å after drying) 3.07, 2.80 and 1.83 Å [29,30]. In the X-ray patterns of IMCA we found the peaks belonging to carbonate crystals and other bands displaced to 3.90 Å (for $CaCO_3$ IMCA) and 3.93 and 6.94 Å (for $BaCO_3$ IMCA).

According to Schwartz and Muller [31], the pKa for monosilicic acid is 9.9, and it has been demonstrated that it decreases to 6.5 for high polymers [32]. Recently, Falcone [33] has experimentally confirmed a previous observation by Iler [34] that silicate solutions begin to adsorb multivalent metal ions at pH values roughly two units below those at which the metal hydroxide is precipitated. Therefore, under the chemical conditions used in the formation of IMCA, we expect the interaction between metal ions and silicate groups and the existence of metal silicate particles in the liquid phase of the silica gel or even on the surfaces of its solid framework. Now, it should be noted that the nucleation and growth of IMCA is in practice controlled by the formation of the carbonate crystals. Thus, in the experimental arrangement for the growth of $CaCO_3$ IMCA (fig. 1b), the $CaCl_2$ solution diffuses through the gel without any appreciable precipitation. Once the carbonate crystals are forming near the central portion of the gel column, the growth and effect of the membrane can be observed: sheaf-of-wheat and "double cone" patterns are formed. Then the precipitation zone moves towards the calcium donor solution. As the growth progresses, the morphologies become more crystal-like, suggesting less membraneous control, as a result of the lower $CaCO_3$ supersaturation [8]. It is indeed possible to obtain structures which look almost exactly like single crystals but which, upon SEM examination, turn out to be polycrystalline. In the case of $BaCO_3$ and $SrCO_3$ IMCA growth such correlation between carbonate concentration and overall morphologies can also be demonstrated. If an experimental system is based only on commercial sodium silicate, with its usual carbonate contamination [35], then twisted ribbons with $\infty 2:2$ or $\infty 4:2$ symmetry are obtained as shown in fig. 3. However, if the carbonate concentration is increased by counterdiffusion of a Na_2CO_3 solution (fig. 1a), a very different kind of twisted ribbon (fig. 7) is obtained, which grows up to 50 mm in length. Thus, a dramatic change in the symmetry of the crystal aggregate morphology is related to the carbonate concentration. If the morphology, for reasons point out in 3.1, is controlled by the growth mechanism of the membrane, these results suggest that CO_3^{2-} groups could be one of the components forming the matrix which enhances the hydration of the calcium silicate particles existing in the gel. This can be explained by considering that, as has been demonstrated, carbon dioxide accelerates the hydration of calcium silicate in cement pastes, giving materials with compressive strengths greater than samples hydrated under normal conditions [36–39]. In the case of IMCA, this catalytic effect explains (a) the absence of metal hydroxide co-precipitation during the hydration of the metal silicate, (b) the control of the precipitating material by the carbonate concentration, (c) the carbonate nature of the 3D crystalline phase of the forming composite, and (d) the X-ray difraction patterns obtained from the $CaCO_3$, IMCA matrix, which are different from those of CSH formed in silicate garden experiments or cement hydration.

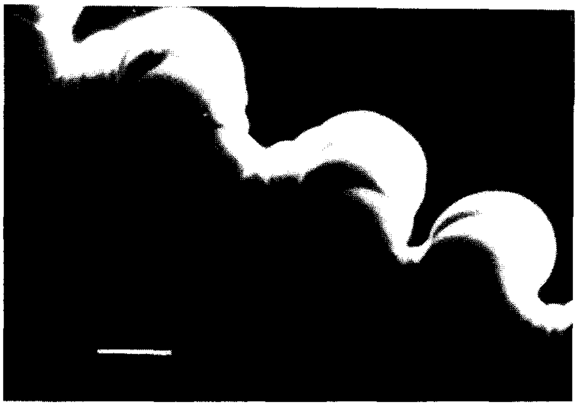

Fig. 7. Twisted ribbon obtained when increasing the carbonate concentration. IMCA of $BaCO_3$. Scale bar 0.2 mm.

In the absence of more extensive and direct data on the composition and structure of the matrix, the nature of the IMCA-forming membrane cannot be unambiguously identified at present. Nevertheless, the above arguments lead one to postulate that it has a metal (Ca, Ba or Sr) carbonate silicate nature. For the case of calcium, some minerals of this composition, such as spurrite [40], paraspurrite [41] and tilleyte [42] are known, and the existence of its synthetic hydrated forms has also been reported [43]. Further work on this matter is in progress.

3.3. On the morphogenesis of IMCA

Morphogenesis is one of the most interesting problems related to IMCA growth. In the second step of the model used by Birchall, Howard and Double, these authors make use of a morphogenetical mechanism proposed in the early literature on silicate gardens [17,44,45]. This mechanism depends on the precipitating CSH being a semipermeable membrane. Coatman et al. [23] have recently demonstrated this semipermeable character by means of a Pfeffer experiment. In order to equilibriate the difference of Ca concentrations inside and outside the membrane an influx of water occurs, creating an osmotic pressure within the membrane (see fig. 6) which eventually breaks out at the weaker points. The opening of the membrane provokes the formation of a new and outer CSH, with a morphology locally controlled by the resulting jet of Ca solution. From a chemical viewpoint, the picture for IMCA is clearly different. Before (or simultaneously with) silicate matrix formation, we have here a precipitation phenomenon and not a dissolution phenomenon. Nevertheless, in spite of its different chemical nature, the morphogenesis in both IMCA and silicate gardens must be regulated by the same physical processes.

Most of the morphologies observed can be well described in terms of symmetry, and can be built up from certain simple geometrical laws. It is difficult to believe that morphologies like those seen in figs. 2, 3 and 7, are created exclusively by a breakage growth process. It is also important to note that the morphological behavior of IMCA ranges from these morphologies to absolutely irregular ones. Thus, the active morphogenetical mechanism, must be able to generate such a wide range of shapes. Although the present author has not carried out laboratory experiments on silicate gardens, it can be concluded from literature that such a wide range of morphologies exist in this case also (see, for example, refs. [16,18,46]).

The growth morphology is related to the silicate matrix growth conditions. Birchall et al. [26] have suggested that the membraneous character of the silicate garden arises from the fact that it nucleates in the region of the so-called non-classical nucleation. However, this would appear to be too mechanistic an application of the theory, one that disregards some important features of these precipitates. For an ideal solution growth system (isobaric, isothermic, and free from impurities) the main variables are the supersaturation ratio $\sigma = IAP/Ks$ and the supersaturation growth rate $R_\sigma = \mathrm{d}\sigma/\mathrm{d}t$. Due to the low solubility product of the silicate matrix and to its large unit cell, it is expected that nucleation will occur within the non-classical zone [27,28] or close to it, i.e. the zone in which critical clusters are smaller than the unit cell of the growing compound. An amorphous phase will therefore be formed. For a compound which normally displays a three-dimensional periodic structure (for example, calcium phosphate) this creates amorphous spherical phases. As σ and R_σ decrease, a transition to a crystalline phase occurs [47,48]. However, in IMCA and silicate gardens, we are dealing with a precipitation phenomena in which one of the reactants presents a certain degree of condensation. In fact, the very structure of the silicate matrix [14,30] prevents three-dimensional layer stacking. Therefore, the possibility of disorder generated at very high supersaturation is here restricted to a two-dimensional surface. If an appropriate range of growth conditions is chosen, one should obtain a large variation of membraneous structures, from a highly disordered surface to a quasi-perfect two-dimensional crystal. This is in harmony with the morphological sequence obtained in some IMCA experiments (fig. 8). The matter can be illustrated as follow. In a suitable glass reservoir, a sodium silicate solution containing a low concentration of carbonate is gelled at pH 9.5. After gelling, a $BaCl_2$ solution (0.5N) is poured on it. Near the interface, irregular crystal aggregates can soon be observed but as time goes on, the precipitation zone moves away from the interface, i.e. to lower supersaturation regions, giving more and more regular morphologies.

Without an appropriate knowledge of the matrix crystal structure and the local chemical conditions a formal morphogenetical model cannot be developed at the moment. However, it would be noted that the above discussion suggests several mechanisms which could be active, for instance,

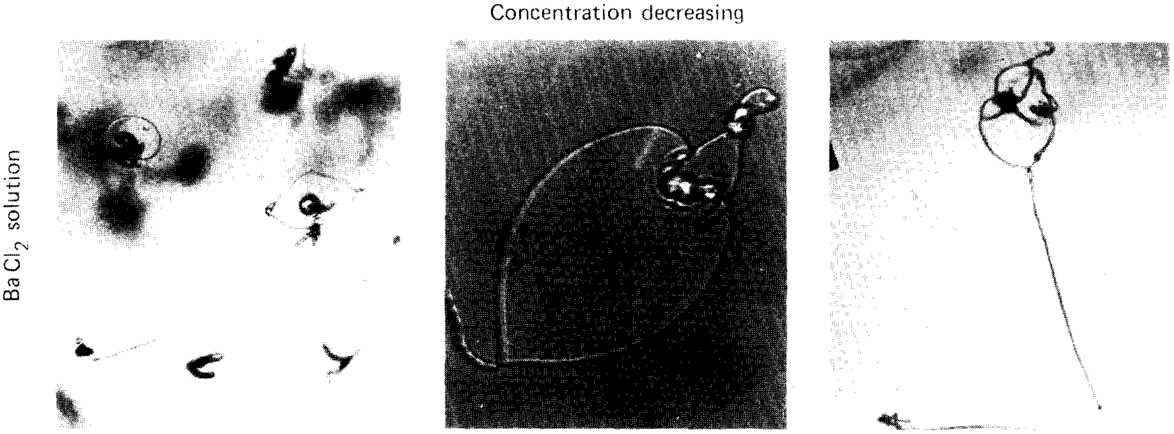

Fig. 8. Morphological evolution found during the growth of $BaCO_3$ IMCA. Experiment arrangement as in fig. 1a.

the existence of rotation defects (disclinations), which are possible in ordered membranes [49]. This kind of defect can explain the generation of three-dimensional objects, such as twisted ribbons, 180 rotations, cones, etc., from 2D surfaces [50]. It is also important to consider that we are dealing with a chemical reaction-transport system, one in which waves of chemical composition may propagate with a variety of structures. This viewpoint could be a very powerful theoretical tool explaining, for instance, the banding observed in IMCA (figs. 2a and 5). This is clearly not related to any kind of periodicity imposed on the system, and therefore must be explained as a self-organization process under conditions far from equilibrium. Also in this context, some of the morphologies observed (for example, see fig. 9) together with the very nature of the phenomenon suggest that IMCA growth could be analyzed in terms of a development of unstable interfaces. One can think, for instance, of the Rayleigh–Taylor instability which occurs when a light fluid pushes heavier fluid or of a Kelvin–Helmholtz instability which is related to discontinuities in the tangential component of the displacement rate across the interface [51]. Work along these lines is under way, but there is also a clear need for more experiments on the formation of IMCA, with special emphasis on quantitative data relating to: (a) textural and morphological characterization; (b) its morphological evolution;

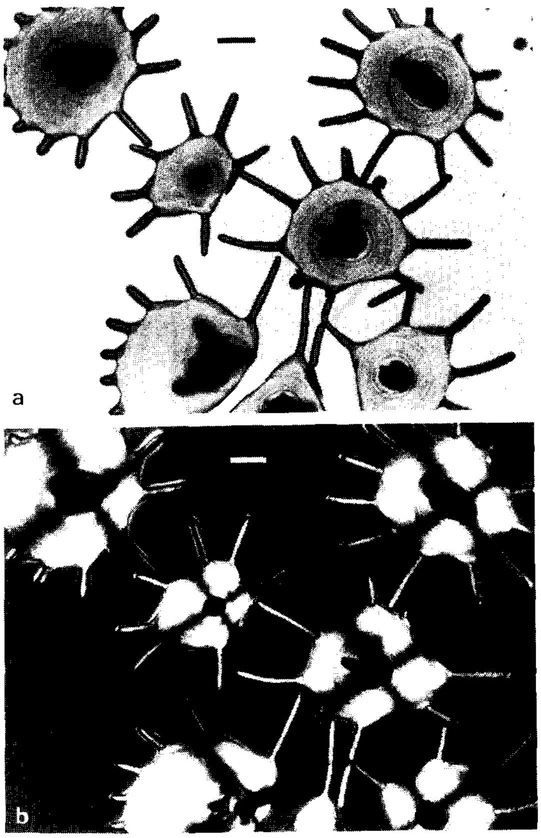

Fig. 9. Finger-like growth obtained in induced morphology crystal aggregate of $CaCO_3$. Ordinary light. (b) Crossed polarizers; scale bar 0.5 mm.

(c) local chemical conditions and their relation to the initial conditions of the experiment; (d) the search of new kinds of induced morphology crystal aggregates by changing the membraneous support and the crystalline phase.

4. Conclusion

In this paper it is shown that the results obtained during the formation of induced morphology crystal aggregates of metal (Ca, Ba or Sr) carbonates in silica gel at pH 8.5–10 are consistent with the following interpretation.

The crystalline phase has a catalytic role in the hydration of the metal silicate particles which exist in the gel. As a result, a hetereocoagulation of the polymeric matrix with crystalline clusters occurs. Due to the low solubility of the precipitating material, nucleation takes place in the non-classical region, giving a disordered arrangement of minute amorphous or poorly crystalline particles. The crystalline side of the coagulate can act as a nucleation site for further epitaxial carbonate crystal growth. The next growth steps depend sensitively on the local chemical conditions. At high supersaturation, due to the very polymeric structure of the matrix, which avoids 3D layering, the precipitate works just like a growing membrane displaying non-crystallographical branching. As supersaturation decreases, both the 2D order in the membrane and the amount of the carbonate crystalline phase in the aggregate increases. Near the equilibrium concentration, the percentage of the crystalline phase is so important that the composite product can acquire a quasi-crystallographic symmetry, although the effect of the matrix is clearly evidenced by the polycrystalline nature of these "crystals".

This picture leads one to discuss a fundamental point of the induced morphology concept. The co-existence of two phases, a 3D periodic crystalline one and membraneous one is an essential condition for IMCA. Indeed, the two phases must be simultaneously formed during IMCA growth. The existence of a previous membraneous substrate on which a crystalline phase is later grown, even when epitaxial relations between the two components are expected, does not necessarily led to the morphological behavior observed in IMCA. In other words, induced morphology crystal aggregates are composites with a self-organized morphology.

Acknowledgements

This paper was writted during a stay of the author in the Material Research Laboratory, Pensylvania State University. Finantial support from the NATO Spanish Scientific Program is acknowledged. It is a pleasure to thank Dr. H.K. Henisch for helpful discussions and revision of the manuscript. I would like also to acknowledge S. Dominguez for figs. 2a and 9.

References

[1] J.M. Garcia-Ruiz, PhD Thesis, Universidad Complutense, Madrid (1980).
[2] J.M. Garcia-Ruiz and J.L. Amoros, J. Crystal Growth 55 (1981) 379.
[3] J.M. Garcia-Ruiz and J.L. Amoros, Bull. Mineral. 104 (1982) 107.
[4] J.L. Amoros and J.M. Garcia-Ruiz, Invest. Ciencia 71 (1981) 107.
[5] N. Watabe, in: Inorganic Biological Crystal Growth, Ed. B.R. Pamplin (Pergamon, Oxford, 1981) p. 99.
[6] J.D. Birchall and A. Kelly, Sci. Am. 248 (1983) 6.
[7] S. Dominguez Bella, unpublished results.
[8] S. Dominguez Bella and J.M. Garcia-Ruiz, Bol. Real. Soc. Espan. Hist. Nat., Secc. Geol., in press.
[9] J. Farran, Rev. Matér. Construct. Trav. Publ. 492 (1956) 191.
[10] A.D. Buck and W.L. Dolch, J. Am. Concrete Inst. 63 (1966) 755.
[11] H.F.W. Taylor, in: The Chemistry of Cement, Royal Institute of Chemistry Lecture Series No. 12 (1966).
[12] R.B. Willianson, Progr. Mater. Sci. 15 (1972) 189.
[13] T.D. Giach, J.E. Gillot, E.G. Swenson and P.J. Sereda, Cement Concrete Res. 1 (1971) 13.
[14] R.B. Willianson, J. Crystal Growth 3/4 (1968) 787.
[15] S. Dominguez Bella and J.M. Garcia-Ruiz, to be published.
[16] R. Coparisow, Kolloid-Z. 9 (1912) 353.
[17] R.E. Liesegang, in: Chemische Reaktionen in Gallerten (Steinkopf, Dresden, 1924).
[18] L. Cramer, Kolloid-Z. 9 (1912) 116.
[19] W.J.C. Ross, J. Proc. Soc. NS Wales 44 (1910) 583.
[20] D.D. Double, A. Hellawell and S.J. Perry, Proc. Roy. Soc. (London) A359 (1978) 435.

[21] D.D. Double and A. Hellawell, Nature 261 (1976) 486.
[22] D.D. Double, Silicates Ind. 11 (1977) 233.
[23] R.O. Coatman, N.L. Thomas and D.D. Double, J. Mater. Sci. 15 (1980) 2017.
[24] J.D. Birchall, A.J. Howard and J.E. Bayley, Proc. Roy. Soc. (London) A360 (1978) 445.
[25] J.D. Birchall, Cement Concrete Res. 11 (1981) 299.
[26] J.D. Birchall, A.J. Howard and D.D. Double, Cement Concrete Res. 10 (1980) 145.
[27] G.W. Sears, J. Chem. Phys. 65 (1961) 1738.
[28] N. Stoyanov, in: Current Topics in Materials Science, Vol. 3, Ed. E. Kaldis (North-Holland, Amsterdam, 1979) p. 421.
[29] L. Heller and H.F.W. Taylor, in: Crystallographic Data for the Calcium Silicates (Her Majesty's Stationary Office, London, 1956).
[30] R.H. Smith, P. Bayliss, B.R. Gamble and R.H. Mills, Cement Concrete Res. 2 (1972) 559.
[31] R. Schwartz and W.D. Muller, Z. Anorg. Allg. Chem. 296 (1958) 273.
[32] V.N. Belyakov, N.M. Soltiuskii, D.N. Strazhesko and V.V. Strelko, Ukr. Khim. Zh. 40 (1974) 236.
[33] J.S. Falcone, in: Soluble Silicates, Ed. J.S. Falcone (American Chemical Society, Washington, DC, 1982) p. 133.
[34] R.K. Iler, in: The Chemistry of Silica (Wiley, New York, 1979) ch. 6.
[35] E.R. Banks, P. Chianelly and E. Pintochousky, J. Crystal Growth 18 (1973) 185.
[36] R.L. Meyers, Rock Products 52 (1949) 96.
[37] I. Leker and F.A. Blakey, J. Am. Concrete Inst. 28 (1956) 295.
[38] B. Kroone and F.A. Blakey, J. Am. Concrete Inst. 31 (1959) 479.
[39] R.L. Berger, J.F. Young and K. Leung, Nature 240 (1972) 16.
[40] R.F. Klevtsova and N.V. Belov, Soviet Phys.-Cryst. 5 (1961) 659.
[41] A.A. Colville and P.A. Colville, Am. Mineralogist 62 (1977) 1003.
[42] L. Louisnathan and J.V. Smith, Z. Krist. 132 (1970) 288.
[43] J. Pluth and J.V. Smith, Acta Cryst. B29 (1973) 73.
[44] T.H. Hazlehurst, J. Chem. Educ. 18 (1941) 286.
[45] T.C. Powers, J. Portland Cement Assoc. Res. Develop. Labs. 3 (1961) 47.
[46] R.E. Liesegang, Kolloid – Z. 9 (1912) 298.
[47] J.M. Garcia-Ruiz, V. Lopez-Acevedo and J.L. Amoros, in: Urolithiasis, Clinical and Basic Research, Ed. L.H. Smith (Plenum, New York, 1981) p. 459.
[48] V. Lopez-Acevedo and J.M. Garcia-Ruiz, Estud. Geol. 17 (1982) 227.
[49] M. Kleman, in: Dislocations in Solids, Vol. 5, Ed. F.R. Nabarro (North-Holland, New York, 1980).
[50] J.M. Garcia-Ruiz, in: Forma y Criterio, Ed. J.L. Amoros (Universidad Complutense, Madrid, 1981) p. 69.
[51] D.H. Sharp, in: Fronts, Interfaces and Patterns, Ed. A.R. Bishop (North-Holland, Amsterdam 1984) p. 3.