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TEXTURES IN INDUCED MORPHOLOGY CRYSTAL AGGREGATES OF $CaCO_3$: SHEAF OF WHEAT MORPHOLOGIES

S. DOMINGUEZ BELLA and J.M. GARCIA-RUIZ

Departamento de Geología, Facultad de Ciencias, Universidad de Cádiz, Apdo. 40, Puerto Real Cádiz, Spain

Three different kinds of textures have been found in induced crystal aggregates of $CaCO_3$ sheaf of wheat morphologies, grown in silica gel at pH = 10. One of them showing concentric banding can be explained by a simple aggregation model of stacked rhombohedra along its c axis. The second does not present concentric banding and is formed by fibers with 3 m symmetry. Finally, the third has a more complicated fiber design with periodical units arranged in a helical pattern, which has not been explained by any simple model of $CaCO_3$ crystal aggregation. The morphogenetical role of the silicated matrix must be particularly important in this last case.

1. Introduction

Induced morphology crystal aggregates (hereinafter IMCA) are composites with self-organized morphologies, which are formed by a silicated non-crystalline phase (calcium silicate hydrate-like phase) and a crystalline phase ($CaCO_3$ in the present case) [1]. They show several morphologies with non-crystallographic symmetry [2]. Of these, the most interesting with regards to their application in the fields of biomineralization and prosthesis are those presenting sheaf of wheat morphology.

The aim of this paper is to present a textural study of this kind of induced morphological crystal aggregates which has been carried out using optical and scanning electron microscopy. A model explaining the observed textures is also proposed.

2. Experimental

Induced morphology crystal aggregates of $CaCO_3$ were obtained in a U-shaped glass cassette. The geometry and dimensions of the device are displayed in fig. 1.

A sodium silicate solution (specific gravity = 1.06 g/cm^3 and pH = 11.2) acidified with HCl (1N) to pH 10, was injected into the cassette up to the level L–L′, leaving two empty branches on either side. After gelling, solutions of $CaCl_2$ (0.5M) and Na_2CO_3 (0.5M) were injected into the branches as seen in fig. 1, in such a way that counter-diffusion of both solutions through the gel occurs. After ten days at room temperature, the first precipitate appears at $x = 25$ mm from the $CaCl_2$ solution (see fig. 1). As the precipitation evolves towards the $CaCl_2$ solution, different kinds of morphologies appear. Each one of these evolves with time, a process which will be described elsewhere. Of these, we have chosen for this textural study, those presenting sheaf of wheat morphology.

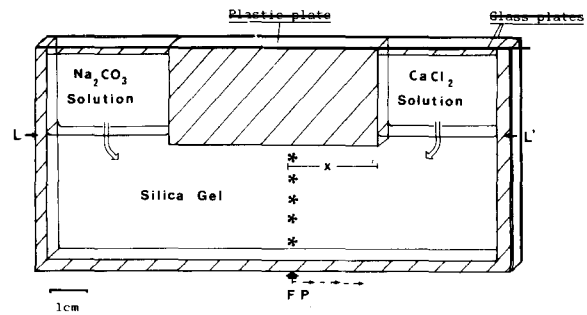

Fig. 1. Arrangement for the growth of induced morphology crystal aggregates. F P stands for the position of the first precipitate. Arrows indicate the advance of the precipitation front (see text).

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The crystal aggregates were recovered from the silica gel by mechanical manipulation, enhanced by gel dissolution with NaOH solutions. Once washed with doubly distilled water and dried, each aggregate was fixed with double-faced adhesive tape to an aluminium base. For a scanning electron microscopy study, they were then coated with Au.

X-ray diagrams (powder method) show that $CaCO_3$ (calcite) is the crystalline phase forming the aggregates.

This study was carried out on two kinds of precipitates: those grown in the gel and those grown on the gel–glass interface. In the last case, the glass was placed directly onto the aluminium base and fixed with silver tincture, and also coated with Au.

3. Textural study; description and explicatory model

Optical and scanning electron microscopic studies reveal the existence of several kinds of textures in crystal aggregates with sheaf of wheat morphology.

3.1. Sheaf of wheat with banding structure

The first presents clear banding structure, i.e., the existence of concentric bands of low and high density of particles as shown in fig. 2A. Each one of these bands is itself formed by microsheaf of wheat aggregates radially arranged (fig. 2B). These microsheaves of wheat are constituted by radial fibers emanating from a growth center. Thus, the low density zone belong to the geometrical locus

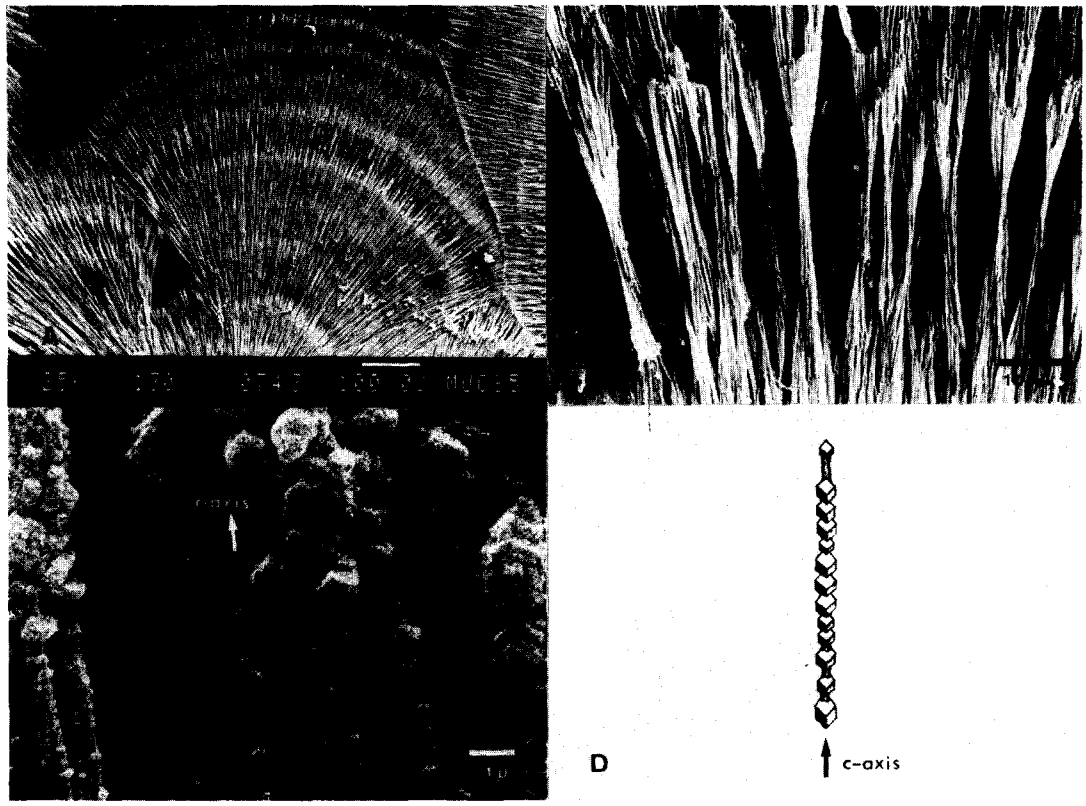

Fig. 2. SEM vies of sheaf of wheat aggregates with banding structure: (A) general view of one aggregate; (B) SEM view of microsheaves of wheat; (C) enlarged view of fibers, showing $\{10\bar{1}1\}$ rhombohedra arranged along its *c*-axis; (D) diagram of a fiber.

of the points displayed by the center of the sheaves. Each fiber is built of a set of $\{10\bar{1}1\}$ cleavage rhombohedra arranged along its c axis (figs. 2C and 2D). Thus, each fiber is a crystal aggregate working optically as a single crystal, which explains the pseudo-uniaxial Maltese cross that appears when IMCA are observed under crossed-nicols and polarized light. We have not observed either linear or Liesegang patterns [4] between the bands forming the aggregate. In fact, just in the growth front of the aggregate we can see several rhombohedra crystals of $CaCO_3$ displaying the above described orientation and without physical contact between them (figure 3). This can only be explained by the existence of such a matrix. An explanation for the rhythmic behaviour of these aggregates including kinetic data has been describes elsewhere [5].

Fig. 3. Rhombohedral crystals of $CaCO_3$ (R), without physical contact between them, in the growth front of the aggregate. Small arrow shows fiber direction. Large arrow shows growth direction.

3.2. *Sheaf of wheat without banding structure*

The second kind of aggregates does not present rhythmic structure (fig. 4A).

These aggregates are composed of fibers arranged radially from the center of the sheaf. Another difference to the aggregates described in the previous paragraph is that in this case, the fibers have a very different morphology and texture. Here, the morphology of each fiber is formed by three ribs arranged with a 3m symmetry, the threefold axis being the fiber-axis (see fig. 4B)

This fiber morphology can evolve to a more complicated and amazing design as shown in fig. 4C, with each rib showing serrated profiles. Similar morphologies to this have been recently described by Folk at al. [6], the so-called "bizarre" morphologies of $CaCO_3$ in hot-spring travertines from central Italy. This fiber pattern is mainly localized in those aggregates growing near the $CaCl_2$ solution, and is also developed by non-sheaf of wheat aggregates growing just on the interface of gel–$CaCl_2$ solution.

As this kind of texture also shows the pseudo-uniaxial Maltese cross under crossed-nicols, it is obvious that the existence of optical continuity is also a feature to be fulfilled by any model explaining the textural relations between the crystals forming the aggregate.

It is clear from the SEM views that the axis $\bar{3}$ of the cleavage rhombohedra is again the fiber axis, and that the morphological unit of the fibers is a combination of acute $\{02\bar{2}1\}$ and cleavage $\{10\bar{1}1\}$ rhombohedra. However, the stacking pattern of these rhombohedra is very difficult to establish without ambiguity. Therefore, for this texture, the authors propose a description and only a tentative model, which has been inferred from the SEM views at different stages of the time evolution of the aggregates. Each fiber is formed by three ribs at angles of 120° to each other. Each rib is formed by a series of units arranged along its axis. Each unit can be described from a morphological viewpoint as the combination of two domes (fig. 4D). Therefore, each rib presents a mirror plane which contains the axis of the fiber. Fig. 5 is a diagrammatic representation of this morphological unit.

However, unlike the previously described text-

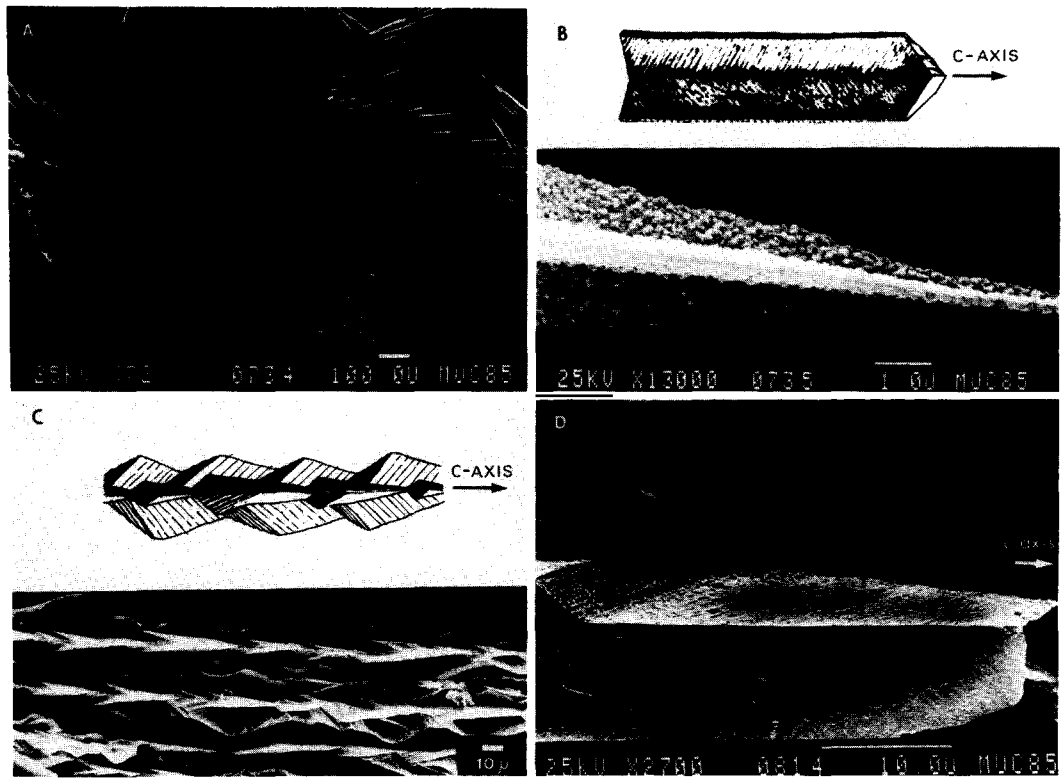

Fig. 4. SEM views of sheaf of wheat aggregates without banding structures: (A) general view of one aggregate; (B) enlarged view of (A) showing a fiber with 3m symmetry and its schematic representation; (C) SEM view of a set of serrated fibers and a diagram of one; (D) enlarged view of (C) showing a morphological unit form by two domes (see text).

ural arrangements, these units and therefore the ribs which they form are not related by a ternary axis. In fact, as shown in fig. 4C, a certain helical pattern appears. The authors have no quantitative data to confirm that a true screw axis exists along the fiber, although in many cases qualitative considerations support such a hypothesis.

In each unit, the dome placed nearer to the growth front of the fiber presents planar surfaces and the dome nearer to the center of the aggregate presents stepped surfaces, the steps being formed by aggregation units stacked on its rhombohedral faces. It is important to note that the term dome must be used bearing in mind that we are dealing with crystal aggregates and not single crystals. The edge of the dome presents a kinked surface which is formed by rhombohedra stacked with one of its mirror planes parallel to the mirror plane of the rib. Thus, as seen from these data, both domes could be explained by a unique aggregation process of units, each unit being a combination of acute $\{02\bar{2}1\}$ and cleavage $\{10\bar{1}1\}$ rhombohedra (fig. 5).

This aggregation model leaves unexplained some important aspects of these unusual textures. In fact, any model built up on the basis of $CaCO_3$ crystal aggregation cannot explain either the rhythm and morphology of the units forming the ribs or the helical pattern of the whole fiber. Therefore, the morphogenetical role of the ill-defined silicated matrix, the existence of which in IMCA has been experimentally demonstrated [3] and checked for the present aggregates must be as important as in the case of the so-called "braids"

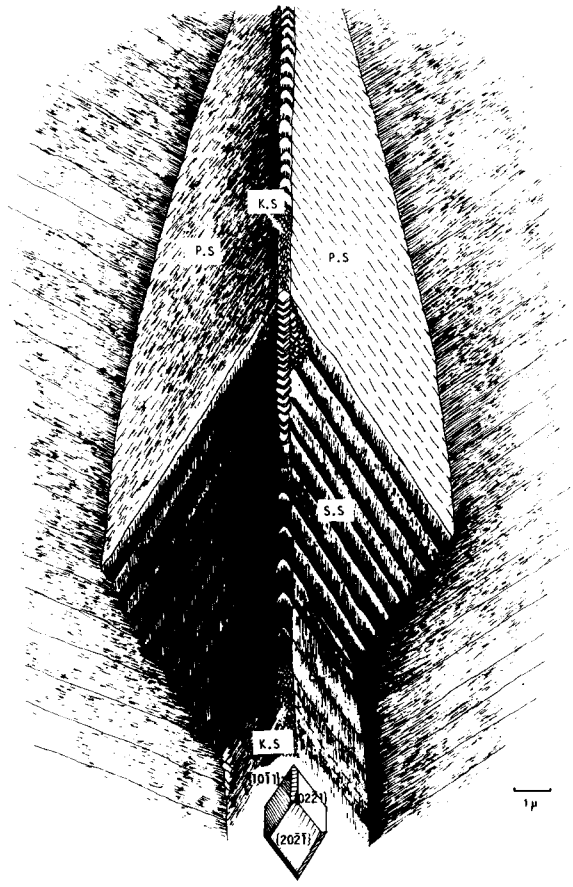

Fig. 5. Diagrammatic representation of a morphological unit observed in fig. 4D, showing the orientation of the aggregation unit ({10$\bar{1}$1} and {02$\bar{2}$1} rhombohedra). PS: planar surfaces; SS: stepped surfaces; KS: kinked surface on the edge of the dome.

of $BaCO_3$ IMCA [2,3]. However, the way this matrix works has not been understood up to the present.

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