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Structure and morphology of synthetic magnesium calcite

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The X-ray crystal structure refinements of two synthetic calcite single crystals containing 3.1 and 5.7 mol% magnesium were carried out. The structure of the second crystal was also refined at -80 °C. No significant structural difference from biogenic magnesium calcite was found. Magnesium within the crystals of calcite forms a solid solution over the compositional range investigated. The principal axes of vibration ellipsoids at -80 °C resemble very closely those of calcite suggesting that the large thermal parameters in magnesium calcite reflect increased thermal vibrations more than positional disorder. The crystals of magnesium calcite express new rhombohedral faces due to the interaction of magnesium with growing crystals. The role of magnesium in the morphology of single crystal and globular aggregates of magnesium calcite is discussed in view of its possible relevance in both biomineralization and crystal growth.

Magnesium is a major component of biogenic calcite crystals and its incorporation into the calcite lattice represents a well known problem of interest not only for biomineralization, but also for materials science and sedimentary geology.[1] Considerable quantities of magnesium were found in the calcite lattice of various marine biological skeletal elements.[2] However, obtaining relatively high magnesium concentration in calcite structures precipitated *in vitro* has so far proved problematic under conditions comparable to those used in biogenic counterparts.[3]

Crosslinked gelatin films can promote the crystallisation of calcite containing up to 12 mol% magnesium by probable reduction of the hydration sphere of magnesium ions through diffusion processes inside the collagenous matrix. The morphology and layered organisation of the magnesium calcite crystals grown into crosslinked gelatin films with entrapped poly-L-aspartate resemble some structural features of radial calcitic ooids.[4]

Fernández-Díaz *et al.* crystallised calcite, aragonite and magnesium calcite containing up to 15 mol% magnesium by diffusion of calcium and carbonate ions from opposite ends of a silica gel column.[5] The magnesium calcite crystals obtained from these experiments were described as compositionally zoned. They exhibit different morphologies ranging from spherical aggregates to single crystals depending on the magnesium content and supersaturation at the point of the column, where nucleation occurs.

Recently we showed that magnesium calcite with unusually high magnesium content up to 14 mol% crystallises from water–alcohol mixtures.[6] These results support the hypothesis that hydration of magnesium partially inhibits its entrance into the calcite lattice,[7] even if effects due to the high supersaturation in these solvents can not be completely excluded. No evidence of physical and chemical heterogeneities were found in the single crystals of magnesium calcite grown from water–alcohol mixtures. The crystals containing up to about 7 mol% magnesium were single and suitable for an accurate X-ray structure analysis.

The crystal structure refinement of a biogenic calcite containing 10 mol% magnesium was carried out by Althoff,[8] and structure refinements of two biogenic calcites isolated from echinoid fragments containing 6.4 and 12.9 mol% magnesium respectively were carried out by Paquette and Reeder.[9] Synthetic magnesium calcite crystals are typically very small, thus a detailed X-ray structure refinement proved difficult. On the other hand the discrepancy between the properties of biogenic and synthetic magnesium calcite, as the variation of the unit cell volume and the *c*/*a* ratio with magnesium content and the difference in stability, aroused interest for a comparison between the structural parameters of biogenic and synthetic single crystals.[10,11]

Here we report the X-ray crystal structure refinements of two synthetic calcite single crystals containing 3.1 (Mg3) and 5.7 (Mg6) mol% magnesium as well as the results of an investigation on the effect of magnesium ions on the morphology and architectural assembly of calcite. X-Ray data were collected at room temperature for the crystal Mg3 and at room temperature and -80 °C for the crystal Mg6. The results allow insight into the possible structural origin of the difference in stability between biogenic and synthetic minerals, as well as into the variations caused by the presence of magnesium in the morphology of calcite.

Experimental

Samples crystallisation

Crystals were grown by very slow diffusion of ammonium carbonate vapour into water–alcohol mixtures (3 ml) containing calcium chloride (10 mM). Different Mg^{2+}/Ca^{2+} molar ratios were obtained by adding the required mass of magnesium chloride.

Crystals Mg3 were obtained from water–ethanol (25% v/v) with Mg^{2+}/Ca^{2+} molar ratio of 1 and crystals Mg6 from water–propan-1-ol (25% v/v) with Mg^{2+}/Ca^{2+} molar ratio of 2.5.[6] The biogenic magnesium calcite was obtained from the teeth of sea urchin.

Samples characterisation

Magnesium contents determined by atomic spectrometry induced coupled plasma (Varian 2100) were 4.2 ± 0.5 and 5.5 ± 0.5 for the crystals Mg3 and Mg6 respectively, and 8.1 ± 0.5 mol% magnesium for the biogenic sample. The data were obtained from three independent sets of analyses.

Morphological investigations were carried out using a Philips XL-20 scanning electron microscope.

The IR spectra of ground samples dispersed in KBr pellets were recorded using a Nicolet 250 FTIR spectrometer.

X-Ray diffraction patterns of the ground samples were recorded with a Philips PW1050/81 PW1710 system equipped with a graphite monochromator in the diffracted beam, using Cu-K radiation.

The least squares method was used to calculate the unit cell parameters from the well determined positions of the three most intense reflections. The peaks positions were corrected using silicon as internal reference.

Crystal structure refinement

Mg3 and Mg6 crystals of dimensions of *ca.* 0.08 × 0.07 × 0.04 mm and 0.09 × 0.04 × 0.04 mm, respectively, were mounted on a Enraf-Nonius CAD-4 diffractometer equipped with a Mo-Kα radiation source ($\lambda = 0.710\,69$ Å). The unit cell parameters shown in Table 1 were determined by least-squares refinements of the setting angles of 25 well centered high 2θ reflections. The reflections were measured in the range $5 < \theta < 45°$ using the omega scan mode, with a scan interval of 1.7°, a pre-scan speed of 5.3° min^{-1} and a pre-scan acceptance of $\sigma(I)/I = 0.5$. Reflections that did not match the acceptance conditions were measured at a desired $\sigma(I)/I = 0.02$ for a maximum time of 120 s. The index ranges *hkl* were −9 to 8, 0–9, 0–33.

All computations were performed using the SHELXL-93 package[14] of crystallographic programs. Refinement proceeded by block-diagonal least-squares methods using the space group ($R\bar{3}c$, no. 167) and the starting coordinates of calcite.[13] An empirical absorption correction was applied by the method of Walker and Stuart.[15] In the last refinement cycles anisotropic atomic displacement parameters (a.d.p.s) were used. The magnesium occupation factors (O.F.) were fixed at the values obtained from the Bishoff equation[12] using single crystal cell volumes, considered the best way to detect the amount of magnesium really present in the calcite structure. The calcium O.F. were fixed as [1−(magnesium O.F.)]. At the end of the refinement procedures, the magnesium O.F. was freed to make a check on composition and no appreciable variation was detected. The O.F. correspond to a magnesium content of 3.1 and 5.7 mol% magnesium for Mg3 and Mg6, respectively. These values and those determined by ICP and by the unit cell volumes obtained from powder data are reported in Table 1 together with the final agreement indexes. The refined positional parameter for the oxygen atom and the atomic displacement parameters are reported in Table 2. The principal axes of vibrational ellipsoids are reported in Table 3 together with equivalent isotropic temperature factors.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/82.

Results and Discussion

Magnesium contents of the calcite crystals determined from powder and single crystals data compare well with the values obtained by means of ICP analysis (Table 1). The discrepancies which are within three times the standard deviations cannot be considered significant.

The IR spectrum of selected crystals of Mg6 is shown in Fig. 1 together with the IR spectra of synthetic pure calcite and calcite from sea urchin teeth. The characteristic IR absorption peak of calcite at 875 cm^{-1} shifts to 874 cm^{-1} and that at 712 cm^{-1} shifts to 714 and 715 cm^{-1} for Mg6 and the biological sample, respectively. As previously reported[16] these shifts are characteristic of magnesium substitution. Magnesium calcite displays peak broadening with respect to pure calcite

Table 1 Magnesium content, unit cell parameters and agreement indexes[a]

sample	Mg%(SC)	Mg%(PO)	Mg%(ICP)	a/Å	c/Å	V/Å^3	R_1[b]	wR_2[b]
CAL[c]	—	—	—	4.988(1)	17.061(1)	367.6(1)	0.022	n.r.
Mg3	3.1(3)	4.3(2)	4.2(5)	4.978(2)	16.988(2)	364.5(3)	0.0224	0.0468
Mg6	5.7(2)	6.8(3)	5.5(5)	4.963(1)	16.957(6)	361.6(2)	0.0256	0.0606
Mg6[d]	5.7(2)	6.8(3)	5.5(5)	4.952(7)	16.92(2)	359.3(9)	0.0265	0.0535

[a]Here and in the following tables the estimated standard deviations are reported in parentheses. SC: magnesium mol% (relative to the sum of the cations) calculated using the equation proposed by Bischoff *et al.*[12] from the unit cell volumes determined from single crystals data at room temperature. PO: calculated using the equation proposed by Bischoff *et al.*[12] from the volume of the cells determined from powder data. ICP: Mg content determined by ICP. [b]Indexes for $I > 2\sigma(I)$; $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)]^2\}^{0.5}$. [c]The data reported for calcite (CAL) in all tables are taken from ref. 13 and are relative to a mineral crystal containing 0.2 magnesium mol%; n.r. = not reported in the referenced paper. [d]Refined at −80 °C.

Table 2 Refined coordinate (× 10^4) and a.d.p.s (× 10^3/Å^2)

	M		C		O				
sample	β_{11}	β_{33}	β_{11}	β_{33}	x	β_{11}	β_{22}	β_{33}	β_{23}
CAL	12.2(5)	0.85(3)	12(1)	0.8(1)	2567(2)	14.2(7)	25.6(8)	1.59(5)	−2.2(1)
Mg3	15(1)	0.89(7)	13(1)	0.96(7)	2577(2)	17(1)	30(1)	1.71(7)	−2.05(7)
Mg6	16(1)	0.96(7)	15(1)	1.03(7)	2574(3)	19(1)	33(1)	1.85(7)	−2.14(8)
Mg6[a]	14(1)	0.83(6)	12.9(9)	1.10(7)	2578(2)	16(1)	25(1)	1.59(7)	−1.09(7)

[a]Refined at −80 °C.

Table 3 Principal axes of vibrational ellipsoids R_n (10^3/Å) and equivalent isotropic temperature factors B_{eq} (10^2/Å^2)

	M			C			O			
sample	R_1, R_2	R_3	B_{eq}	R_1, R_2	R_3	B_{eq}	R_1	R_2	R_3	B_{eq}
CAL	108(2)	112(2)	94(3)	107(5)	111(7)	93(5)	99(4)	125(3)	179(2)	151(4)
Mg3	117(2)	116(2)	111(7)	112(3)	117(3)	103(8)	110(3)	138(3)	185(3)	174(8)
Mg6	120(2)	120(3)	118(7)	117(2)	122(3)	111(8)	114(4)	145(4)	193(5)	189(7)
Mg6[a]	110(3)	113(3)	103(8)	110(3)	126(4)	103(8)	110(4)	139(4)	166(4)	158(8)

[a]Refined at −80 °C.

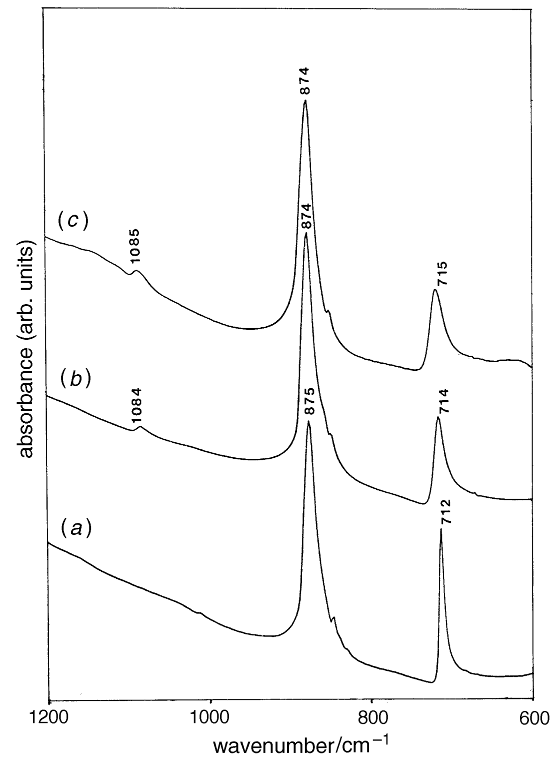

Fig. 1 FTIR spectra of: (*a*) pure calcite; (*b*) sample Mg6 containing 5.7 mol% magnesium; (*c*) biogenic calcite from sea urchin teeth containing 8.1 mol% magnesium

and an additional broad peak around 1084 cm^{-1} in agreement with the data reported by Aizenberg *et al.*[17]

The powder X-ray diffraction patterns of Mg3 and Mg6 samples are compared with that of pure calcite in Fig. 2. The shift of the peaks of magnesium calcite with respect to those of pure calcite indicates a reduction of the unit cell dimensions. Peak broadening increases with magnesium content. Furthermore it is possible to note in addition pronounced wings as already reported for biological and synthetic magnesium calcite.[10]

The increases of peak broadening of the IR spectra (Fig. 1) and X-ray powder diffraction patterns (Fig. 2) on increasing magnesium ion concentration may be due either to compositional inhomogeneity or to disorder caused by the presence of magnesium. Bischoff *et al.*[11] ascribed the broadening of Raman bands in both synthetic and biogenic samples of magnesium calcite to increasing positional disorder of the CO_3^{2-} group with magnesium content. On the basis of an accurate analysis[18,19] of the X-ray diffraction profiles of biological and synthetic magnesium calcite, the angular spread of the crystalline domains in synthetic magnesium calcite, which was found to be an order of magnitude larger than that of pure calcite, was ascribed to the presence of magnesium. Furthermore the texture of the crystals indicated an isotropic distribution of magnesium within the crystals.[19]

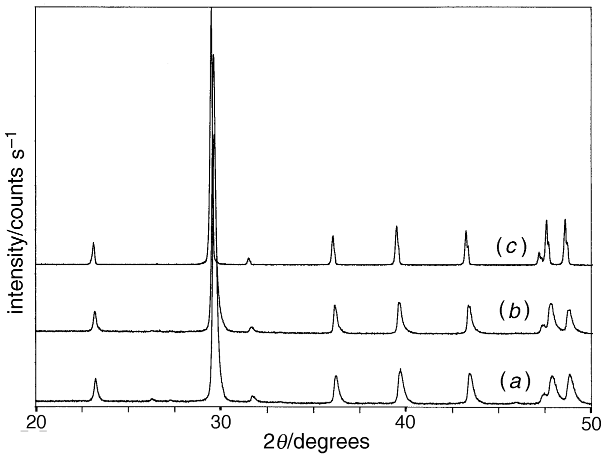

Fig. 2 Powder X-ray diffraction patterns of: (*a*) sample Mg6 containing 5.7 mol% magnesium; (*b*) sample Mg3 containing 3.1 mol% magnesium; (*c*) pure calcite

Table 4 M—O distances and coordination polyhedra parameters

sample	M—O/Å	octahedral volume/Å^3	octahedral QE[a]
CAL[b]	2.3595(5)	17.479(5)	1.0013(2)
Mg3	2.3502(6)	17.28(1)	1.0013(2)
Mg6	2.3450(7)	17.16(1)	1.0014(2)
Mg6[c]	2.3389(6)	17.02(2)	1.0015(2)

[a]Calculated according to Robinson *et al.*[20] [b]Calculated on the basis of anisotropic refinement data. [c]Refined at −80 °C.

The results of the crystal structure analysis indicate that magnesium within the crystals of calcite forms a solid solution over the compositional range investigated in agreement with the findings of Paquette and Reeder[9] for biogenic magnesium calcite. The distortion of cation octahedra was calculated and compared with that of calcite (Table 4) in order to verify a possible correlation with the behaviour and stability of magnesium calcite. No significant increase in distortions with respect to calcite was found. Furthermore the variation of the M—O bond lengths and of the cation octahedra volumes as a function of magnesium content was that expected for substitutional solid solutions and in good agreement with the data obtained for biogenic crystals.[9]

Going from room temperature to −80 °C the axes of vibrational ellipsoids and the equivalent isotropic temperature factors decrease approaching the thermal parameters of calcite at room temperature (Table 2 and 3). This suggests that the rather large atomic displacement parameters in magnesium calcite are due to thermal motions caused by the substitution of a smaller cation on a larger site rather than to some positional disorder of the atoms.

The crystals of magnesium calcite express new rhombohedral faces due to interaction of magnesium with growing crystals. Different indexes were assigned to these planes of interaction.[5,21,22] Because of the roughness of these planes this assignment is difficult. We found that the most probable indexes were {01.1} on the basis of the angle between the {10.4} rhombohedral and the new expressed faces. Crystals Mg3 [Fig. 3(*a*)] show striations and grooves parallel to the rhombohedron {01.1}. The tips of the crystals are open with hollows on the {10.4} rhombohedral faces [Fig. 3(*b*)]. The surface texture of newly expressed {01.1} faces shows the presence of {01.1} steps closed by {10.4} faces [Fig. 3(*c*)]. No morphological changes were observed in pure calcite crystals grown from water-alcohol mixtures, which were always rhombohedra {10.4}. More pronounced inhibition yielded Mg6 crystals with large stepped {01.1} faces[6] [Fig. 3(*d*)]. These crystals are elongated in the direction of the *c* axis and capped with more or less pronounced rhombohedral {10.4} faces. A possible mechanism for magnesium interaction with growing calcite has been proposed by Albeck *et al.*[22] Magnesium might be adsorbed by the newly expressed faces composed by alternating anionic and cationic surface areas. In water–alcohol mixtures partially dehydrated ions might be more easily adsorbed on the surface with a consequent greater inhibition of crystal growth.

When the crystallisation from water occurs in the presence of crosslinked gelatin films the size of magnesium calcite crystals in the direction perpendicular to the *c* axis decreases

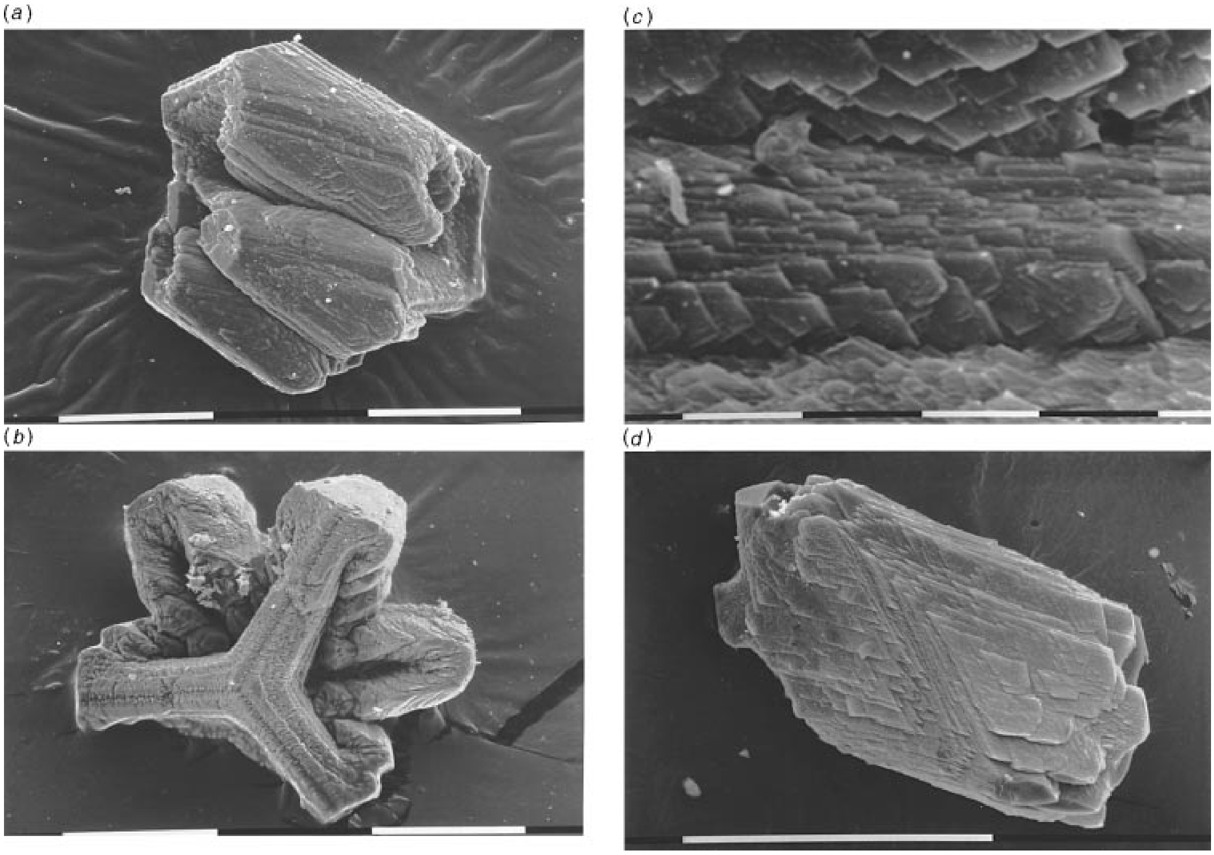

Fig. 3 SEM images of magnesium calcite crystals grown from water–alcohol mixtures: (*a*) sample Mg3 showing newly expressed rhombohedral faces belonging probably to the {01.1} family; (*b*) view along the *c* axis of sample Mg3; (*c*) surface of the newly expressed {01.1} rhombohedral faces and (*d*) sample Mg6. Scale bars: (*a*), (*b*), (*d*) 100 μm; (*c*) 10 μm.

with the increase of the magnesium content in solution. The single crystals aggregate with an angular spread of the hexagonal *c* axis of a few degrees. During growth the spread increases until the aggregate attains a spherical shape[4] (Fig. 4). The aggregate surface is modulated by the tips of the acicular crystals capped by {10.4} faces. Similar aggregates of magnesium calcite form under controlled supersaturation conditions by the counter diffusion of Ca^{2+} and $CO_3{}^{2-}$ ions through a silica gel column.[5] In the absence of magnesium ions calcite grows as rhombohedra {10.4}, whereas in its presence the habitus of calcite changes progressively from single crystals with stepped rombohedral faces through dumbbell shaped to the spherical aggregates containing up to 15 mol% magnesium. Similar stages of the self-assembled growth of acicular crystals to give spherical aggregates were described for fluoroapatite crystallised by diffusion into gelatin.[23] All these processes of architectural assemblies of acicular crystals seem to be controlled by ion diffusion in gels.

Magnesium was considered responsible for polymorphism control of calcium carbonate. In fact magnesium, which gives rise to high thermal vibrations, destabilises calcite inhibiting its growth in such a way as to induce mainly the crystallisation of aragonite from water solution when magnesium/calcium molar ratio becomes >4.[24] However, it has been shown that calcite or aragonite selectivity may be controlled in the absence of magnesium and that the microenvironment where nucleation occurs is important in determining the calcite or aragonite precipitation.[4,25] Although magnesium seems not essential to control calcium carbonate polymorphism, its presence in solution causes considerable changes in morphology, which may be important in the construction of architectural assembly by organisms.

In fact, although the microenvironment of the gel system plays the leading role in the construction of the architectural assembly of acicular crystals, the presence of magnesium ions seems to be a necessary stage for the formation of spherical aggregates. Thus the habitus of magnesium calcite crystals and their preferential growth in the direction of the hexagonal axis might give a major contribution to the final shape of skeletal elements of organisms, at least when the biological microenvironment is not so stiff to overcome the pressure due to the growing crystal.

Conclusions

Large thermal vibrations seem to represent the main structural factor influencing the relative thermodynamic stability of magnesium calcite. However the presence of a small amount of other foreign ions and occluded organic matrix in the biogenic calcite crystals must be taken into account when physical and chemical properties are considered, even if their presence is not revealed in the electron density distribution obtained by the X-ray single crystal analysis. Although magnesium ions are not essential to control calcium carbonate polymorphism in organisms, their presence in the crystallisation microenvironment can be of relevance in determining stability, morphology and architectural assembly of calcite crystals.

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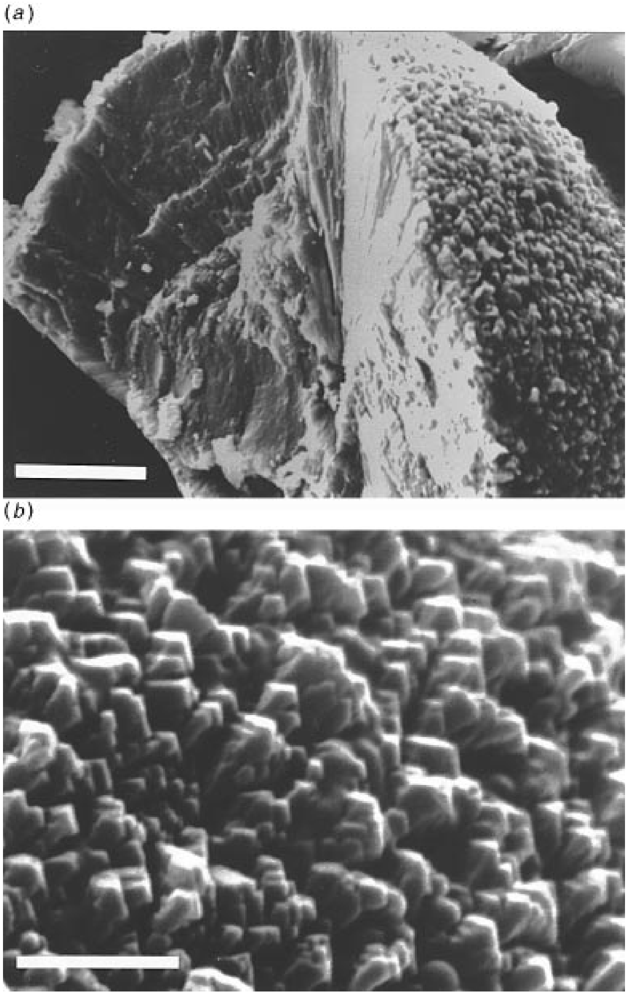

Fig. 4 SEM images of a globular aggregate of magnesium calcite crystals grown in the presence of gelatin films: (*a*) fractured sample showing radially oriented acicular crystals elongated in the *c* axis direction; (*b*) enlarged image of the aggregate surface showing the acicular crystal capped by {10.4} rhombohedral faces. Scale bars: (*a*) 10 μm; (*b*) 2 μm.

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