Magnesium calcite crystallization from water–alcohol mixtures

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Magnesium calcite with unusual magnesium contents up to 14 mol% crystallizes from water–alcohol mixtures. Morphological changes result from interactions of solvent and Mg^{2+} with specific planes of the growing crystals.

Studies on calcium carbonate biogenic crystals[1] are of great interest in inorganic materials chemistry[2,3] and for the biomineralization processes in which organisms are able to exert control over polymorphism, crystal morphology and chemical composition.[4] Chemical compositions are sometimes unusual, as in the case of biogenic calcite from parts of sea-urchin skeleton containing as much as 40 mol% magnesium,[5] whereas a maximum reproducible incorporation of *ca.* 6 mol% magnesium has been reported[6] under *in vitro* conditions close to the biological ones.

Magnesium when present as a cosolute of calcium inhibits the crystal growth of calcite and leads almost completely to the crystallization of aragonite when the magnesium : calcium molar ratios exceed 4.[7] The larger hydration sphere associated with the magnesium ion can represent a barrier to the entrance of this ion into the denser aragonite structure, whereas magnesium can be accommodated inside the calcite structure where it causes a pronounced inhibition of crystal growth. This inhibition has been ascribed to the adsorption of magnesium ions into the growing crystal sites.[8]

This study focuses on the ways in which the reduction of energy of solvation of magnesium ions in water–alcohol mixtures influences the chemical composition, crystal growth and morphology of calcite.

It is known that alkaline-earth metal ions are solvated more weakly in methanol than in water.[9,10] The solvation enthalpies of different alcohols are similar as far as the ion–solvent bond is considered.[11] However, it is reasonable to assume that the perturbation of ions on the bulk structure of the solvent depends on the hydrocarbon chain length and structure of the alcohol. When alcohol–water mixtures are considered the ion solvation has to be intermediate between those of the pure solvents.[11] Thus we infer that the solvation energy of alkaline-earth metal ions decreases on increasing the concentration and the hydrocarbon chain length of the alcohol.

On the basis of these considerations magnesium inhibition of the crystal growth of calcite should decrease in water–alcohol mixtures from methanol to ethanol to propan-1-ol and when the alcohol concentration is increased. Magnesium ions were introduced into water–alcohol solutions of growing calcite crystals with varying magnesium : calcium ratios.† Crystals of calcium carbonate were characterized by powder X-ray diffraction (Philips PW1050/81-PW1710, Cu-Kα radiation), Fourier-transform infrared spectroscopy (FTIR) (Nicolet 250 FTIR spectrometer), inductively coupled plasma emission spectroscopy (ICP; ICP Varian 2100) and scanning electron microscopy (SEM Philips XL20).

We obtained mineral phases containing only calcite or mixtures of calcite and aragonite polymorphs; vaterite was never found. The alcohols cause an increase of the nucleation density which increases with alcohol concentration. The calcite contents of the mineral phases are reported in Table 1 together with the magnesium content within the calcite crystals, as deduced from the reduction of the unit-cell dimensions.[12] Calcite content decreases upon increasing the magnesium concentration in water–alcohol mixtures, but it still accounts for 35% of the mineral phase even for a magnesium : calcium ratio of 5, which does not give any calcite in pure water. The aragonite cell dimensions and IR absorption spectrum do not vary with the magnesium and alcohol content in solution, indicating that magnesium does not enter into the aragonite crystal lattice. In contrast, the magnesium content of calcite crystals increases up to 14 mol% upon increasing the magnesium : calcium molar ratio and alcohol concentration in solution. The characteristic IR absorption peak of calcite at 876 cm^{-1} shifts toward lower wavenumbers (to 872 cm^{-1}) for calcite crystals at higher degrees of magnesium substitution. The peak at 711 cm^{-1}, which shows a characteristic shift in magnesium calcite, cannot be observed since it is overlapped with a band at 713 cm^{-1} due to aragonite.[13,14] The total magnesium content of the mineral phases determined by ICP is invariably greater than that of calcite crystals deduced from X-ray data. Since X-ray and IR spectra indicate that aragonite crystals do not contain appreciable amounts of magnesium the remainder must be adsorbed on the surface of the crystals or located on the boundaries of the crystalline domains, as suggested by Aizenberg *et al.*[15] Besides the higher magnesium content of the calcite crystallized from water–alcohol solutions, it should be noted

Table 1 Calcite content of the mineral phases and magnesium content within calcite crystals

Mg/Ca[a]	% alcohol[b]	% calcite[c]	% Mg[d] (XRD)
1	0	30(5)	3.5(2)
1	25 MeOH	90(5)	4.3(2)
1	25 EtOH	95(5)	4.3(2)
1	25 PrOH	100(5)	5.4(2)
1	50 MeOH	100(5)	3.9(2)
1	50 EtOH	100(5)	4.2(2)
1	50 PrOH	100(5)	4.8(2)
2.5	0	10(5)	4.5(4)
2.5	25 MeOH	20(5)	5.5(4)
2.5	25 EtOH	20(5)	6.4(4)
2.5	25 PrOH	75(5)	6.8(3)
2.5	50 MeOH	55(5)	5.4(4)
2.5	50 EtOH	60(5)	5.9(3)
2.5	50 PrOH	90(5)	6.2(2)
5.0	0	0[e]	—
5.0	25 MeOH	5(5)	10.1(5)
5.0	25 EtOH	5(5)	13.3(5)
5.0	25 PrOH	10(5)	14.1(5)
5.0	50 MeOH	15(5)	9.0(5)
5.0	50 EtOH	15(5)	12.2(5)
5.0	50 PrOH	35(5)	13.3(5)

[a] Magnesium : calcium molar ratio in solution. [b] Volume% of alcohol in solution. [c] The mass percentage of calcite was calculated from the diffraction peak areas using a calibration curve obtained from crystal mixtures of calcite and aragonite with known ratios. [d] Magnesium content deduced from the reduction of the unit-cell dimensions.[12] [e] Only aragonite formed.

that the amount of magnesium incorporated in the crystal lattice increases going from methanol to propan-1-ol.

Calcite crystals grown in the absence of magnesium ion from alcohol–water mixtures always form rhombohedra that exhibit only the {104} family of hexagonal faces. Typical morphologies of magnesium calcite crystals indicating specific interactions of solvent and Mg^{2+} ions with growing crystals are shown in Fig. 1. The morphology of magnesium calcite crystals grown from water has been previously described.[16,17] These crystals express {011} faces indexed on the basis of the angle formed with the *c*-axis as described by Albeck *et al.*[17] Crystals of the same morphology, but with grooves parallel to the edges of the rhombohedron {011} and hollows on the {104} rhombohedral faces, grow from water–alcohol solutions with 25% *v*/*v* of alcohol and a magnesium : calcium molar ratio of 1 [Fig. 1(*a*)]; the hollows and grooves become deeper going from methanol to propan-1-ol. Crystallization from water–alcohol (25% *v*/*v*) and with a magnesium : calcium molar ratio of 2.5 yielded calcite crystals with well developed {011} stepped faces and very small {104} faces reminiscent of the morphology of synthetic crystals obtained from the recrystallization of a solution of dissolved sea urchin spines containing 7.5 mol% magnesium[17] [Fig. 1(*b*)]. This suggests that the presence of the alcohol enhances the specific interaction of magnesium ions with {011} faces with a consequent retardation of crystal growth in the direction perpendicular to these faces. When the concentration of the additives increases they interact nonspecifically with growing calcite crystals. In fact, when the magnesium : calcium molar ratio in solution is 5, polycrystalline aggregates of calcite were observed. These aggregates consisted of oval-shaped units with spheroidal outgrowth [Fig. 1(*c*)].

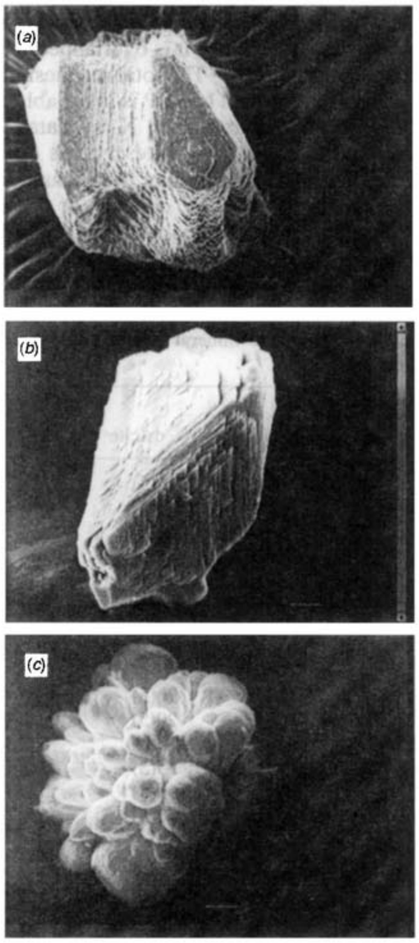

Fig. 1 Scanning electron micrographs of magnesium calcite crystals grown from water–alcohol mixtures containing: (*a*) Mg : Ca molar ratio 1 and 25% *v*/*v* of MeOH, bar = 10 μm; (*b*) Ma : Ca molar ratio 2.5 and 50% *v*/*v* of PrOH, bar = 10 μm; (*c*) Mg : Ca molar ratio 5 and 50% *v*/*v* of EtOH, bar = 10 μm

A mechanism similar to that suggested for the interaction of magnesium and intracrystalline macromolecules of sea-urchin spines[17] with growing calcite crystals can be invoked to explain the changes in morphology and chemical composition of magnesium calcite crystallized from water–alcohol solutions. The reduction of the hydration layer around each magnesium ion caused by the presence of alcohol in solution makes the adsorption of the ions on the crystal surface easier with consequent inhibition of growth in specific directions and control of crystal morphology. Then the partially dehydrated magnesium ions can enter into the crystal lattice and form a solid solution up to a content of 14 mol%, unusual for a synthetic calcite obtained from solution at room temperature.

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Footnote

† Synthetic calcium carbonate crystals were grown by slow diffusion of ammonium carbonate into water–alcohol mixtures (3 ml) containing calcium chloride (10 mmol dm^{-3}) and magnesium chloride. Different magnesium : calcium molar ratios (0, 1.0, 2.5, 5.0) and different concentrations of methanol, ethanol or propan-1-ol (0, 25, 50% *v*/*v*) were used.

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