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Polymorphs and morphologies of calcium carbonate induced by inorganic and organic additives

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Calcium carbonates are common minerals precipitated in both modern and ancient environments. Biological activities have the ability to control the morphologies and polymorphs of calcium carbonates (e.g. calcite, aragonite, vaterite etc.) [1-2]. Series of synthetic calcium carbonates were obtained by the reactions with aqueous solutions of calcium chloride and sodium carbonate in the existence of various inorganic and organic additives in normal pressure and temperature (NPT, P≈1atm, T≤25°C). The precipitates are analysed via scanning electron microscope (SEM) for observation of morphologies and X-ray diffractions (XRD) for phase detection.

In the presence of magnesium chloride, rhombic calcite and spherical vaterite occur, while aragonite is rare (Figure 1 A). With the addition of aluminium chloride, the synthetic products are numerous crystals of rhombic calcite, which aggregate into a cauliflower-like morphology (Figure 1 B).

In the medium of 5% agar gel, three polymorphs of calcium carbonate including calcite, aragonite and vaterite are obtained with various morphologies of rhombic, spherical, fascicular and their aggregated forms. With the increase in concentration of reaction materials, the numbers of nucleations increase accordingly (Figure 1 C). In the presence of glucose, the precipitate consists only of rhombic calcite and their aggregations (Figure 1 D).

Different polymorphs and morphologies of calcium carbonate are induced in the presence of acidic to alkaline amino acids. In acidic amino acids (i.e. L-aspartic acid and L-glutamate) solutions, both rhombic calcite and spherical vaterite existed; moreover, the content of vaterite was higher than that of calcite. However, under the influence of neutral amino acids (L-serine and L-glycine), the only product was spherical vaterite (Figure 1 E), whereas in alkaline amino acids, only micron-sized rhombic calcite was precipitated.

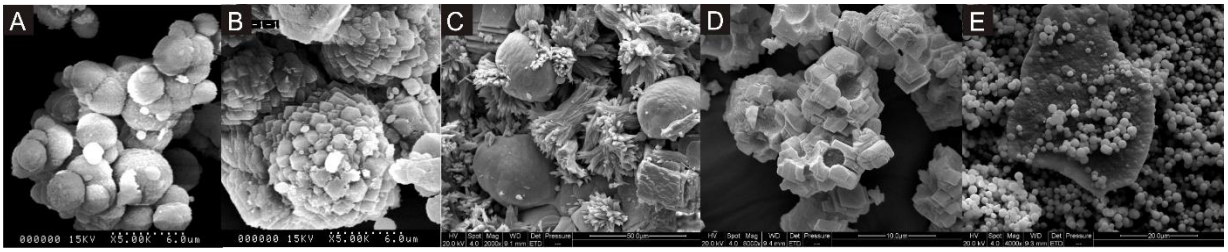

Figure 1: Synthetic calcium carbonates precipitated in the presence of inorganic and organic additives. *A. Spherical vaterite in 0.003 mol $MgCl_2$ solution; B. Cauliflower-like calcite in the solution of 0.1 mol $AlCl_3$;*

C. Calcite and aragonite in the medium of 5% agar gel; D. Aggregations of micro-sized rhombic calcite in 0.1 mol glucose liquid; E. Vaterite precipitated in 0.01 mol L-serine solution.

In summary, these experimental results indicate that both inorganic additives like Mg^{2+} and Al^{3+}, and organic additives like agar and amino acids, all significantly influence the morphologies and polymorphs of calcium carbonates during the crystal growth.

References:

[1] Addadi L et al. (1998) Chem Eur J 4(3): 389-396
[2] Weiner S et al. (2005) Science 309: 1027-1028