

## The Crystallisation of $(\text{Ca,Sr})\text{CO}_3$ on Calcite $\{10\bar{1}4\}$ surfaces: an AFM Study

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It is well known that the presence of foreign ions in a growth medium can substantially affect the crystallisation process modifying the growth rate of the faces, the shape and height of the steps and the composition of the growing phase (Chernov 1984, Sangwal, 1993). Eventually, the presence of certain ions can promote the nucleation and subsequent growth of a secondary phase. A complete understanding of such possible effects requires the knowledge of (1) the thermodynamic and kinetic behaviour of the solid solution- aqueous solution (SS-AS) system and (2) the role that crystal surfaces play in the incorporation of growth and foreign units in the solid phase.

In this work we present an experimental study of the crystallisation of  $(\text{Sr,Ca})\text{CO}_3$  on calcite  $\{10\bar{1}4\}$  faces from an aqueous solution. In this system, the difference between the radii of the cations is large and there is not a complete solid solution between end-members. Moreover, two limited solid solutions are possible: one with a calcite-type structure and one with an aragonite-type structure. Crystal growth experiments were carried out in situ in a fluid cell of an Atomic Force Microscope (AFM) at 25°C.  $\text{Ca}^{2+}\text{-Sr}^{2+}\text{-CO}_3^{2-}$  aqueous solutions were prepared by mixing  $\text{Na}_2\text{CO}_3$ ,  $\text{Sr}(\text{NO}_3)_2$  and  $\text{CaCl}_2$  aqueous solutions. Different concentrations of  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  were used in each experiment maintaining constant supersaturation with respect to calcite ( $\beta=5$ ).

In all experiments step advancement was immediately observed after injecting the solution. In order to avoid solution/sample equilibrium a fresh solution was injected at intervals of about 30 seconds. When the amount of  $\text{Sr}^{2+}$  present in the solution was low, a "normal" step advancement on the calcite surface was observed. However, when these steps reached a newly

formed surface, the advancement of the steps was momentarily stopped, exactly reproducing the previous surface topography. Then a dendritic step advancement occurred. On the other hand, when the amount of  $\text{Sr}^{2+}$  was higher, AFM images showed simultaneous dissolution and growth processes on the calcite surface. Experiments carried out using the same reactive concentrations, but injecting fresh solution only at the beginning of the experiments showed a similar behaviour. Growth occurred after injecting the solution, but then a subsequent dissolution process was observed. The dissolution affected not only the newly produced surface but also the previous substrate. Images taken in different areas of the surface showed the formation of a secondary phase, probably  $\text{SrCO}_3$  orthorhombic (strontianite). AFM as well as SEM images revealed a structural control of the calcite surface on the strontianite nucleation.

The interpretation of the crystallisation phenomena must be made taken into account the structural, thermodynamic and kinetic factors. So, the presence of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  in solution leads to the growth of a phase with the calcite structure. Moreover, after a certain waiting period, when the concentration of  $\text{Sr}^{2+}$  in the solution adjacent to the crystal surface is high enough, thermodynamic and kinetic factors overcome the crystallographic control and strontianite nucleates on the calcite surface. A coupled process of calcite dissolution-strontianite growth takes place.

Chernov AA, *Modern Crystallography III*, Springer-Verlag, (1984).

Sangwal K, *J. Crystal Growth*, **128**, 1236-1244, (1993).