Influence of silicic acids on the growth of calcite

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Carbonate minerals frequently show non-crystallographic morphologies. They are often referred to be of biologic origin if grown in natural medias. However, non-crystallographic habits (also called Induced Morphology Crystal Aggregates, ICMA) can as well be obtained by crystallization of carbonates in silica gels at high pH (e.g., Garcia-Ruiz, 1985). The pores of these gels contain silicic acids (Si_{aq}) which act as growth modifier. Silicic acids are present in nearly all plants and animals. Therefore besides amino acids, silicic acids are among the most important factors in biomineralisation. To study the influence of silicic acids on the growth of calcium carbonate we performed gel growth experiments and growth experiments with atomic force microscopy (AFM). The gel growth experiments allowed us to obtain macroscopic calcites (ca. 500 μm in size) with modified morphologies. Whereas the AFM experiments allowed us to investigate the $\{104\}$ face of calcite *in situ* and in molecular resolution. In the AFM experiments calcite $\{104\}$ surfaces grew from aqueous solutions with supersaturations between β_{Calcite} = 2.9 and 31 at a pH of 10.2. Silica concentrations ranged from 10 ppm to 200 ppm. The main findings of both the gel growth and the AFM experiments are: i) Si_{aq} has a double effect on the advance rates of the steps: it enhances the growth at low concentrations and inhibits growth at concentrations above about 20 ppm. ii) Growth on the $\{104\}$ surfaces occurs via the nucleation of two dimensional islands. These islands become elongated along the [42-1] direction, i.e. along the trace of the c-glide plane. This elongation is pronounced with increasing Si_{aq} content. iii) Simultaneously to the elongation of the 2D-islands we observe that the steps become rounded. A possible explanation is that silica blocks the kink positions that separate the junction between *acute* and *obtuse* steps. iv) The inhibitory effect of silica on the growth of calcite is similar to the effect of magnesium (Davis *et al*., 2004). It leads to an elongation along the c-axis and stabilises the faces parallel to these axis. From these findings we conclude that silica acts as both a growth inhibitor and a growth promotor of calcite. The inhibitory effect might be explained by *Step-Pinning*, whereas the promotor effect might be explained by changes in the surface energy. Moreover silicic acids enhance the two dimensional nucleation and lead to catastrophic three dimensional nucleation. Silicic acids therefore are key substances in biomineralisation as they interact with both ions and proteins in the extrapallial fluid of almost all organisms.

References

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