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Nanoscale observations of crystal growth of calcite in the presence of sulfate ions: An AFM study.

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Sulphate is a dominant ionic species of seawater as well as occurring in many natural waters. It is known that a growing calcite crystal can incorporate sulphate into the crystal lattice [Frisia et al, 2005]. In situ atomic force microscopy (AFM) has been used to compare the growth of pure calcite and the growth of calcite in the presence of sulphate ions from aqueous solutions at a constant value of supersaturation (S.I. = 0.9) with respect to calcite, in an attempt to specify where on a growing crystal surface the SO_4^{2-} is incorporated. Supersaturated solutions with a Ca:CO_3 ratio 1:1 and pH of 10.0 were prepared and sulphate was added as Na_2SO_4. The solution composition was readjusted to keep the supersaturation and pH constant. PHREEQC was used to determine relevant solution concentrations and *in situ* AFM experiments of calcite growth were made using a fluid cell and flowing solutions over a freshly cleaved calcite surface. Growth rates were determined from the closure of the rhombohedral etch pits induced by an initial dissolution with pure water. The spreading rate of 2-dimensional nuclei was also measured. At low concentrations of sulphate ($<$0.5mM), no effect on the growth rate of the calcite was observed. At higher concentrations (2 to 3mM) of sulphate, the growth rate increased, while at much higher concentrations (up to 60mM) the growth rate was substantially decreased. The morphology of 2-dimensional growth nuclei became increasingly elongated with increasing sulphate content. Measurements of step height showed that newly grown steps were approximately 1Å higher when grown in high sulphate concentrations, compared to steps grown in sulphate free so-

lutions. AFM experiments indicate that the new growth has incorporated sulphate into the calcite surface. Macroscopic growth experiments have been carried out to attempt to quantify the composition of calcite grown in the presence of sulphate.

Reference:

Frisia, S., Borsato, A., Fairchild, I.J., Susini, J., **2005**. Variations in atmospheric sulphate recorded in stalagmites by synchrotron micro-XRF and XANES analyses. Earth and Planetary Science Letters, 235, 729– 740.