Role of polysaccharides in calcite (re)crystallisation

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Polysaccharides are often suspected for inhibiting chalk recrystallisation. Well known is the dual role of polymers in crystallisation control. They act as inhibitors when free in the solution, but when immobilized at surfaces, they can promote mineralization. This duality is shown in [1] where calcite growth, initially inhibited by alginate, resumed after alginate immobilization at the surface. Independent of supersaturation, induction time for resuming calcite growth drastically increases (Fig.1) when adsorbed concentration approaches its maximum 7.5E-4 g/m^2. At maximal adsorption, alginate can no longer serve as a good template for calcite overgrowth. Alginate molecules spread and arrange in flat positions at the surface, where all their carboxylic groups are occupied in binding on Ca^{2+} that is part of the mineral structure, thus retarding ion transport to the surface. Under these conditions, diffusion becomes rate determining for calcite growth. Because of extremely low supersaturation, this is not the case when alginate inhibits calcite recrystallisation and the overall process proceeds in the surface kinetics range. This is the reason why the relative inhibition of calcite recrystallisation is much lower than that of calcite precipitation.

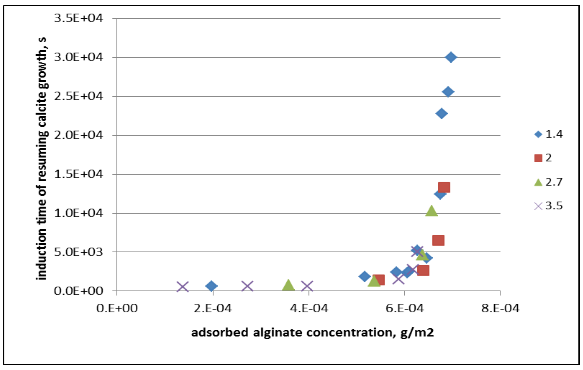

Figure 1. Induction time for calcite growth to resume after inhibition as a function of adsorbed alginate concentration for a series of solution supersaturations.

[1] Lakshtanov *et al*.. (2011) Geochim. Cosmochim. Acta, **75**, 3945-3955.

Direct Measurements of Isotopic Fractionation Factors of Water Vapor over Ice for Temperatures below 235 K

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The use of the isotopic composition of water vapor as a tracer for convective and microphysical processes is complicated by the fact that isotopic fractionation factors have not previously been directly measured at the temperatures characteristic of much of the upper troposphere (< 235 K). Instead, fractionation factor values used in models are extrapolated from measurements made at higher temperatures [1, 2]. We report on the first direct determination of the equilibrium fractionation of HDO/H2O between water vapor and ice at temperatures below 233 K, obtained during the ISOCLOUD measurement campaign at the AIDA cloud and aerosol chamber. The ISOCLOUD campaign involved a series of adiabatic expansion experiments over a range of temperatures between 190 and 233 K, during which measurements were made of water vapor and total water (vapor + ice) and their isotopic compositions. Modeling of vapor sources, sinks and ice cloud formation during the expansion experiments then allowed determination of the degree of preferential condensation of the heavier isotopologues.

[1] Merlivat, L. & G. Nief (1967) *Tellus* **19**, 122-127. [2] Ellehøj, M. (2010) Ph.D. thesis, *University of Copenhagen*

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