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Arctic hot-springs and self-organized rimstone terraces at Spitsbergen

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The 'Troll' springs are located along a major fault zone along the Western shore of Bockfjorden, Spitsbergen at 80°N and probably represent the northernmost thermal springs ever reported. The springs are dominated by sodium and bicarbonate. Six active springs have deposited travertine terraces along an approximately 800 m long section. Terrace formation is still ongoing and we have studied a spectacular arrangement of travertine terraces comprising an area more than 100 m across around one of these springs. The total range in water temperature, pH, and CO_2-content from source to terrace rims recorded in the field was: 27.4-11.3°C, 6.6-8.4, and 372-140 mg/l, respectively. Carbonate precipitation rates driven by the CO_2-degassing ranged from zero to about 2 mm/year based on measured precipitation on fine-grained limestone chips located around in the pools. The highest precipitation rate was measured at terrace edges.

The self-organized generation of the terrace patterns is related to the coupling between the hydrodynamics and the rate of carbonate precipitation. We have carried out numerical and physical experiments to study how terrace-formation is controlled by coupled precipitation and fluid flow. The experiments demonstrate how fluid flow down an initially smooth slope with small initial perturbations leads to the growth of terraces. Terrace edges migrate downstream, and the pools coarsen with time as smaller pools are flooded and disappear.

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NMR study of citrate coprecipitation with calcite

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Interaction of organic ligands with mineral surfaces during precipitation is an important consideration in a number of areas, including biomineralization and contaminant transport and retention. Complexation with organic ligands can control mineral phase and morphology and affect metal incorporation in the mineral phase. We are investigating the effect of organic molecules on calcite precipitation. Calcite was synthesized by the constant addition method, with citric acid added to the $CaCl_2$ solution. The precipitates, finely crystalline, were filtered, rinsed repeatedly in deionized water and dried at 60°C. XRD indicates calcite as the only solid phase. A small amount of the solid was subsequently re-dissolved in high-purity HCl solution and analyzed for citrate by ion chromatography. The IC results indicate the calcite contains approximately 0.5 wt. percent citrate. Molecular-scale structural interaction between the citrate and calcite host was investigated by ^{13}C and ^{1}H NMR spectroscopic methods.

The $^{13}C\{^{1}H\}$ CP-MAS spectra of the calcite/citrate coprecipitates at natural ^{13}C abundance contain broad peaks at chemical shifts near 183, 78, and 47 ppm consistent with the carboxyl, central C-OH, and secondary carbons of citrate. In addition, a narrow peak of similar intensity occurs near 168.7 ppm, corresponding to carbonate that must occur in close spatial proximity to hydrogen. However, ^{1}H-NMR spectra are dominated by signals from quasi-rigid water molecules. Comparison with samples prepared in D_2O, and without citrate in H_2O, indicate that approximately five water molecules accompany each citrate in the structure. Detailed examination of the ^{13}C-^{1}H cross polarization dynamics and 2-dimensional $^{13}C\{^{1}H\}$ heteronuclear correlation (HETCOR) spectra on samples prepared with ^{13}C-enriched carbonate show unambiguously polarization transfer between the carbonate carbons and hydrogen on the citrate. In particular, the carbonate trace in the HETCOR spectra of a sample prepared in D_2O contains a broad spinning sideband envelope consistent with the methylene protons on the citrate. These data indicate that the citrate is bound in the calcite structure, with citrate-carbonate distances of a few Å. Some additional data were obtained for incorporation of aspartic and glutamic acids, present at concentrations about 50 times lower than observed for citrate, whereas signal from phthalic acid could not be detected. These results suggest that, in addition to metal-ligand complexation, the structural role of water and hydrogen bonding interactions may need to be considered to understand organic/calcite interactions.