

CaCO₃ polymorph growth and stabilization in water-ethanol mixtures

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Alcohol-water mixtures can control the mode of precipitation and morphology of crystalline CaCO₃. However, these two characteristics are sensitive to experimental parameters such as concentration, calcium source, temperature, precipitation method and mixing speed. An understanding of the growth of CaCO₃ in alcohol-water mixtures is important because control of the precipitating polymorph and its morphology are two central parameters for successful biomineralization of CaCO₃.

We used a simple, homogeneous precipitation method, where we fixed temperature (24 °C) and total concentration of CaCl₂ and Na₂CO₃ (25 mM) and varied the proportion (10 and 50%) of alcohol, shaking speed, type of alcohol (ethanol, 1-propanol and 2-propanol) and reaction time (1 h to 4 m). Diffraction and imaging results show that shaking speed and alcohol concentration are the determining parameters for vaterite and aragonite stabilization. They also control vaterite morphology, which varies from cauliflower shaped aggregates to dendrites (Figure 1). We also present an equation for controlling the synthesis of aragonite:vaterite and aragonite:calcite ratios.

The evolution of the precipitates over time lead us to conclude that this system is described by classical growth with twinned aragonite and spherulitic vaterite and aragonite. Solutions with a low water activity can be used as a switch for control of polymorph and morphology and thus define new possible pathways for biomineralization processes.

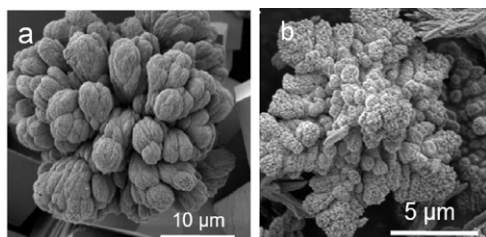


Figure 1: Vaterite precipitated in (a) 10% and (b) 50% alcohol under vigorous shaking. With gentle shaking, vaterite did not form in experiments with 50% alcohol.

Electron donating properties of humic substances and implications for pollutant phototransformation

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Humic substances (HS) play a key role in many biogeochemical and pollutant electron transfer reactions. Past research primarily focused on HS redox properties under anoxic conditions. This contribution will present the results of a systematic characterization of the electron donating properties of a diverse set of HS under oxic conditions and, for selected HS, relate their antioxidant properties to inhibitory effects on the indirect phototransformation of organic pollutants.

Electron donating capacities (EDCs) were measured by electrochemical oxidation using 2, 2'-azino-bis (3-ethylbenzothiazoline-6-sulphonic acid) radicals to mediate electron transfer from HS to the working electrode [1]. The number of oxidizable moieties at constant pH and applied reduction potential, E_h , increased from microbial to terrestrial HS and was highest for mixed aquatic-terrestrial HS. For a given HS, EDC values increased with increasing pH and E_h . Strong positive correlations of EDC with HS titrated phenol contents and, for mixed terrestrial-aquatic HS with aromaticities indicates that phenols and hydroquinones are the major electron donating moieties in HS.

HS may decrease indirect phototransformation rates of organic pollutants by donating electrons to oxidized reaction intermediates [2]. Combined electro- and photo-chemical experiments with anilines as model pollutants showed that the inhibition efficiencies of HS on pollutant phototransformation increased with their EDCs. Furthermore, the inhibition efficiency for a given HS increased with increasing pH, in parallel with increasing EDC. Pre-treatment of HS with chemical oxidants, including ozone and chlorine dioxide, reduced the number of electron donating moieties, reflected by significant reduction in both inhibition efficiency and EDC values. These results suggest that EDC and inhibition efficiency on organic pollutant phototransformation are determined by the number and potential distribution of hydroxybenzene moieties present in HS.

[1] Aeschbacher, A. M. Sander, & R.P. Schwarzenbach (2010) *Environmental Science & Technology*, **44**, 87–93. [2] Wenk, J. U. von Gunten, & S. Canonica (2011) *Environmental Science & Technology*, **45**, 1334–1340.