

Silica influence on calcium carbonate precipitation

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Precipitation of calcium carbonate is known to occur extensively in many natural coastal and marine environments. Moreover, it is a source of major interest to industry because it forms scale in boilers, cooling towers, etc. Calcium carbonate plays a significant role in the geochemical behaviour and balance of trace elements. It is known to adsorb and incorporate di- and trivalent metals, but much less is known about the interaction of carbonates with silicon. Even though replacement of carbonate minerals by silica polymorphs in geological environments is a common phenomenon in sedimentary rocks.

The aim of the present work was to investigate the effect of dissolved silica on the kinetics of spontaneous precipitation of calcium carbonate under various degrees of supersaturation and $\text{SiO}_{2(\text{aq})}$ concentration.

Experiments were performed in the beakers, closed to the atmosphere, by quickly mixing CaCl_2 and NaHCO_3 solutions, with or without dissolved silica. pH of solutions was measured to monitor the kinetics of homogeneous nucleation. After the lapse of a certain time after mixing of solutions (induction period), formation of calcium carbonate began, resulting in a drop of pH.

As expected, the induction time decreases with increasing supersaturation. Increasing silica concentration shortens the induction time. All experiments yielded a mixture of vaterite and calcite but dissolved silica promotes the formation of calcite. It can be assumed that the initially nucleated calcium carbonate polymorph was vaterite. Dependence of the induction time on supersaturation may be used to estimate the surface free energy of the nucleating phase, σ . For a 'pure' system without silica, $\sigma \approx 42 \text{ mJ m}^{-2}$ agrees well with that reported in literature for vaterite and indicates some degree of heterogeneous nucleation. This can occur because of the relatively low degrees of supersaturation used for the experiments. σ values obtained in the presence of silica (37 and 34 mJ m^{-2} for 1 and 2 mmole silica) indicate a higher degree of heterogeneous nucleation provided by increasing amounts of polymeric silica.

Mineral-solution partitioning and sedimentary organic carbon fluxes

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A complex soup of assorted dissolved organic compounds can be found in lakes, rivers and oceans. Some of this organic matter (OM) is associated to mineral phases and the composition of the dissolved organic compound mixture is largely dictated by the adsorption efficacy and availability of mineral surfaces. In sediments, about 90% of the OM is bound – to some extent reversibly – onto minerals, leaving a mere 10% in discrete organic debris [1]. The presence of a sizeable mineral-bound OM pool implies that porewater dissolved organic matter (DOM) concentrations are well buffered by surrounding mineral phases and by the OM that they provisionally retain. We show, through laboratory simulations, that DOM is strongly partitioned between mineral surfaces and ambient waters. Through stable isotope analysis, we demonstrate that the composition of porewater DOM is regulated by an exchange mechanism of organic matter between the solids and the solution. Partitioning is influenced considerably by the mineralogy of the solid phases. In particular, authigenic iron and manganese oxides, formed through diagenetic processes are typically concentrated at or near the sediment-water interface, increase the efficiency of DOM sorption in sediments. The presence of a strongly sorbing layer located in the uppermost sediment layers will play an important role in regulating the magnitude and composition of diffusive sedimentary DOM fluxes.

[1] Hedges & Keil (1995) *Marine Chem.* **49**, 81-115.