

## Crystal growth and dissolution in terms of the rates of attachment of ions from solution and their detachment

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Traditionally, rates of mineral growth and dissolution are measured against the bulk saturation state of the system, e.g. relative to a bulk solubility product constant. It has been recently shown that the growth rate of two common step orientations of calcite vary while exposed to solutions with a fixed saturation index but variable aqueous calcium-to-carbonate ratio.[1] Specifically, obtuse step orientations grow faster under solutions containing high calcium ratios, where acute step orientations grow faster under low to moderate calcium ratios. Additionally, putative dissolution features were observed on the surfaces exposed to solutions containing high calcium-to-carbonate ratio. Similar anomalous dissolution under supersaturated conditions is observed for another sparingly soluble salt, barite. The apparent contradiction between the bulk thermodynamics of the system and reaction of individual step reactivities is addressed by examining the change in step-edge energy with changing ratio.

A theory is derived where step velocity is expressed as a function of independent rates of attachment and detachment of ions to and from the step. Attachment rates are believed to be driven by diffusion, ligand exchange reactions of the aqueous ion and mineral surfaces whereas detachment reactions are believed to be controlled by bond breakages from the surface. Supporting this interpretation, fitted rate constants for attachment compare favorably to the rates of water exchange reactions for the aqueous ions and simulations of rates of attachment of aqueous ions to planar calcite surfaces.[2]

[1] Stack, Grantham (*in press*) Cryst. Growth Des. [2] Kerisit, S. Parker, S. C. (2004) Free energy of adsorption of water & metal ions on the {1014} calcite surface. *J. Am. Chem. Soc.* **126**, 10152–10161.

## Fossilized microbes in methane-derived carbonates: False interpretation or the true evidence?

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The ability of living microorganisms to mediate carbonate precipitation is an important geobiological action of our planet. Still little is known about the role and coupling of microorganisms to the formation of individual carbonate minerals. In methane-saturated sediments, carbonate mineralisation is resulted from chemosynthetic carbon fixation by prokaryotes via anaerobic oxidation of methane (AOM). The lack of possibilities of carrying out culture experiments with anaerobic methanotrophs leaves a gap in the knowledge on the biogeochemical binding of two phenomena: AOM and associated carbonate genesis.

AOM-related carbonate precipitation results in partial incorporation of methane-derived carbon into a carbonate lattice. We applied a combination of inorganic and organic molecular tools, including diverse microscopy methods accompanied with U/Th dating, lipid biomarker study and stable carbon and oxygen isotope measurements for several pieces of fossil carbonate towers outcropping into the water column at the peripheral part of the Amon mud volcano (Eastern Mediterranean). The polarized light microscopy accompanied with cathode-luminescent and scanning electron microscopy revealed a number of structures morphologically resembling mucus-secreting microbial mats, consortia of archaea and sulfate reducing bacteria catalyzing AOM, filamentous bacteria, and other microbe-like shapes in fossil preservation. All carbonates were composed by almost pure aragonite with a negligible admixture of secondary high-Mg calcite and scarce crystals of dolomite. High-Mg calcite was dominantly found around microbial-like 'cells' structures. The  $\delta^{13}\text{C}$ -CaCO<sub>3</sub> and  $\delta^{18}\text{O}$ -CaCO<sub>3</sub> measurements from visually different parts of a carbonate sample, where assumed 'cells' were observed, revealed a noticeable variation in  $\delta^{13}\text{C}$ -CaCO<sub>3</sub> values and relatively stable  $\delta^{18}\text{O}$ -CaCO<sub>3</sub>. Lipid biomarker analysis from the same parts of the carbonate showed different AOM-mediating anaerobic methanotrophs. On this scales, our presentation will deal with microbial and mineral mapping within several methane-derived carbonate precipitates. We will discuss whether fossilized shapes are preserved microbes or they are a false impression that supposedly relate to mineral/organic diagenesis. The paper compares obtained detailed data with currently known and novel insights on methane-derived carbonate development.