

Calcite step growth velocities; a function of saturation index and the Ca^{2+} to CO_3^{2-} activity ratio

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Calcite (CaCO_3) growth rate has an impact on many natural and industrial processes, ranging from biomineralisation to carbon storage and pipe scaling. Larsen *et al.* [1] noted that Ca^{2+} to CO_3^{2-} activity ratios in natural waters are rarely unity and demonstrated that growth velocities of the calcite acute and the obtuse steps varied with the Ca^{2+} to CO_3^{2-} ratio at constant states of supersaturation. We have extended the work of Larsen *et al.* to quantify the growth rates for acute and obtuse steps as a function of saturation index (SI) and Ca^{2+} to CO_3^{2-} activity ratios. Microscopic analysis of growth spirals show that absolute growth velocities change with SI. We have also observed that, independent of SI, acute step velocities are higher than obtuse velocities at low Ca^{2+} to CO_3^{2-} ratios, whereas obtuse step velocities are higher at higher Ca^{2+} to CO_3^{2-} ratios (Fig. 1). This shift is certainly related to the different geometries of the acute and obtuse steps.

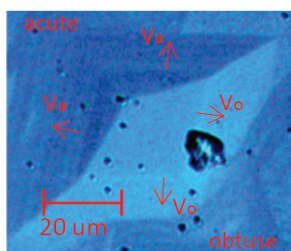


Figure 1. Growth spiral at a $\text{Ca}^{2+}/\text{CO}_3^{2-} = 50$. The obtuse step velocities are faster (V_o) and apex shifts toward the acute corner.

These results have implications for current models of calcite growth and reaffirm that calcite growth cannot simply be described using classical crystal growth theory intended for the high order symmetry of cubic atomic lattices. The rhombohedral symmetry of the calcite atomic structure must be considered.

[1] Larsen *et al.* (2010). *Geochimica et Cosmochimica Acta* **74**, 2099-2109

Quantification of organic matter redox states by mediated electrochemical analysis

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Electron transfer reactions involving organic matter (OM) play a key role in carbon and element cycling in wetlands. Under anoxic conditions, OM may act as terminal electron acceptor in anaerobic microbial respiration. Reduction of OM may competitively suppress electron transfer to CO_2 and hence methanogenesis. Under oxic conditions, OM is susceptible to enzymatic oxidation, which ultimately leads to OM mineralization and hence CO_2 emissions. Despite the widely recognized importance of OM redox reactions to the biogeochemistry of wetlands, these reactions were difficult to study in past work as direct quantification methods were missing. We recently introduced mediated electrochemical analysis as a novel approach in which water-soluble organic mediator compounds are used to facilitate electron transfer and redox potential equilibration between OM and electrodes. The approach includes two types of measurements: (i) Mediated electrochemical reduction and oxidation directly quantify (changes in) the numbers of electrons that small OM samples accept and donate in electrochemical cells with well defined redox conditions. (ii) Mediated potentiometric redox potential measurements can be used to determine (changes in) the reduction potentials E_h of OM samples and on the thermodynamics of redox reactions involving OM. The unique capabilities of mediated electrochemical analysis for the analysis of OM redox dynamics in wetlands will be highlighted by results of two mechanistic laboratory studies. In the first study, mediated electrochemical analysis was used to quantify changes in the redox states of different OM over successive microbial reduction and O_2 -oxidation cycles. The results demonstrate that electron transfer to and from OM was fully reversible, that system thermodynamics controlled the extents of microbial OM reduction, and that OM accepted electrons over wide E_h ranges. In the second case study, OM oxidation during incubation with phenoloxidases (i.e., laccases) was quantified, and fast, extensive and irreversible enzymatic oxidation of phenolic moieties in OM was demonstrated. Implications for OM redox dynamics in wetlands under anoxic and oxic conditions will be discussed.