Nonmonotonic Coupled Dissolution-Precipitation Reactions at the Mineral–Water Interface

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Dissolution is inherent to fluid-mineral systems. Yet its impact on minerals reacting with electrolytes is overlooked. Here, a novel nonmonotonic behavior for the surface interactions of carbonates (calcite and Mg-calcite) with organic acids is reported. Applying a bioinspired approach, Mg-calcite sensors via amorphous precursors, avoiding any preconditioning with functional groups are synthesized. A quartz crystal microbalance is used to study the mass changes of the mineral on contact with organic acids under varying ionic conditions, temperatures, and flow velocities. Supported by confocal Raman microscopy and potentiometric titrations, nonmonotonous mass developments are found as a function of Ca$^{2+}$ concentration and flowrate, and attributed to three coupled chemical reactions: i) carbonate dissolution via Ca$^{2+}$ ion complexation with organic molecules, and the formation of organo-calcium compounds as ii) a surface phase at the mineral–water interface, and iii) particles in the bulk fluid. These processes depend on local ion contents and the precipitation onset (i.e., saturation index) of organo-calcium salts, both of which substantially differ in the bulk fluid and in the fluid boundary layer at mineral interfaces. This continuum between dissolution and precipitation provides a conceptual framework to address reactions at mineral interfacial across disciplines including biomineralization, ocean acidification and reservoir geochemistry.

1. Introduction

Dissolution is intrinsic to all mineral–fluid systems. This is exemplified by biomineralization processes,[1] the discoloration of monuments,[2] fluid displacement in rock formations,[3] weathering of rocks,[4] and mineral (in)stability in acidified oceans.[5] In any attempt to understand, quantify, and model these mineral–solute interactions, substrate solubility is an intrinsic factor to consider. Yet the ion and colloidal interactions between solutes and minerals are often described without any account of mineral dissolution.

Constituting a significant fraction of the Earth’s crust, carbonate minerals participate in carbon exchange between land, oceans, and the atmosphere. Carbonates are particularly amenable to surface modifications with organic species, utilized for the biological and biomimetic synthesis of fascinating crystalline structures and also for manufacturing composite materials.[1,6] Despite its fundamental and technological importance, our scientific understanding of the interfacial interactions of carbonate minerals with various solutes is incomplete. An important lack of insight pertains to the substantial dissolution rates of carbonate minerals, which can yield a half-life on the order of seconds for the surface sites (Figure 1a). In relation, for poorly soluble minerals such as quartz, this half-life can be several days.[7] The high reactivity of carbonates has severely limited experimental attempts at addressing the transfer mechanisms of solute species between bulk fluids and carbonate surfaces in various disciplines including:

a) Biomineralization: Living systems exploit organic–inorganic interactions to produce fascinating skeletal structures from ionic and colloidal crystal precursors.[3] A key concept explaining the consistent crystallographic features of biominerals is stereochemical complementarity between macromolecules and crystal facets. However, X-ray reflectivity measurements identify a distorted interfacial mineral structure to depths of six unit cells associated with highly structured water layers.[8] Also biominal-associated proteins often lack a fixed 3D structure.[9] Together these evidences question the scope of “lock and key” interactions between (bio)macromolecules and mineral surfaces. Yet numerous instances of macromolecules binding selectively to crystal-facets have been reported, for instance in phage display libraries.[10] This contrast highlights the need for a
better understanding of the interfacial interactions during biologically-guided crystal growth.

b) Ocean acidification: While it is generally accepted that rising seawater pCO$_2$ levels threaten marine calcification, the assessments of carbonate dissolution in the presence of organic carbon have presented mixed observations. For example, organic matter naturally codeposited with biominerals was found to suppress dissolution of the underlying mineral phase. Yet in simple synthetic systems, negligible effects of organic molecules on the rates of mineral dissolution have also been reported. Moreover, the estimated dissolution rates of coccoliths have been reported as close to those of pristine calcite when close to equilibrium, but much lower when far from equilibrium. With the projected severe consequences for marine calcifiers in the coming decades, these uncertainties and nonlinear relations for the interfaces and (in)solubility of marine carbonates in gradually acidifying environments must quickly be resolved.

c) Carbonate geochemistry: With goals of storing tons of captured CO$_2$ in or extracting oil from underground rock formations, the chemistries of geochemical fluids are thoroughly investigated with intents to tune the surface properties of underground rocks. Researchers anticipate several mechanisms to affect the surface properties of rocks, such as: ion-exchange, mineral dissolution, electrostatic interactions, and changes to the colloidal surface interaction forces. However, the surfaces of microscale carbonate grains within rock formations have only recently gained attention, with rock bound organo-ionic layers identified as a key determinant for mineral reactivity.

With substantial spatiotemporal scales, implementation costs, and ambitious climate goals associated with these geochemical endeavors, there are still many open questions in our fundamental understanding of the interfacial interactions between heterogeneous fluids and natural minerals.

From this, it is clear that the knowledge of mineral–organic interactions involving soluble minerals such as calcium carbonate (CaCO$_3$) is still incomplete and this missing key is essential to address problems across disciplines all centered around the surface reactions of minerals. For an ideal (insoluble) substrate, sorption processes involve “specific” electrostatic interactions with surface sites and “non-specific” interactions such as hydrophobic effects, Van der Waals forces and (de)solvation. However, the soluble nature of minerals necessitates two additional considerations.

First, precipitation processes can involve surface phases formed via interfacial reactions, as illustrated by the chemical equilibria for a metal cation (M$^{2+}$) interacting with a carbonate surface

(a) Adsorption of M$^{2+}$ on CaCO$_3$:

$$\text{CaCO}_3(s) + M^{2+} \leftrightarrow \text{CaCO}_3(s) + M^{2+}$$

(b) Dissolution/Precipitation of M$^{2+}$ as a surface phase (related to the solubility product of the surface phase, $K_{sp}$):

$$\text{MEO}_3(s) + HCO_3^- \leftrightarrow \text{MEO}_3(s) + H^+$$

Figure 1. a) Dissolution rates and estimated half-life of surface groups (>OH or >CO$_3$H) of different minerals, assuming that dissolution rates determine the mean reactivity of surface groups. Reproduced with permission. Copyright 1997, Elsevier. b) Schematic depiction of the time ($t$) development of a boundary layer at the calcite-fluid interface, referring to a region which extends from the mineral surface to a plane beyond which ion concentrations represent thermodynamic equilibria in bulk fluid. Distinct ion contents C(s) and saturation conditions can exist within the boundary layer relative to the bulk solution C(b) under nonequilibrium conditions.
Adsorption and dissolution processes play a key role in the interaction between minerals and organic molecules, often leading to complex reaction pathways. For instance, the dissolution of CaCO$_3$ can be described by the reaction:

$$\text{CaCO}_3 + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} + \text{H}_2\text{O}$$

Dissolution/Precipitation of CaCO$_3$ (related to the solubility product of calcite, $K_{\text{sp, CaCO}_3}$) can be represented by:

$$\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$$

While specifically addressing soluble minerals as sorbents, this surface precipitation model is also limited to inorganic adsorbates.

Second, for soluble minerals, the ionic conditions at fluid-mineral interfaces can substantially differ from the bulk fluid and involve a distinct interface-associated fluid composition termed as a “boundary layer”. Atomic force microscopy and interferometry have shown the existence of fluid boundary layers at mineral interfaces. Originating from carbonate dissolution (Figure 1b), this interfacial fluid boundary layer can be supersaturated with respect to one or multiple mineral phases while the bulk fluid is not. Yet in numerous studies, sorption events involving soluble adsorbents such as CaCO$_3$ are still described by fitting of Langmuir and Freundlich models to adsorption isotherm data, which accounts neither for surface precipitation nor for mineral dissolution. Hence, a mechanistic picture for the interfacial interactions between minerals and organic molecules, that can also sustain a conceptual framework to address the surface reactions in complex natural and synthetic environments, is urgently missing.

In this paper, we show that the dissolution and surface modification of soluble minerals (calcite and Mg-calcite) in the presence of organic acids are interconnected processes and highly responsive to variations in ionic conditions, sorbent type, temperature, and flow velocity. Following a systematic experimental approach, first, the surface characterization of calcite crystals treated with solution mixtures of organic acids and Ca$^{2+}$ ions is performed. Second, using a Quartz Crystal Microbalance with Dissipation monitoring (QCM-D), we investigate with high sensitivity the responses of the mineral mass to applied ionic conditions, nature of organic acids and temperature. For this purpose, we also introduce a new method to functionalize the QCM-D sensors with Mg-calcite. And third, the outcomes for the nonmonotonic organo-mineral interactions are addressed with respect to the bulk saturation for the respective organo-calcium salts and applied flow velocities. Additional compositional and structural insights for the organo-mineral interactions are gained from confocal Raman microscopy and potentiometric titrations. By integrating these analytical approaches, we provide a physical framework to address the organic modifications of soluble minerals in relation to the distinct composition and structure of the mineral-water interface. In this manner, we elucidate a dynamic and nonmonotonic behavior for interface coupled dissolution-precipitation reactions involving organo-ionic complexes and precipitates, beyond the mechanisms assumed by classical isotherms.

2. Results and Discussion

2.1. Nonmonotonic Organo-Calcite Interactions

Adsorption studies generally utilize batch experiments in which analyte fractions bound to a certain amount of the adsorbent material are estimated. Typical experimental approaches involve the quantification of the residual or unbound analyte in the reaction medium at equilibrium. Such batch approaches have been extensively applied to investigate sorption events even on mineral surfaces. However, soluble minerals present key distinctions, such as a dynamic solvent composition on account of mineral dissolution, and thus also the involvement of solution state interactions between the leached ions and organic adsorbates. For these reasons, batch experiments with soluble adsorbents such as CaCO$_3$ do not accurately reflect kinetic rates and thermodynamic parameters such as equilibrium constants and free energies.

Here we apply an alternate—microscopy based—approach to investigate the surface modification of minerals in which a freshly cleaved Iceland spar surface is exposed to carefully controlled fluid compositions. Solution mixtures are generated in an automated titration device system and maintained at constant stirring and temperature conditions (Figure S1, Supporting Information). With porphyrins as biogenic constituents of shale, coal, and sedimentary rocks and also having physiological roles in metal ion homeostasis, protoporphyrin-IX (PP-IX) is applied as a sorbent to the surfaces of (freshly cleaved) Iceland spar. The representative image of a crystal briefly exposed to PP-IX ($5 \times 10^{-6}$ m) at $40 \degree C$ without any externally added Ca$^{2+}$ ions displays a brownish color, clearly indicating surface deposition of the organic anion (Figure 2a).

Prior introduction of Ca$^{2+}$ ions ($1 \times 10^{-3}$ m) into the PP-IX solution, however, largely suppresses coloration and thus obviously diminishes surface uptake. Systematically modified in this manner, the calcite surfaces are characterized by using confocal Raman microscopy.

The Raman spectrum of the untreated calcite (Figure S3, Supporting Information) presents peaks at 155 and 279–282 cm$^{-1}$, corresponding to the lattice modes of calcite, and also a dominant peak at 1084 cm$^{-1}$, representing the $\nu_1$ (symmetric) internal mode of the carbonate ion. In relation, PP-IX treated calcite presents several additional peaks characteristic of the organic molecule (Table S1, Supporting Information). Indicative of the bending deformations of pyrrole-like rings ($1585$ cm$^{-1}$) and asymmetric stretching of $C=\sigma$-$\sigma$ bonds ($1604$ cm$^{-1}$), the integral values of this spectral region from 1500 to 1650 cm$^{-1}$ are used to map the distributions of PP-IX.

To characterize the crystal surfaces, a depth profiling approach is applied. Here large area ($x,z$) scans are performed in a plane perpendicular to the ($x,y$) air-calcite interface by using confocal Raman microscopy (CRM). For calcite treated with a solution of PP-IX ($5 \times 10^{-6}$ m) and CaCl$_2$ ($1 \times 10^{-3}$ m) at $40 \degree C$, the surface deposition of the organic acid is illustrated in Raman maps and also in corresponding intensity profiles of calcite and the organic acid as a function of depth (Figure 2b–d). The spatial distribution of PP-IX across the calcite surface is heterogeneous (Figure 2c), which we attribute to distinct topographical features, such as terraces, pits, and steps of the (even freshly
cleaved) calcite surface. Such surface defects produce local variations in ionic and pH conditions proximal to the mineral-water interface[24] and can result in uneven uptake of organic species by the anisotropic crystalline surface.

Amounts of PP-IX deposited during crystal-fluid contact were estimated for various ambient temperatures and externally added amounts of Ca\(^{2+}\) ions (Figure S4, Supporting Information). Adsorbed contents are represented by average Raman intensities for the organic sorbent at the mineral面部 (Figure 2e). In the absence of added Ca\(^{2+}\) ions, the surface deposition of PP-IX at 40 °C is about two orders of magnitude higher relative to the amount deposited at 10 °C. Increasing the levels of added Ca\(^{2+}\) ions lead to less surface-bound PP-IX at 40 °C. For instance, the introduction of Ca\(^{2+}\) ions (1 × 10\(^{-3}\) M) in the reaction mixture produces about 80% reduction in the calcite bound organic material. At 10 °C, where maximum deposition occurs for 0.25 × 10\(^{-3}\) M added Ca\(^{2+}\), the surface bound organic content also decreases at higher added Ca\(^{2+}\) ion contents.

While divalent ions such as Ca\(^{2+}\) can participate in ion bridging interactions and serve as potential determining ions for CaCO\(_3\) surfaces,[25] the observed interactions between organic acids and carbonate surfaces (Figure 2) do not conform to sorption mechanisms solely based on electrostatic interactions and ion-bridging. First, while the zeta potential of calcite can vary linearly with Ca\(^{2+}\) ion concentration,[25] a corresponding direct dependence on the sorption behavior is absent (Figure 2e). Second, ion bridging interactions have established roles in the surface alteration of relatively insoluble minerals such as apatite, silica, and mica.[26] Assuming a central role of Ca\(^{2+}\) ion mediated bridging interactions for carbonates, the adsorbed contents of the organic acid are expected to positively correlate with the added Ca\(^{2+}\) ion content and then saturate. Instead, increasing Ca\(^{2+}\) ion contents during organic acid-crystal contact produced substantial reductions in the bound organic fractions (Figure 2e). This remarkable nonmonotonic behavior is a key phenomenon that we strive to understand in the subsequent sections by systematically studying its dependence on fluid compositions, temperature and flow velocity in a QCM-D flow cell.

### 2.2. Sensor Functionalization with Mg-Calcite

In the QCM-D method, changes in the sensor mass are reflected in the resonance frequency.[27] In the classical Sauerbrey relation, this is described as

\[
\Gamma = -C \left( \frac{f_n - f_r}{n} \right) = -C \frac{\Delta f_n}{n}
\]

where \(\Gamma\) is the mass change (deposited or removed) of the sensor (mass/area), \(f_r\) is the resonant frequency of the bare sensor, \(f_n\) is the resonant frequency upon a mass change, and \(n\) is the overtone number (3, 5, 7, etc.). The sensitivity factor, \(C\), is a fundamental property of the sensor and is about 177 ng (cm\(^{-2}\) Hz) for an AT-cut quartz crystal with \(f_r = 5\) MHz. Thanks to this ultrahigh sensitivity, QCM-D is a powerful analytical method for investigating various surface phenomena.[28] However, the poor availability of routes to functionalize sensors with inorganic materials and also the high costs and low stability associated with commercial alternatives limit the widespread use of the QCM-D technique. Here we introduce a novel and facile method for the controlled surface growth of Mg-calcite on silica coated sensors by using a bioinspired approach.

Several living systems utilize ionic additives such as Mg\(^{2+}\) ions to control the growth and structure of minerals.[29] Extending this strategy to achieve the growth of carbonates on...
silica sensors, we performed alternate injections of i) a solution mixture of Ca\(^{2+}\) and Mg\(^{2+}\) ions and ii) a (bi)carbonate solution in a flow cell maintained at RT. Over several cycles of injection (black curve, Figure 3), negative increases of $\Delta f_3$ indicate gradual material deposition on the silica surface. After accounting for the frequency change due to the densities of precursor solutions, the mass deposited on the silica surfaces is estimated (under Sauerbrey assumptions) at about 3 $\mu$g cm\(^{-2}\) after 8 injection cycles. In comparison, if we introduce small plugs of deionized water in between the cation (Ca\(^{2+}\)) and anion (HCO\(_3\)) containing solutions, no growth of calcite is observed and the minor variations in frequency can be completely ascribed to the density and viscosity changes of the injected fluid\(^{[30]}\) (red curve, Figure 3). Hence, we conclude that the alternating injection of the Ca\(^{2+}\)/Mg\(^{2+}\) and (bi)carbonate solutions leads in every cycle to a layer of the previous solution that is gradually replaced from above by the following solution. This results in the repetitive formation of a liquid–liquid interface between Ca\(^{2+}\) ion- and (bi)carbonate-rich solutions that acts as a moving reaction boundary and finally results in the deposition of the carbonate minerals (Figure 3).

To characterize the composition and growth mechanisms of the mineral deposits, silica surfaces treated with 3, 6, and 8 injection cycles were briefly rinsed with ethanol, dried with N\(_2\) gas, and then characterized with CRM. As shown in Figure 4a, the Raman spectrum of mineral deposits obtained after 3 reaction cycles presents a band at $\approx$1078 cm\(^{-1}\), indicative of a symmetric C–O stretch ($v_1$) in a Mg\(^{2+}\) ion stabilized amorphous carbonate phase.\(^{[31]}\) With increased number of reaction cycles (Figure 4b,c), this band decreases in intensity and a corresponding $v_1$ band (1086–1089 cm\(^{-1}\)) indexed to crystalline CaCO\(_3\) emerges. Relative to the $v_1$ band of pristine calcite (1086 cm\(^{-1}\)), the blueshift reveals the occlusion of Mg\(^{2+}\) ions within the calcite structure.\(^{[32]}\) With this initial evidence of an amorphous-to-crystalline transition during the growth of Mg-calcite, the mineralized surfaces are further characterized by using Raman imaging methods.

Brightfield images of the mineralized surfaces show distinct morphological transitions from dendritic to euhedral forms with increasing injection cycles (Figure 4d–f). Regions of interest (boxed areas) are mapped for carbonate phases by image reconstructions based on integrals of the spectral region from 1076 to 1095 cm\(^{-1}\). Corresponding Raman maps (green, Figure 4d–f) confirm the compositions of both the dendritic and the euhedral deposits as carbonate phases. To characterize the crystallinity of surface carbonate phases, maps are also generated by applying a crystallinity index defined as

$$\text{Crystallinity} \, \% = \frac{I_{1086}}{I_{1078} + I_{1086}} \times 100$$

where $I_{1078}$ and $I_{1086}$ are values count values at 1078 and 1086 cm\(^{-1}\) (indicative of the $v_1$ band for amorphous and crystalline CaCO\(_3\), respectively).\(^{[22,33]}\) Distributions of the crystallinity index confirm the amorphous and crystalline compositions of the dendritic structures and euhedral particles, respectively (Figure 4d–f). The consumption of an amorphous phase during the surface growth of Mg-calcite confirms the involvement of an Ostwald–Lussac ripening of the surface bound amorphous precursors (analogous to certain biominerals).

Previous studies demonstrate CaCO\(_3\) functionalization of QCM sensors using electrocrystallization and self-assembled monolayers.\(^{[33]}\) In comparison, our “alternate injection” approach circumvents any preconditioning with organic functional groups and enables direct in situ monitoring of mineral growth in a typical QCM-D flow cell. While previous investigations identify reaction boundaries during crystallization in gel media (e.g., Liesegang rings\(^{[34]}\) and counter-diffusion crystallization\(^{[35]}\)), here we manipulate a moving reaction boundary to achieve the heterogeneous growth of Mg-calcite crystals on silica surfaces by alternating fluid injection. Formed at the interface between fluids containing high contents of ionic precursors, this moving reaction boundary can present a dynamic composition, involving a time development of nonclassical crystallization pathways from ion clusters to liquid condensed phases and amorphous precursors and finally to crystalline particles.\(^{[36]}\) Coupled with the role of Mg\(^{2+}\) ions in transiently stabilizing gel- or fluid-like mineral phases,\(^{[37]}\) the observed amorphous-to-crystalline transitions (Figure 4d) can also involve wetting interactions between transiently stabilized fluidic precursors and the silica surface. Further investigations on additive- and temperature-guided crystal growth could expand this functionalization approach not only to other CaCO\(_3\) polymorphs but also to exotic materials beyond the existing capabilities of sensor design and fabrication.
2.3. Calcite-Organic Acid Interactions: QCM Study

Having successfully functionalized our QCM-sensors with Mg-calcite, we now systematically investigate sorption/dissolution reactions at the mineral–fluid interface in variable fluid compositions. In QCM-D experiments, the changes in resonance frequency and energy dissipation are measured in relation to their values measured for a clean or “untreated” sensor in a reference atmosphere or fluid. Therefore, it is essential to establish a stable baseline before any “treatment” is applied to the Mg-calcite sensors. Given the pH dependent solubility of CaCO₃ phases, we found a relatively stable frequency signal in alkaline environments, generated by injecting a NaOH solution. Accordingly, QCM-D experiments were performed in a consistent and stepwise manner (Figure 5). A typical experiment involved four stages: i) initial deposition of Mg-calcite using the “alternate injection” method (Figure 3), ii) achievement of a stable resonance frequency (i.e., minimal baseline drift) by continuously injecting a NaOH solution (pH 10.5) at 50 µL min⁻¹, iii) injection of a solution mixture (pH 10.5) of Ca²⁺ ions and the organic acid of interest for 1 h under constant flow, and iv) injection of alkaline solution again (repeating step iii). In both the alkali regimes

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**Figure 4.** Representative Raman ν₁ band (continuous line) in air for carbonate phases synthesized after a) 3, b) 6, and c) 8 reaction cycles, fitted by two Gaussians (dashed line) centered at 1078 cm⁻¹ and between 1086 and 1089 cm⁻¹ representative of amorphous and crystalline Caₓ(Mg₁₋ₓ)CO₃, respectively. d–f) Bright field microscopy (left) and CRM-derived false color images representing distributions of Mg-calcite (green, middle) on SiO₂ sensors and the associated crystallinity (right), after d) 3, e) 6, and f) 8 reaction cycles. Boxed areas are mapped using a step size of 0.5 µm in x and y directions. Scale bars represent 40 µm (micrographs) and 10 µm (color maps).
The interaction factor ($F_{\text{int}}$) defined as 

$$F_{\text{int}} = \frac{\Delta f_{\text{organic}}}{\Delta f_{\text{calcite}}}$$

(7)

based on the third overtone frequency responses during Mg-calcite deposition ($\Delta f_{\text{calcite}}$) in late step i) and subsequent mineral dissolution or sorption in the presence of the organic acid ($\Delta f_{\text{organic}}$) during the initial regime of step iv). Since $\Delta f_{\text{calcite}}$ is always negative (Figure 5), the sign of $F_{\text{int}}$ is an indicator of either mineral dissolution (negative) or the sorption of organic molecules (positive). As both $\Delta f_{\text{calcite}}$ and $\Delta f_{\text{organic}}$ are measured under identical conditions of fluid composition, flow rate, and temperature (Figure 5), the utilization of $F_{\text{int}}$ values eliminates the contributions of viscosity and density changes, allowing to ascribe changes in $F_{\text{int}}$ primarily to mass variations. Note that the $F_{\text{int}}$ values reflect changes in the overall sensor mass, also consequent of simultaneously occurring dissolution and surface precipitation reactions.

Figure 6 shows the responses, quantified by the interaction factor $F_{\text{int}}$, of Mg-calcite functionalized sensors upon exposure to solutions of PP-IX and HA as a function of Ca$^{2+}$ concentration for a series of different temperatures. The resulting curves display a—at first glance—rather complex behavior, yet three main observations are made.

First, mineral dissolution, represented by a negative sign of $F_{\text{int}}$, is limited to solutions of HA at very low Ca$^{2+}$ concentrations (Figure 6b). Considering the poor solubility of carbonates under alkaline conditions, we infer that this dissolution of solid mineral is mediated by the organic acid, via the chemical reaction

$$\text{MCO}_2\text{R} + > \text{MCO}_2\text{R} + 2\text{RCOO}^- \rightleftharpoons \text{MCO}_2\text{R} + \text{M}^{2+} \text{(RCOO}^-)_2\text{aq} + \text{CO}_3^{2-}$$

(8)

where M$^{2+}$ denotes the Ca$^{2+}$ or Mg$^{2+}$ ions constituting the Mg-calcite layer. Hence, we attribute mineral dissolution to the formation of solute complexes between the divalent cations and hexanoate species. The continued dissolution is sustained by the steady influx of free acid species and efflux of metal ion-organic acid complexes under the continuous flow conditions. In contrast to HA, solutions of PP-IX never induce any mineral dissolution regardless of the concentration of added Ca$^{2+}$ ions (Figure 6a). Although for PP-IX an equilibrium similar to (8) may exist, it does not become as prominent as it does for HA (see below).

Second, for hexanoate solutions with low to moderate Ca$^{2+}$ content, $F_{\text{int}}$ presents positive values, indicating surface deposition. In this concentration regime (2–10 $\times$ 10$^{-3}$ M added Ca$^{2+}$ depending on temperature), this deposition positively correlates with added divalent ion contents (Figure 6b). This trend is also observed for PP-IX interacting with Mg-calcite at 10 $^\circ$C for Ca$^{2+}$ up to 100 $\times$ 10$^{-3}$ M (Figure 6a) and confirmed by CRM maps, which depict the colocalization of the organic acid with Mg-calcite particles (Figure S5, Supporting Information). Consistent with the surface precipitation model for inorganic sorbents, we attribute the Ca$^{2+}$ ion-mediated surface deposition of organic acids to two chemical equilibria

(a) Adsorption of organic species on MCO$_2\text{R}$ as a monolayer

$$> \text{MCO}_2\text{R} + 2\text{RCOO}^- + \text{Ca}^{2+} \rightleftharpoons \text{MCO}_2\text{R} + > \text{Ca}^{2+} \text{(RCOO}^-)_2$$

(9)
(b) Formation of a organo-calcium surface phase as a multilayer (related to the solubility product of the organo-calcium salt $K_{sp_{organo-Ca}}$)

$$\text{Ca}^{2+}(\text{RCOO}^-)_2 + 2\text{RCOO}^- + \text{Ca}^{2+} \rightleftharpoons \text{Ca}^{2+}(\text{RCOO}^-)_{2\text{org}} + > \text{Ca}^{2+}(\text{RCOO}^-)_2$$

(10)

Multilayer sorption of organo-calcium salts (10) is also indicated by the continuous decrease in $\Delta_{\text{organic}}$ (i.e., mass increase to about 10 µg cm$^{-2}$ under Sauerbrey conditions) on injecting the solution mixture (Figure 5).

We remark here that in the absence of externally added Ca$^{2+}$ ions, the dissolution of Mg-calcite is the only source of divalent ions available for the ion bridging and surface precipitation reactions (9, 10). In this scenario, one might anticipate surface passivation via organic molecules to completely inhibit mineral dissolution$^{[49]}$ and thereby limit the availability of Ca$^{2+}$ and Mg$^{2+}$ ions for any further organic interactions. However, the adsorption of organic anions on the Mg-calcite surface does not show saturation as long as the influx composition is maintained (Figure 5). This could be explained by the topographical and chemical heterogeneity of carbonate surfaces, producing local variations in dissolution rates (i.e., distinct ionic and pH conditions at carbonate surfaces$^{[24]}$) and leading to nonuniform surface distributions of the organo-calcium salt (Figure 2b). Also the aspect of heterogeneous nucleation is important. Deposition of an organo-calcium multilayer on a preformed monolayer (9) is energetically more favorable compared to the same process on a bare carbonate surface$^{[40]}$. This preferential multilayer deposition of the organo-calcium phase can leave the mineral surface available for further dissolution. Both mechanisms can preclude a complete inhibition of mineral dissolution and thereby explain the continuous type sorption behavior in the QCM-D experiments (Figure 5).

The third outcome of the organo-mineral interplay is the gradual reduction in adsorbed organic material (reflected by decreasing yet positive $F_{\text{in}}$ values) as the added Ca$^{2+}$ ion content in the injected fluids is increased toward the highest values (Figure 6). For HA, Ca$^{2+}$ concentrations above $5 \times 10^{-3}$ M at 10 °C and above $10 \times 10^{-3}$ M at 25 and 40 °C lead to gradual reductions in the surface bound organo-calcium material (Figure 6b). A similar trend is observed for protoporphyrin applied to Mg-calcite at 10 °C, where $200 \times 10^{-6}$ M of added Ca$^{2+}$ ions cause a 80% reduction in deposited mass compared to the maximum at around $100 \times 10^{-6}$ M Ca$^{2+}$ (Figure 6a). However, PP-IX shows a different behavior at elevated temperatures (25 and 40 °C): here the maximum surface deposition on the Mg-calcite surfaces occurs in the absence of externally added Ca$^{2+}$ ions. Any incorporation of Ca$^{2+}$ ions in the injected fluids results in the diminished sorption of protoporphyrin at 25 and 40 °C, in agreement with Figure 6a. We attribute this third consequence of decreased adsorption of the organic anions to a high driving force for bulk precipitation of the organo-calcium salts

$$\text{Ca}^{2+} + 2\text{RCOO}^- \rightleftharpoons \text{Ca}^{2+}(\text{RCOO}^-)_{2\text{org}} \rightleftharpoons \text{Ca}^{2+}(\text{RCOO}^-)_{2\text{solid}}$$

(11)

Formation of bulk organo-calcium precipitates by reaction (11) can deplete free organic species, which otherwise could participate in either mineral dissolution (8) or surface deposition (9, 10) reactions.

2.4. Bulk Versus Surface Precipitation of Organo-Ionic Phases

The QCM-D experiments thus reveal that the interactions of organic acids with calcite (Figure 2) and Mg-calcite (Figure 6) produce three different outcomes primarily determined by the Ca$^{2+}$ ion contents of the reaction media. For soluble metal carbonates (Figure 1a), the dissolution of the mineral phase assists the formation of organo-ionic phases, in setting the nonzero lower thresholds for Ca$^{2+}$ ions. Therefore, to develop any holistic picture of the surface modification of soluble minerals, the relative precipitation propensity of organo-calcium salts must be considered along with the dissolution behavior of carbonate minerals.

While the calcium salts of fatty acids typically involve the association of two organic chains with a single Ca$^{2+}$ ion (e.g., Ca(HA)$_2$ for calcium hexanoate), the binding stoichiometries for calcium-protoporphyrin IX salts are unclear. We use potentiometric titration with a Ca$^{2+}$ ion selective electrode to elucidate the Ca$^{2+}$ ion complexation behavior of PP-IX. Herein, a gradual addition of Ca$^{2+}$ ions to PP-IX solutions allows measuring the delay in the appearance of free Ca$^{2+}$ ions as an indicator of ion complexation (Figure S6, Supporting Information). Applying a simple Langmuir model to describe the fraction of bound versus total Ca$^{2+}$ ions, the binding stoichiometry revealed the association of two Ca$^{2+}$ ions with one PP-IX molecule (Table S2, Supporting Information), indicated as Ca$_2$(PP). This number is in accordance with the metal ion binding capacity of the carboxylate groups and also with the ion coordination ability of the porphyrin group$^{[20,41]}$.

Using these stoichiometries of Ca(HA)$_2$ and Ca$_2$(PP), the solubility products of the organo-calcium salts were determined (Figure S7, Supporting Information), by estimating the nonprecipitated contents of the organic acid and calcium ions in solution mixtures after prolonged aging. Both organo-calcium salts present retrograde solubility, i.e., decreased solubility products at elevated temperatures (Figure S7, Supporting Information). Typically prograde solubility behavior is presented by long chain fatty acids (<C$_n$) and their soaps$^{[42]}$. Hence the decreased solubility of Ca(HA)$_2$ at higher temperatures suggests the existence of a certain crossover for the fatty acid chain length, at which the entropy-driven water release during Ca$^{2+}$-carboxyl association becomes as crucial as the hydrophobic interactions between the alkyl chains$^{[42,43]}$. Solubility estimates for the organo-calcium phases allow us to examine the relations between the surface interactions of carbonates and the bulk precipitation propensities of the organo-calcium salts.

The thermodynamic driving force for nucleation in bulk environments is generally expressed in terms of the saturation index (S)

$$S = \log \frac{IAP}{K_{sp}}$$

(12)
which relates the ion activity product (IAP) and solubility product (Ksp) for the forming phase. With the sparingly soluble nature of the organo-calcium salts (Figure S8, Supporting Information), their respective IAP values are expressed as

\[
IAP_{\text{Ca}[^{2+}]_{\text{extern}}} = \{HA\} \cdot \{\text{Ca}[^{2+}]_{\text{extern}} + \text{Ca}[^{2+}]_{\text{mineral}}\} 
\]

(13)

\[
IAP_{\text{Ca}[^{2+}]_{\text{PP}}} = \{\text{PP}\} \cdot \{\text{Ca}[^{2+}]_{\text{mineral}}\}^2
\]

(14)

where \{Ca[^{2+}]_{extern}\} represents the Ca[^{2+}] ion activity of the injected fluid and \{Ca[^{2+}]_{mineral}\} denotes the ion activity in equilibrium with the mineral phase. At low electrolyte contents, activities are estimated using the Debye–Hückel limiting law. Since the temperature dependent solubility values of Mg-calcite are reported congruous with those of pristine calcite, we utilize the latter as \{Ca[^{2+}]_{mineral}\} estimates.[44] Following this approach, the mass changes of Mg-calcite interacting with solution mixtures of Ca[^{2+}] ions and organic acids (F_{int} values) are discussed in terms of the saturation indices (i.e., bulk precipitation propensities) of both organo-calcium salts.

Remarkably, all three types of the organo-mineral interplay (discussed above) occur in undersaturated solutions (Figure 7a,b). At low S values (S < −2.2), the bulk fluid is vastly undersaturated with respect to the organo-calcium phase and even the Ca[^{2+}] ions originating from carbonate dissolution are inadequate to trigger any precipitation of the organo-calcium phase. With the continuous influx of organic anions and the efflux of aqueous organo-calcium complexes, mineral dissolution is sustained under continuous flow. For solutions with intermediate S values (−2.2 < S < −1.4), the surface deposition of organo-calcium phases positively correlates with the bulk precipitation propensity (Figure 7a). While the heterogeneous nucleation of minerals on organic surfaces in undersaturated bulk conditions is established,[45] to the best of our knowledge, our observations

![Figure 7](image-url)

**Figure 7.** a) Distributions of F_{int} values for Mg-calcite treated with PP-IX (star symbols) and HA (square symbols) in relation to the saturation index (S) of the respective organo-calcium surface phases at different temperatures. b) Schematic diagram for the outcomes of organo-mineral interactions, reflected by mass changes at the mineral interface (ΔMass) and the saturation index of the organo-ionic salt. Mineral surfaces can undergo 1) dissolution (black), 2) surface alteration with organo-ionic phases positively correlated with saturation index (blue), and finally 3) decreased surface deposition at higher saturation indices (pink). c) Schematic of the distinct modes of coupled dissolution-precipitation processes at the carbonate-water interface involving 1) mineral dissolution and the release of Ca[^{2+}] ions, 2) formation of organo-ionic solute clusters, 3) precipitation of organo-calcium salts within the fluid boundary layer and at the mineral surface, and 4) the formation of organo-ionic precipitates in the bulk fluid. d) Formative stages of organo-calcium phases involving the complexation of Ca[^{2+}] ions by the organic molecules as ion clusters, followed by the nucleation of a solid phase.
of the nucleation of organo-ionic matter on mineral surfaces under undersaturated conditions are new. In our experiments, the heterogeneous nucleation of organo-calcium surface phases is promoted by additional enrichment of the interfacial fluid environments with Ca\(^{2+}\) ions originating from mineral dissolution (Figure S5, Supporting Information). Such localized enrichment of ionic and organic precursors might also transiently form precursors, such as ion-clusters and amorphous phases at the mineral interface.\[^{46}\] Furthermore, even the surfaces of inert impurities can substantially reduce the barrier for nucleation.\[^{49}\] Thus, the carbonate surface, which itself provides the Ca\(^{2+}\) ion precursor, is evidently effective in reducing the local energy barrier for the formation of surface precipitates.

With increasing tendencies of bulk precipitation (\(\sim 1.4 < S\)), the surface deposition of the organic acids gradually decreases. In this regime, the bulk fluid is still undersaturated with respect to the organo-calcium phase (Figure 7a). Again, the Ca\(^{2+}\) ions released upon mineral dissolution are sufficient to trigger the bulk precipitation of organo molecules as calcium salts. However, because of the strong enrichment of Ca\(^{2+}\) ions in the injected fluids, the driving force for nucleating organo-calcium phases now is sufficient further away from the mineral surface. The supersaturation as a function of distance from the mineral surface is now also determined by diffusive fluxes, from the bulk to the mineral and vice versa. In other words, the precipitation fronts can “fizzle out” before substantial contact with the carbonate surfaces, thereby precluding the nucleated organo-metal particles from binding to the carbonate surfaces. Established in the crystallization mechanisms for Liesegang bands and silica gardens,\[^{34}\] this contribution of dynamic precipitation fronts is one factor explaining the third outcome of the solute and mineral interactions. At the same time, divalent cations such as Ca\(^{2+}\) are common nucleating species in the formation of both metal carbonates and organo-metal phases. Following Le Chatelier’s principle (common-ion effect), with increased Ca\(^{2+}\) concentrations from mineral dissolution, the precipitation of the more sparingly soluble substance viz., the organo-calcium salts (Figure 8) will occur at higher rates and thereby can promote the nucleation of organo-calcium particles even in the bulk fluid. While here we primarily consider the differences in ionic conditions, key distinctions also exist between the chemical environments of the boundary layer at crystal-fluid interfaces and the bulk solvent. For instance, the mobility of solvent molecules\[^{35}\] and potential determining ions\[^{36}\] and also the structure of hydration\[^{47}\] are distinct at the mineral-water interface, also affecting the organo-mineral interactions.

Precipitation of the organo-calcium salts in bulk fluid is anticipated only for \(S \geq 1\). Yet, the surface deposition of organo-calcium salts on carbonates clearly occurs at a fraction of this threshold value (Figure 7). This reflects the substantially lowered free energy for precipitation of organo-metal surface phases on carbonate surfaces, originating from multiple factors such as the local enrichment of Ca\(^{2+}\) ions at the mineral surface, contributions of the common-ion effect and also likely (hetero) epitaxial interactions between the growing organo-calcium surface phase and the mineral surface. For these connected chemical equilibria and interface phenomena, the nucleating species present in injected fluids and released from mineral dissolution are key regulators of the surface interactions of carbonates. By coupling the surface and bulk reactions (8–11), Ca\(^{2+}\) ions emerge critical in modulating the local saturation for organo-calcium phases (Figure 7). Distinct compositions of bulk and interfacial fluids in contact with carbonate minerals elucidate the nonmonotonic modifications of carbonate surface (Figure 6), induced by both organic anions and their calcium salts. As an immediate consequence, we can identify i) the fluid chemistry of the boundary layer at carbonate-water interfaces, ii) the roles of local Ca\(^{2+}\) concentrations in regulating the coupled equilibria (8–11), and iii) precipitation reactions propagating from the bulk fluid to mineral surfaces as interconnected factors regulating organo-mineral interactions.

2.5. Coupled Dissolution-Precipitation at Dynamic Interfaces

Thin fluid layers at carbonate interfaces present positive rates for the formation of organo-calcium phases, while the bulk fluid is still undersaturated (Figure 7). Like for other (inorganic)
modifiers of minerals,[18a] the ion activities and thermodynamic solubilities in the bulk fluid are not representative for the interfacial fluids. While $[\text{Ca}_{\text{ionic}}]$ is generally considered equivalent to the ion activity in fluids equilibrated with the mineral phase (Figure S8, Supporting Information), the mineral solubility is not fully indicative of the ion contents within the fluid boundary layer. Ultimately, the bulk and boundary fluids will reach equilibrium with the mineral phase, and become (de facto) compositionally indistinguishable. However, with the constant influx of fresh solution mixtures enriched with organic anions in our QCM-D cell, such an equilibrium is never attained. Even in air, calcite surfaces can undergo structural rearrangements on the atomic scale.[48] While the local thermodynamic equilibrium for mineral dissolution emerges as a key factor governing the interfacial reactions between solutes and mineral phases, direct evaluation of this local reactivity of mineral surfaces is beyond the capabilities of the QCM-D method. Nonetheless we anticipate that the hydrodynamic characteristics of the interfacial fluid layer will impact the surface reactions of carbonate minerals.

To explore the relevance of diffusive boundary layers for the interface coupled dissolution and precipitation reactions, we performed QCM-D experiments at variable injection rates. Specifically, we monitored the evolution of the frequency shifts upon injecting 3 mL of solutions of pure PP-IX ($50 \times 10^{-6}$ M) and HA ($10 \times 10^{-3}$ M) at flow rates ranging from 15 to 400 µL min$^{-1}$, corresponding to flow velocities of 0.02–0.7 m min$^{-1}$. Used as an industrial descaling agent and in chelation therapy, we also apply ethylenediaminetetraacetic acid (EDTA) ($1 \times 10^{-4}$ M) to study the flow dependent modifications of Mg-calcite.

For applied flow velocities, the values of Peclet number ($Pe$) are estimated in the range of $3.6 \times 10^3$ to $126 \times 10^3$ (diffusion coefficient of $\text{Ca}^{2+}$ ions, $D = 13 \times 10^{-10}$ m$^2$ s$^{-1}$ and sensor diameter, $L = 14$ mm). These high $Pe$ values reflect advectively dominated distributions of dissolved and dissolving $\text{Ca}^{2+}$ ions and a failure in homogenizing the concentration fields within the QCM-D cell. Even so, these high $Pe$ values are pertinent to several real world phenomenology from cytoplasmic streaming in living cells to fluid displacement in rock formations.[49] The applied flow conditions set up the distinct compositions of the bulk and boundary fluids in our QCM-D experiments. These experiments were carried out without any externally added $\text{Ca}^{2+}$ ions.

For all three organic species, the mass signals turned out to vary nonmonotonically with the flow rate, as shown in Figure 8a. This demonstrates the existence of an optimal residence period for sorbent molecules at the mineral interface to either induce maximal mineral dissolution or to undergo maximal surface precipitation. While PP-IX displays increasing deposition at low flow velocities followed by a maximum and a subsequent decrease toward weak dissolution at the highest velocities, HA and EDTA display the opposite trend: increasing dissolution at low flow velocities followed by a maximum dissolution and subsequently a decrease toward weaker dissolution rates.

These seemingly opposing trends can be rationalized within a single consistent reaction-diffusion-advection scheme in combination with the highly different solubilities of the organo-calcium complexes of the two salts. At the highest flow rates, the solutions of PP-IX, HA, and EDTA lead to the relatively limited interactions with the substrate. This can be explained if the organic anions are depleted from the region close to the mineral surface. In this case, the behavior of the system is exclusively determined by the bare calcite in contact with the pure water, leading to a strong continuous flux of $\text{Ca}^{2+}$ ions away from the surface in the presence of a thin boundary layer at high flow rates.[50] Indeed, this behavior is also found in separate control experiments with pure water (Figure S9, Supporting Information), in qualitative agreement with observations made with holographic microscopy.[53]

Upon reducing the flow rates, the organic anions have enough time to diffuse toward the Mg-calcite surface leading to appreciable concentrations of both $\text{Ca}^{2+}$ ions and organic anions in the fluid boundary regions. Note that the mineral surface is the only source of $\text{Ca}^{2+}$ ions in this experiment. As a consequence, anions and cations associate to form organo-calcium complexes, proximal to the mineral–water interface. However, due to the vastly different solubilities of $\text{Ca}^{2+}$ and organo-$\text{Ca}^{2+}$ complexes is very different for each organic compound. $\text{Ca}^{2+}$ (PP) quickly precipitates onto the calcite surface leading to an increasingly positive interaction factor $F_{\text{int}}$ (Figure 8a), despite the fact that some $\text{Ca}^{2+}$ is scavenged from the mineral as well. In contrast, Ca-hexanoate complexes remain soluble. Their formation, however, reduces the calcium concentration in the vicinity of the calcite and thereby further enhances the dissolution rate (Figure 8b). EDTA presents a flow rate determined dissolution trend analogous to hexanoate, however at higher magnitudes on account of the higher $\text{Ca}^{2+}$ ion chelation capacity reflected in the stoichiometry of the organo-calcium as $\text{Ca(EDTA)}$[52] and relatively stable solute complexes.

For the lowest flow rates, the $\text{Ca}^{2+}$ ion species with the highest diffusion coefficient of the ions involved, diffuses progressively deeper into the bulk of the solution. For instance, the diffusion coefficient of $\text{Ca}^{2+}$ ions ($13 \times 10^{-10}$ m$^2$ s$^{-1}$) is about 2–3 times higher than that of small organic molecules (e.g., EDTA: $5.5 \times 10^{-10}$ m$^2$ s$^{-1}$).[53] With the common ion effect, the precipitation of Ca-PP-IX is no longer limited to the interfacial region but also occurs away from the calcite surface. Salts precipitated outside the immediate vicinity of the substrate, however, are flushed away by the flow and are not detectable with the QCM-D. This explains the decrease to negligible deposition as the flow rate is reduced toward zero. Similarly, HA anions form solute complexes with $\text{Ca}^{2+}$ ions already farther away from the surface and therefore reduce the concentration of $\text{Ca}^{2+}$-scavenging free hexanoate species in the immediate vicinity of the substrate. Hence, the dissolution rate eventually decreases toward zero, analogous to the depletion of organic solutes as $\text{Ca}_{2}(\text{PP})$ (Figure 7).

Trends of mineral reactivity depending on flow velocities are consistent with a picture in which distinct chemical potential gradients exist at the mineral–water interface, with the fluid boundary layer or bulk fluid becoming more supersaturated with respect to $\text{Ca}^{2+}$-containing phases. Assuming an identical advective flux under laminar conditions, the flow velocity also affects the composition and organization of the boundary layer (with thickness, $\delta$).[50] Both factors must be taken into consideration in order to address the nonlinear associations between flow velocity and surface reactions of minerals. This is
illustrated in Figure 8b, where we sketch the resulting scenario of physicochemical processes within the fluid boundary layer for a low solubility organo-calcium salt such as Ca₂PP. At high flow rates, the formation of Ca₂⁺ ion enriched yet thin fluid boundary layers lead to surface limited interactions between the organic acids and the mineral surface. In relation, thicker boundary layers, formed at lower flow velocities, produce transport limited interactions. Thus, it is possible for local supersaturation of the organo-calcium phase to develop exclusively at the mineral–fluid or the boundary layer-bulk fluid interfaces. The proximity of carbonate interfaces to the precipitation front is an important factor driving the respective propensities of surface and bulk reactions.

For more soluble organo-calcium salts such as EDTA and hexanoate, the injected solutions present relatively high capacities to accommodate Ca₂⁺ ions before triggering any nucleation of organo-calcium phases. For such electrolytes, from low to moderate velocities, increased Mg-calcite dissolution can sustain the formation of organo-ion solute complexes on short timescales of tens of picoseconds away from the carbonate surface and then their continuous efflux. Whereas at high flow rates, the reduced thickness of the fluid boundary layer renders the depletion of organic acids from the Ca₂⁺ abundant boundary layer. This in turn diminishes the formation of the hybrid organo-ionic complexes and the contributions of ion complexation events toward mineral dissolution. This mechanistic picture suggests that variations in the velocity profile alone can steer the local saturation conditions at fluid-mineral interface. Though a switch between the outcomes of mineral dissolution and surface precipitation is not evident (Figure 8a), the applied flow velocities evidently control the magnitude of these interfacial processes. Thus, both the chemical compositions and organization of the fluid boundary layer guide the nature of interfacial interactions between solutes and carbonate minerals. Further investigations are needed to explore such relations between complex velocity profiles of reaction media and the local reactivity of fluid-mineral interfaces.

2.6. Coupled Reactions at Fluid-Mineral Interfaces: From Biominalization to Rock Formations

Based on a continuum from mineral dissolution to the surface and bulk precipitation of organo-calcium phases, our conceptual picture explains the nonmonotonic relations of mineral reactivity with bulk saturation and flow velocity, and is highly relevant to various biological and geological minerals. Exploring the evolutionarily optimized strategies of crystallization, there are several reports of specific or “lock and key” interactions between macromolecules and crystal phases or facets, which address the selective emergence of metastable phases and crystal structures. In relation, our study shows that the surface precipitation of organic molecules as calcium salts occurs on both calcite and Mg-calcite crystals and dissolving as well as dissolved ionic species have key roles in controlling these organo-mineral interactions.

From a fundamental viewpoint, Wulff’s construction predicts the equilibrium shape of the crystal based on the minimization of the net interfacial energy of all facets. This implies that the surface areas of crystal faces with low surface free energy are always retained at the expense of high energy surfaces. And from Ostwald–Lussac law of stages, phase transformations always produce a thermodynamically stable state following an energetically downhill sequence. Yet apparent deviations from Wulff’s rule, i.e., the expression of high energy facets in crystals and the extended stabilization of metastable mineral phases (e.g., amorphous CaCO₃ and vaterite) are often observed in the biological pathways of mineralization.[1,6a,29]

Our results portray that the interactions of minerals with organic molecules are guided by the local saturation for organo-calcium surface phases, not affected only by the amounts of organic molecules. The availability and localization of divalent metal ions, which affect the local saturation for organo-metal matter, are equally important. Through this mechanism, the stages of surface restructuration and phase transformation or crystal ripening can themselves kinetically determine the mineral phase- or facet-specific binding of solutes. The high translational and rotational mobility of ionic species on high energy surfaces (including those of amorphous phases) can alone favor the surface precipitation of anionic adsorbates and present an apparent nature of binding specificity or a “lock and key” interaction. This relation between phase stability (solubility) and the surface precipitation of (bio)molecules also elucidates the prevalence of intermediate states of the Ostwald step rule in the biological world. We argue that the higher propensities for the surface precipitation of organic species in presence of more soluble, metastable phases and high energy surfaces inherently favor the confinement based stabilization of transient amorphous phase.[55] This is supported by several instances of the transient stabilization of otherwise metastable CaCO₃ phases in the presence of proteins,[56] peptides, and polymers[57] bearing functional groups with metal ion binding characteristics. Thus, the interfaces of even transiently existing out-of-equilibrium material states have functional roles in the selective emergence of phases, morphologies, and organizations of biological materials.

Our results showcase the spectacular feat of biological systems at manipulating the local equilibria for coupled dissolution and surface precipitation. Extending beyond stereoechemical complementarity, the specificity of bio-inorganic interactions can originate from subtle differences in the dissolution rates of mineral phases and surface energies of crystal faces. Living systems emerge adept at exploiting this local nonequilibrium to gain control over material genesis at larger length scales. This also brings attention to the design features of biological and biomimetic additives guiding the growth of synthetic crystals.[36b,58] Experimental and computational studies generally assume the crystal facet and/or the additive controlling crystallization reactions as conformationally rigid.[1,6a] However, shown by our QCM-D experiments, the additive specific outcomes of mineral dissolution (induced by EDTA and HA) and surface precipitation (with PP-IX) underscores the need to consider the physicochemical characteristics of both the organic additive and its ionic salt in the molecular design of nucleation and crystallization regulators.

Affected by the bulk saturation of organo-calcium salts (Figure 7) and flow velocity (Figure 8), the distinct nonmonotonic organo-mineral interactions identify the fluid boundary...
layer as the active reaction zone for any surface interaction with soluble minerals. Mechanistic functions of the composition and organization of fluid boundary layers in mineral–organo interactions have key repercussions toward experimental and computational simulations of carbonate geochemistry, from ocean acidification to reservoir engineering.

In view of mineral dissolution in acidifying oceans, our results elucidate previous observations of lower dissolution rates of coccolith calcite only when estimated far from equilibrium and vice versa. [13] Based on coupled dissolution–precipitation reactions (8–11), we explain this observation by an enhanced precipitation flux of organo-calcium salts at the mineral interface, shielding the mineral phase from undersaturated fluids when far from equilibrium (Figure 8). This reflects the spectacular property of soluble minerals being resistant to attack by organic acids due to the likelihood of simultaneously occurring surface precipitation of organo-calcium phases.

This highlights the self-preservation property of biominerals based on evolutionarily optimized design of the material interface, as exemplified by enamel material.[59] Whereas in oversaturated fluids, the organic acids are simply depleted as bulk precipitates.

Addressing mineral dissolution in acidifying waters, previous reports also present mixed observations on the dissolution behavior of carbonates treated with organic acids.[12,19] Though distinct stereochemical complementarity is a proposed explanation for this disparity,[60] our results show that the responses of carbonate interfaces to organic anions are determined also by the solubilities of the corresponding organo-calcium salts rather than the presence of certain functional groups (e.g., carboxyl) alone. This is supported by mineral dissolution predominantly induced by EDTA and hexanoate, additives with a substantial Ca\(^{2+}\) binding capacity prior to nucleation of their organo-calcium salt. In contrast, precipitation prone organic molecules, such as PP-IX are likely to undergo surface or bulk precipitation in the presence of soluble minerals. This explains the ubiquitous and strong association of carbonates with bulky molecules with polar modifications such as certain asphaltenenes,[61] humic acids, fulvic acids,[62] kerogens, porphyrins,[21a] and pigments[63] in varied environments. Even for the salts of long-chain fatty acids, both structural ordering of the side chains within solute clusters occur prior to the nucleation of crystalline solids and elucidates the strong binding (surface precipitation) of long chain fatty acids on calcite surfaces.[39,64] Thus, for the formation of organo-metal surface phases on carbonates, the hydrophobic interactions between the side chains of acid groups become equally crucial to the electrostatic interactions between metal cations and polar groups. In view of the distinct responses of calcifying organisms to gradual ocean acidification, we infer that resistance of (bio)minerals to dissolution is reflected not in the mere presence of an outer organic covering,[65] but also the microscale interactions of constitutive organic molecules with dissolved ion species at the aqua-organo-mineral junction.

It is important to consider first that both biological and geological fluids, such as connate/formation water (pH 6.8), sea water (pH 8), and serum (pH 7.4), are acidic relative to the applied pH in our experiments. Acidsic conditions enhance carbonate dissolution, releasing more divalent ions to interact with organic solutes. At the same time, low pH promotes the protonation of acid groups (e.g., COO\(^{-}\)), reducing the availability of calcium-binding functional groups. Both factors will affect the chemical gradients of reacting species and the dissolution and depositional rates at mineral surfaces. Nonetheless, the precipitation propensity or saturation of an organo-metal salt, even at low pH, will determine how it eventually modifies the mineral surface. This notion also finds agreement with previous studies conducted at initial pH ≈8, wherein the aromaticity of organic acids correlated with their calcite-binding ability[66] and higher affinities for CaCO\(_3\) surfaces were found for fatty acids with longer alkyl chain lengths.[67]

Remarkably the nonlinear effects of aqueous fluids on the properties of carbonate interfaces are established in the field of geoengineering, yet poorly understood. Surface active organic materials are both physically and chemically adsorbed on to underground rocks. These surface layers impact the equilibrium of carbonate surface with surrounding fluids by physically isolating the mineral surface and by lowering the surface free energy of the mineral phase.[14a,15] First, in order to remove mineral bound organic matter and render the surface properties of rocks “water wet”, exposure to aqueous solutions highly undersaturated with respect to mineral phase is ideally anticipated. Yet brine compositions of intermediate saturation are often reported as optimal.[68] Here interface coupled dissolution–precipitation reactions involving organo-calcium salts provide more holistic insights into these surface reactions (8–11).

In Ca\(^{2+}\) ion enriched fluids, organo-ionic layers can remain stable and surface bound. On the other extreme, high rates of mineral dissolution in undersaturated brines produce a fluid boundary layer abundant in Ca\(^{2+}\) ions and can strengthen the flux for the precipitation of organic acids at the carbonate interface. Based on this explanation, we propose that water compositions oversaturated with respect to underlying mineral phase and at the same time undersaturated with respect to the bound organo-ionic layer are optimal for removing rock bound organo-ionic matter. Consistent with the molecular characteristics of carbonate bound molecules as bulk aromatic hydrocarbons with polar modifications[61] and the physical nature of the rock bound organic matter as organo-ionic surface phases,[69] this mechanism brings forth the rich interconnectivity between multiple bulk and surface equilibria involving organic and inorganic species in underground formations.

Second, in carbonate rocks, the equilibration of propagating fluids is widely presumed to occur over a distance of millimeters.[13] In contrast, our study shows that mineral dissolution can even occur under alkaline conditions in the presence of organic acids. Thus, in naturally occurring compositionally heterogeneous and turbulent fluids, carbonate equilibration with a flowing aqueous medium is not practically instantaneous and presents local fluctuations. Due to the inherently heterogeneous pores and fine migration within natural formation,[69] nonuniform flow profiles naturally develop within rock formations and thus can modulate the local equilibrium for mineral dissolution and (de)adsorption of organic matter during CO\(_2\) injection or oil displacement. Complex flow profiles, transitioning between laminar and turbulent, are prevalent in nature. Such dynamic flow will also affect the composition and dimensions of boundary layers and impact the surface
reactions of minerals. For instance, in simple micromodels, laminar to turbulent flow transitions influence the mixing of mineralizing solutions and also the detachment of oil from mineral surfaces.\cite{3f}

Moreover, surface reactions of carbonates can occur on time-scales of few seconds to minutes\cite{38} and as a result, geochemical reactions emerge mainly controlled by the local equilibria for dissolution and precipitation of minerals and organo-metal salts. Interestingly these effects are reflected in the difficulties to realize wettability alterations of rough calcite surfaces and highly microporous rocks\cite{72} where the high dissolution rates of carbonates can produce considerable saturation of the boundary layer with respect to the organo-calcium surface phases.

And third, the surface precipitation model for organic acids also addresses the mixed wettability of rock formations, in which certain mineral phases present higher propensities toward wettability alterations by bound organic matter.\cite{73} Here we attribute the ability of organic molecules to deeply modify carbonate surfaces relative to less soluble minerals, to the Ca\textsuperscript{2+} ion enriched fluid boundary layers of carbonates favoring the surface precipitation and retention of organo-calcium salts. With ambitions of CO\textsubscript{2} storage and oil recovery on vast spatiotemporal scales,\cite{1b,68} our observations of the nonmonotonic reactions of carbonate minerals capture the complex dynamics of fluid-mineral interfaces at the microscale. Such chemically coupled equilibria (8–11) represents an important stratum in the hierarchical structure of all geochemical endeavors, ranging from fluids and rocks interacting at the nanoscale to fluid displacement over kilometers.

In addition to biological, synthetic, and geological carbonates, our results have wide implications toward fundamental studies on adsorption involving soluble sorbents. In all standard isotherms, the sorption capacity increases and then saturates with increasing adsorbate contents. However, the solubility limit of the applied sorbent is often overlooked, see Equation (11). Especially the utilization of reaction media, highly enriched with sorbate molecules, can promote intermolecular interactions driving self-association. Depleted as either condensates or precipitates, these sorbent fractions could be mistaken as “substrate bound”, especially in batch adsorption experiments involving filtration and centrifugation steps. With numerous instances of decreased sorption at higher adsorbate contents in literature (Table S3, Supporting Information), we surmise that the observed transitions from surface to bulk precipitation of organic molecules interacting with carbonate surfaces is ubiquitous and extends to other sorbent molecules such as asphaltennes, polysaccharides, proteins, polymers, and ions interacting with diverse surfaces.

Therefore, we caution against the unqualified application of standard isotherms to sorption data, without first considering the physicochemical properties of the individual sorbent and sorbate materials, in order to acquire accurate values of thermodynamic constants and kinetic rates.

3. Conclusion

In conclusion, we report that the interfacial interactions between organic molecules and minerals encompass i) coupled chemical equilibria for dissolution and precipitation at fluid-mineral interfaces and ii) the composition and structure of the fluid boundary layer at mineral surfaces. Especially for relatively soluble carbonate minerals, even subtle perturbations to local thermodynamic equilibria for mineral dissolution, ion complexation, and precipitation reactions have substantial bearing on the global equilibrium of various fluid-mineral systems of biological, synthetic, and geological origins. For surface reactions occurring within the fluid boundary layer, calcium ions, temperature, and even flow velocity affect the continuum from mineral dissolution to the surface and bulk precipitation of organo-metal salts. These findings provide new ways to understand the dynamic nature of carbonate interfaces across fields, such as biominalization, additive-guided crystallization, climate change, and reservoir engineering. Finally, the nonmonotonic relations show that direct extrapolation of laboratory data to complex biological and geological systems is not straightforward, also establishing that at the interface neither the mineral nor the fluid is equivalent to its bulk counterpart.\cite{50}

4. Experimental Section

Materials: Calcium carbonate utilized in experiments includes freshly cleaved Iceland spar (Ward’s Science) and synthetic Mg-calcite grown on surfaces of silica sensors (described below). Aqueous solutions of Sigma-Aldrich reagent grade chemicals (calcium chloride (CaCl\textsubscript{2}), magnesium chloride hexahydrate (MgCl\textsubscript{2}·6H\textsubscript{2}O), sodium bicarbonate (NaHCO\textsubscript{3}), and sodium hydroxide (NaOH)) were prepared using deionized water (18.2 M\textsubscript{Ω} cm, Milli-Q). Solutions of organic acids (EDTA, HA, and disodium salt of protoporphyrin IX (PP-IX)) from Sigma-Aldrich were prepared with deionized water.

Quartz Crystal Microbalance: The QCM-D technique enables monitoring changes in the resonance frequency and energy dissipation during shear oscillation of a quartz crystal sensor. Mass developments of sensors were monitored by using a QCM-D (E4) instrument from Q-sense (Gothenburg, Sweden). Prior to use, silica sensors from Biolin Scientific (Gothenburg, Sweden) were cleaned with steps of gentle flushing with acetic acid (2% w/w), immersion in aqueous solution of sodium dodecyl sulfate (1%) for 10 min and then immediate rinsing with deionized water. Sensors were then dried in a stream of nitrogen and cleaned in a UV Ozone ProCleaner (Bioforce) for 20 min.

Growth of Mg-calcite on silica sensors was performed in a Q-Sence E4 flow cell at a constant temperature of 25 °C. Alternate injections of equal volumes (200 µL) of freshly prepared i) solution mixture of CaCl\textsubscript{2} (0.25 m) and MgCl\textsubscript{2}·6H\textsubscript{2}O (0.25 m) and (ii) NaHCO\textsubscript{3} solution (0.5 m) were performed at a rate of 100 µL min\textsuperscript{-1} by using a peristaltic pump (IPC-N 4, Ismatec). After mineral deposition, the QCM cell was flushed with a NaOH solution (pH 10.5) at 50 µL min\textsuperscript{-1} until a stable baseline with minimal drift (<0.1 Hz min\textsuperscript{-1} for the third overtone) was obtained. During this regime, the flow cell temperature was adjusted as required for investigating subsequent sorption processes. The sorption experiments were performed by injecting an aqueous mixture (pH 10.5) of either HA (10 × 10\textsuperscript{-3} m) or PP-IX (50 × 10\textsuperscript{-6} m), or EDTA (1 × 10\textsuperscript{-3} m) and Ca\textsuperscript{2+} ions for 1 h at a flow rate of 50 µL min\textsuperscript{-1} (unless stated otherwise). Finally the NaH solution (pH 10.5) was injected again at 50 µL min\textsuperscript{-1}.

Potentiometric Titration: An automatic potentiometric titration system (HI-931-02, Hanna Instruments) equipped with a Ca\textsuperscript{2+} ion selective electrode (ISE) and computer controlled dosing unit was used (Figure S1, Supporting Information). All titrations were performed in a temperature-controlled reaction vessel equipped with an overhead stirrer operated at 600 rpm. The ISE was calibrated by continuous CaCl\textsubscript{2} addition to DI water (pH 10.5, 100 mL) at 10 and 40 °C. Glassware, electrodes, stirrer, and burette tip were rinsed with acetic acid (5%) and cleaned with DI water after each experiment run.

To investigate the deposition of organic acids on calcite surfaces, distinct solution compositions were prepared by the slow addition of a
CaCl₂ stock liquid to a PP-IX solution (pH 10.5) at a rate of 100 μL min⁻¹ while stirring and maintaining a constant temperature. On attaining the desired solution composition, a cm-size Iceland spar crystal was immersed for 2 min and then dried in a stream of nitrogen.

To characterize ion binding interactions, a calcium chloride solution (0.05 m) was gradually added (at 100 μL min⁻¹) to an aqueous solution of PP-IX (200 × 10⁻⁶ m, pH 10.5). Meanwhile, the free Ca²⁺ ion concentration was monitored with the ion-selective electrode. The binding stoichiometry and equilibrium constant were estimated using a Langmuir-type binding model, in which \( n \) Ca²⁺ ions are assumed to associate with one molecule of PP-IX (P)

\[ n \text{Ca}^{2+} + P \rightarrow \text{Ca}_nP \] (15)

and the fraction of bound calcium ions is expressed as

\[ \frac{[\text{Ca}]_{\text{bound}}}{[\text{Ca}]_{\text{add}}} = \frac{c_{\text{max}} + [\text{Ca}]_{\text{add}}}{[\text{Ca}]_{\text{add}}} \] (16)

where \( K_i \) is the Langmuir constant, \( c_{\text{max}} \) is the Ca²⁺ ion binding capacity of the protoporphyrin (at concentration [P]), and \([\text{Ca}]_{\text{add}}\) is the added Ca²⁺ content. After fitting \( K_i \) and \( c_{\text{max}} \) from the titration data, the binding stoichiometry is estimated as

\[ n = \frac{c_{\text{max}}}{[P]} \] (17)

Solubility Estimation: Solubilities of organo-calcium salts were estimated by prolonged incubations of 100 mL solutions containing CaCl₂ and an organic acid (viz., a) \( 100 \times 10^{-3} \) m CaCl₂ and \( 50 \times 10^{-6} \) m protoporphyrin and b) \( 10 \times 10^{-3} \) m CaCl₂ and \( 2.5 \times 10^{-6} \) m HA) in sealed bottles at 10, 25, and 40 °C for 3 weeks with intermittent mixing. The mixtures were thereafter quickly filtered through a polyethersulfone (PES) filter membrane (0.2 μm) and centrifuged at 4000 g for 10 min to remove precipitates. Obtained supernatants were analyzed for residual Ca²⁺ and centrifuged at 4000 g for 10 min to remove precipitates. Obtained µ40 of 600 g mm⁻¹ microscope equipped with a 532 nm excitation laser was used. A Iceland spar and sensor surfaces, a WITec Alpha-300R confocal Raman microscope (1600 objective (NA = 0.56), a) 100 × 10⁻³ m CaCl₂ and 2.5 × 10⁻⁶ m HA) in sealed bottles at 10, 25, and 40 °C for 3 weeks with intermittent mixing. The mixtures were thereafter quickly filtered through a polyethersulfone (PES) filter membrane (0.2 μm) and centrifuged at 4000 g for 10 min to remove precipitates. Obtained supernatants were analyzed for residual Ca²⁺ content using the ISE and also for residual organic contents. Residual PP-IX contents were measured from their absorbance values at 380 nm using a Tecan infinite M200 plate reader (Figure S2, Supporting Information). To quantify residual from the absorbance values at 380 nm using a Tecan infinite M200 plate reader (Figure S2, Supporting Information). To quantify residual HA contents, copper reagent of Lowry and Tinsley was prepared by filtering 0.5 g L⁻¹ aqueous solution of cupric acetate and then applied for precipitating copper salts of the fatty acid. After filtering the reaction product through a PES filter membrane (0.2 μm) to remove precipitates, the depletion of Cu²⁺ species was estimated by measuring the absorbance at 380 nm (Figure S2, Supporting Information).

Confocal Raman Microscopy: For the surface characterization of Iceland spar and sensor surfaces, a WITec Alpha-300R confocal Raman microscope equipped with a 532 nm excitation laser was used. A 50× objective (NA = 0.75, Zeiss ECL Planap) and a CCD camera (1600 × 200 pixels, 16 μm pixel size, Andor Newton) were used. A grating of 600 g mm⁻¹ provided a spectral resolution of 2.3 cm⁻¹. To account for the inherent fluorescence of Iceland spar, the spectral datasets were initially baseline corrected using the Witec ProjectFIVE software and next a principal component analysis (PCA) guided denoising was applied. False color distribution maps were generated by integrating the spectral regions of interest for each pixel: from 1076 to 1095 cm⁻¹ for calcite (\( \nu_3 \), in-plane bending) and from 1500 to 1650 cm⁻¹ for PP-IX.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

adsorption, calcium carbonate, dissolution, interfaces, organic acids, QCM-D

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