

Defect-mediated carbonation pathways at the brucite-gas interface

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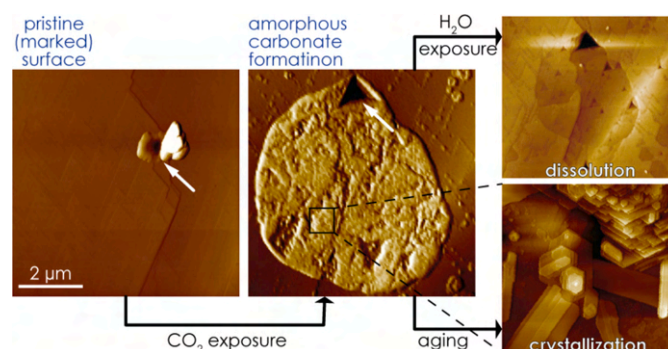
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HIGHLIGHTS

- AFM tracking reveals brucite carbonation under water-lean conditions.
- Carbonation nucleates preferentially at brucite step edges.
- Conformal carbonate layer remains permeable to interfacial transport.
- Carbonate growth propagates beneath crystal terraces.
- Epitaxial nesquehonite probably forms from amorphous precursor layers.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Carbonate formation
Brucite
CO₂
Atomic force microscopy
Mineral surfaces
Interfacial transport
Solid-gas interfaces

ABSTRACT

Hypothesis: Mineral carbonation is governed by water-mediated interfacial transport and nucleation processes. In bulk aqueous environments, dissolution, transport, and precipitation occur in spatially separated domains, preventing direct resolution of interfacial reaction pathways. We hypothesize that under water-lean conditions local mass redistribution can be directly resolved at the reactive interface, enabling carbonation pathways to be determined through direct tracking of redistributed and newly formed interfacial volumes.

Experiments: To isolate the interfacial carbonation pathway, we performed atomic force microscopy on freshly cleaved brucite [Mg(OH)₂] single crystals exposed to CO₂ under hydrothermal equilibrium conditions and specific humidity ~2%. The same surface regions were tracked before and after the treatments, enabling direct nanoscale visualization of morphological evolution due to carbonation while suppressing bulk-solution processes.

Findings: Carbonation initiates preferentially at surface step edges, where defect-mediated nucleation produces nanophases with possible amorphous structure whose volume scales with step height. These transient layers remain permeable to mass transport, enabling sustained subsurface growth beneath crystal terraces instead of immediate surface passivation. Upon aging, the amorphous precursor crystallizes into oriented needle-like aggregates at the brucite-carbonate interface, revealing a non-classical growth pathway governed by defect-controlled flux localization and transport likely through nanoconfined interfacial water films. These findings establish a direct mechanistic link between surface defects, plausible water molecule mediation, and interfacial

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<https://doi.org/10.1016/j.jcis.2026.141596>

Received 16 May 2026; Received in revised form 11 September 2026; Accepted 11 September 2026

Available online 13 September 2026

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carbonate growth dynamics, providing a framework for understanding solid-gas mineralization reactions in confined aqueous environments.

1. Introduction

Alkaline-earth metal hydroxides, and in particular brucite, $\text{Mg}(\text{OH})_2$, represent prototypical solid surfaces for studying CO_2 mineralization at the nanoscale, where interfacial transport, hydration, and phase transformation are tightly coupled yet remain mechanistically unresolved. Brucite carbonation, although in principle possible under dry conditions via dehydroxylation of the mineral [1,2], predominantly proceeds through water-mediated pathways in which dissolved CO_2 species drive dissolution–precipitation reactions that yield magnesium carbonates [3]. While water accelerates carbonation kinetics by enabling ion transport and CO_2 hydration, it also fundamentally alters the reaction pathway by stabilizing hydrated intermediates and decoupling interfacial reactions from local mass balance. Elucidating how water governs these pathways is therefore central to controlling mineral carbonation since its products enable thermodynamically stable long-term storage and feedstocks for industrial reuse [4,5]. Addressing this challenge requires microscopic and spectroscopic approaches capable of probing the solid-fluid interface with molecular-scale resolution, while accounting for the structural properties of the reactive solid that regulate interfacial mass exchange.

The freshly cleaved (001) surface of brucite provides a well-constrained model system for such investigations. A pioneering atomic force microscopy (AFM) study by Kudoh et al. showed that, despite the low solubility of brucite, dissolution of the basal surface in water proceeds via the nucleation of 2D triangular etch-pits bounded by the [100], [010], and $[1\bar{1}0]$ crystallographic directions [6]. The interplay between dissolution and carbonation at the brucite basal surface was later investigated by Hövelmann et al. [7] by introducing dissolved inorganic carbon in the form of hydrogen carbonate solutions. In that study, triangular etch-pits remained a recurrent morphological motif and were followed at later stages by the appearance of additional particulate Mg-carbonate phases on the mineral surface, likely occurring as dypingite $[\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}]$.

A recurring theme in the literature is the pivotal role of confined water at mineral interfaces, where nanometric films act as quasi-two-dimensional reactive environments controlling ion release, transport, and carbonate nucleation. For instance, faster precipitation of Mg-carbonates has been observed in ultrathin water layers compared to bulk solutions, underpinning the emergence of broader “on-water catalysis” concepts at aqueous interfaces [8–14]. Complementarily, operation under water-saturated supercritical CO_2 enhances reaction driving forces and enables *in situ* AFM observations of amorphous magnesium carbonate (AMC) nucleation, which subsequently seeds nesquehonite growth [15,16]. AMC is typically described by a $\text{MgCO}_3 \cdot x\text{H}_2\text{O}$ ($x = 0.5\text{--}1.0$) stoichiometry and exhibits a hydromagnesite-like structure $[\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}]$.

At the nanoscale, $\text{MgO}/\text{Mg}(\text{OH})_2$ systems exhibit strongly humidity-dependent dynamics. Luong et al. tracked the growth of AMC on MgO nanocubes exposed to moist CO_2 in thin water molecule film [17]. AMC, with a stoichiometry of $\text{MgCO}_3 \cdot 2.3\text{--}2.5\text{H}_2\text{O}$, was observed to grow in sub-monolayer to 4 monolayer-thick water films, with formation rates and yields scaling with humidity. However, AMC growth progressively limited the access of water to the reactive MgO core. Exposure to thicker water films partially dissolved these coatings [18], temporarily restoring reactivity until passivation re-emerged. These findings identify a dynamic passivation mechanism that may represent a key bottleneck for efficient CO_2 mineralization in MgO -based systems [19,20].

Very recently, the structural evolution of brucite under controlled humidity at ambient pressure has been probed by indirect analytical techniques, showing that carbonation leads to the formation of a

smooth, conformal coating of hydrated Mg-carbonates at the surface [21].

These studies collectively suggest that carbonation is governed by interfacial processes in confined water films, yet they also report contrasting behaviors, ranging from sustained growth to rapid surface passivation.

In the light of the state of the art, *in situ* AFM studies at the solid-liquid interface have identified the key steps of brucite carbonation, namely the water-triggered dissolution, followed by the attainment of supersaturation conditions for carbonate precipitation and the subsequent growth of a hydrated carbonate layer. However, under conditions where the mineral is in contact with a bulk aqueous reservoir, dissolution, transport, and precipitation occur in spatially separated domains. As a result, interfacial mass balance cannot be rigorously established, and the spatial coupling between defect structure, mass transport, and carbonate growth remains unresolved. Indirect spectroscopy techniques have provided complementary evidence, indicating the formation of a conformal layer of hydrated Mg-carbonates and their dependence on environmental conditions and water layer thickness [21].

To overcome these limitations, we confine carbonation to the solid-gas interface under hydrothermal conditions and specific humidity $\sim 2\%$, suppressing bulk-solution processes and enabling direct AFM tracking of the same surface regions. This strategy enables direct access to the intrinsic interfacial pathway of carbonation, disentangled from bulk-mediated processes. We show that carbonation initiates at step edges, forming islands whose volume scales with step height, and subsequently propagates beneath terraces. The nascent carbonate layer remains permeable to mass transport, while aging drives crystallization into oriented needle-like crystals at the brucite-carbonate interface which we attribute to nesquehonite with possible epitaxial order. These findings establish a direct mechanistic link between surface defects, nanoscale transport, and interfacial growth dynamics, providing a general framework for solid-gas reactions, likely mediated by confined water films.

2. Materials and methods

2.1. Suppliers for materials and instrumentations

All materials, gases, and consumables used in the hydrothermal treatments are listed here to ensure full reproducibility:

- Nitrogen (N_2 , 99.999%) and carbon dioxide (CO_2 , 99.995%) were supplied by Gruppo Sapio, Milano, Italy, and used as received.
- Municipal tap water from the University of Milano-Bicocca laboratory supply was used exclusively as microwave-absorbing base load and did not come into direct contact with the brucite samples.
- Ultra-pure water used for *in situ* AFM dissolution experiments was produced with a Milli-Q® IQ 7003 Water Purification system, from Merck Millipore distributor, and had a resistivity higher than 18 $\text{M}\Omega \text{ cm}$.
- Brucite lamellae were mounted on quartz slides $[(10 \times 10) \text{ mm}^2]$; kindly provided by Prof. Donato Belmonte] using Super Attak acrylic glue from Loctite® and exfoliated immediately before treatment using Magic™ adhesive tape from Scotch®.
- PTFE perforated vials and the PTFE rack were commercially purchased from Milestone S.r.l, Sorisole, Italy.
- Hydrothermal treatments were performed in a SynthWave microwave synthesizer (Milestone Srl, Sorisole, Italy) equipped with a 900 mL cylindrical PTFE-lined reactor and a 2.45 GHz magnetron source with maximum power of 1500 W.

AFM measurements were performed using a Keysight 5500 scanning probe microscope (Keysight, Santa Rosa, CA, USA) operated in tapping mode with PPP-NCHR-20 silicon probes (NanoSensors™, Neuchâtel, Switzerland; nominal spring constant *ca.* 40 N/m, resonance frequency *ca.* 310 kHz). AFM images were processed using WSxM software, version 5.0.

2.2. Brucite single crystals

Natural lamellar brucite crystal (Fig. S1) was manually cleaved by shock to produce lamellae exposing prevalently the (001) face. This specimen occurs in veins within hydrothermally altered serpentinites. It originates from the Carro mine (Carro municipality, La Spezia, Italy). The chemical composition of brucite, determined by SEM-EDS analysis on polished sections, is close to the end-member composition, $\text{Mg}(\text{OH})_2$, with a maximum Fe^{2+} content of 0.02 apfu [22]. Because of the manual cleavage, lamellae can show different sizes, in the order of few millimeters square. Single lamellae were glued with acrylic adhesive on $(10 \times 10) \text{ mm}^2$ quartz slides to facilitate transportation and placement on the sample holder for AFM measurements and reactor rack for hydrothermal treatments. Before any treatment, the surface of the crystal was exfoliated by adhesive-tape.

2.3. Hydrothermal treatments

Quartz slides with the brucite crystal were placed in PTFE perforated vials in a PTFE-rack which can be inserted in a cylindrical PTFE-lined reactor (900 mL total volume) filled with 200 mL of tap water, forming a 4 cm-high liquid layer. Samples stayed suspended above the water surface. Tap water, containing a fraction of electrolytes, serves as base load facilitating microwave absorption from a magnetron source (2.45 GHz, max power, 1500 W) irradiating from the bottom of the reactor and enables fine temperature monitoring by using an immersed temperature gauge. Tap water was used exclusively as MW-absorbing base load and did not come into direct contact with the samples. The reactor is part of a microwave synthesizer (SynthWave, Milestone), enabling to control the gauge pressure inside the reactor and to program the temperature ramp. After loading the samples at room temperature, the reactor was closed

and gases were injected up to an established pressure. For treatment in pure N_2 atmosphere, N_2 (99.999%) was injected up to a pressure of 10 bar, then temperature was increased linearly up to 80 °C in 10 min, and maintained at 80 °C for 10 min. For treatment in mixed N_2/CO_2 atmosphere, N_2 (99.999%) was injected up to a pressure of 5 bar, then temperature was increased linearly up to 80 °C in 10 min, CO_2 (99.995%) was injected up to a pressure of 10 bar and temperature maintained at 80 °C for 10 min. For treatment in pure CO_2 atmosphere, temperature was increased linearly up to 80 °C in 10 min, then CO_2 (99.995%) was injected up to a pressure of 10 bar and temperature maintained at 80 °C for 10 min. After the 20-min treatments, the reactor was immediately depressurized and the samples were extracted and stored in vacuum-sealed boxes. The external jacket of the reactor was chilled with a flux of water at 8 °C to allow for restarting of a new experiment at room temperature.

Considering that the vapor pressure of water at 80 °C is 0.47 bar, the water-vapor mole fraction at the conditions adopted is $\sim 5\%$. The humidity ratio (ω) of the gas phase is estimated to be $\omega = (M_{\text{H}_2\text{O}} \times P_{\text{sat}}) / (M_{\text{dry}} \times P_{\text{dry}})$, where $M_{\text{H}_2\text{O}}$ is the molar mass of water, P_{sat} is the saturation pressure of water, M_{dry} is the average molar mass of the gas phase excluding water, and P_{dry} its partial pressure. When 10 bar of pure N_2 are adopted, $\omega = (18.015 \times 0.47) / (28.013 \times 10.0) = 0.030 = 3.0\%$; when equal partial pressures of CO_2 and N_2 are adopted [average molar mass $= (0.5 \times 44.010 \text{ g mol}^{-1}) + (0.5 \times 28.013 \text{ g mol}^{-1}) = 36.0115 \text{ g mol}^{-1}$], $\omega = (18.015 \times 0.47) / (36.0115 \times 10.0) = 0.024 = 2.4\%$, decreasing to 1.9% when pure CO_2 is adopted. Corresponding specific humidities [$q = \omega / (1 + \omega)$] are 2.9%, 2.3% and 1.9%, respectively.

Note that at 80 °C the penetration depth of 2.45 GHz microwaves in water is close to the thickness of the base water layer ($\sim 4 \text{ cm}$). This implies that water absorbs a large part of MW irradiation, so that irradiation received by the samples is minimal and their temperature increases *via* vapor convection.

Each kind of treatment was repeated twice, and, for each kind of treatment, three brucite lamellae were placed in the PTFE perforated vial and exposed to the reactor environment. At the end of each treatment, lamellae were transferred inside vacuum-sealed boxes to the AFM instrumentation for the *ex situ* measurements within 12 h.

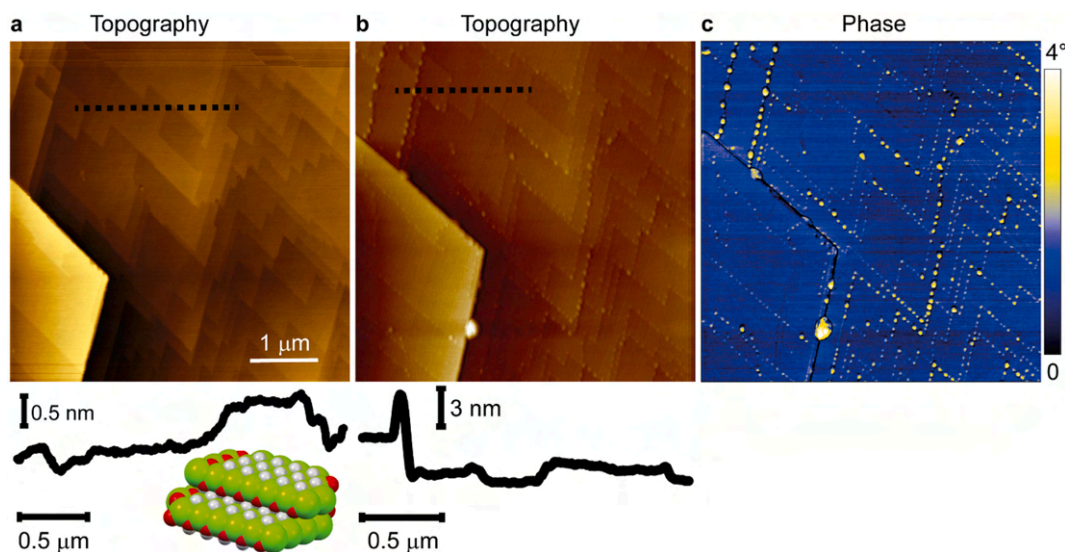


Fig. 1. Pristine brucite surface under hydrothermal conditions and absence of CO_2 . (a) AFM image of a region of the (001) surface of a freshly-exfoliated single crystal of brucite and cross-sectional profile (solid black line; vertical and horizontal scale bars displayed) as taken along the black dotted segment. The structural model in the inset shows the layered structure of the crystal (green: Mg-atoms, red: O-atoms, white: H-atoms), with layers separated by $d_{001} = 0.477 \text{ nm}$. (b) Same region as panel (a) after a 10 min-treatment at 80 °C under $p\text{-N}_2 = 10 \text{ bar}$. A cross-sectional profile (solid black line; vertical and horizontal scale bars displayed) as taken along the black dotted segment is shown. (c) Phase contrast image of the region in panel (b) highlighting round-shaped bulbs decorating the surface step-edges. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

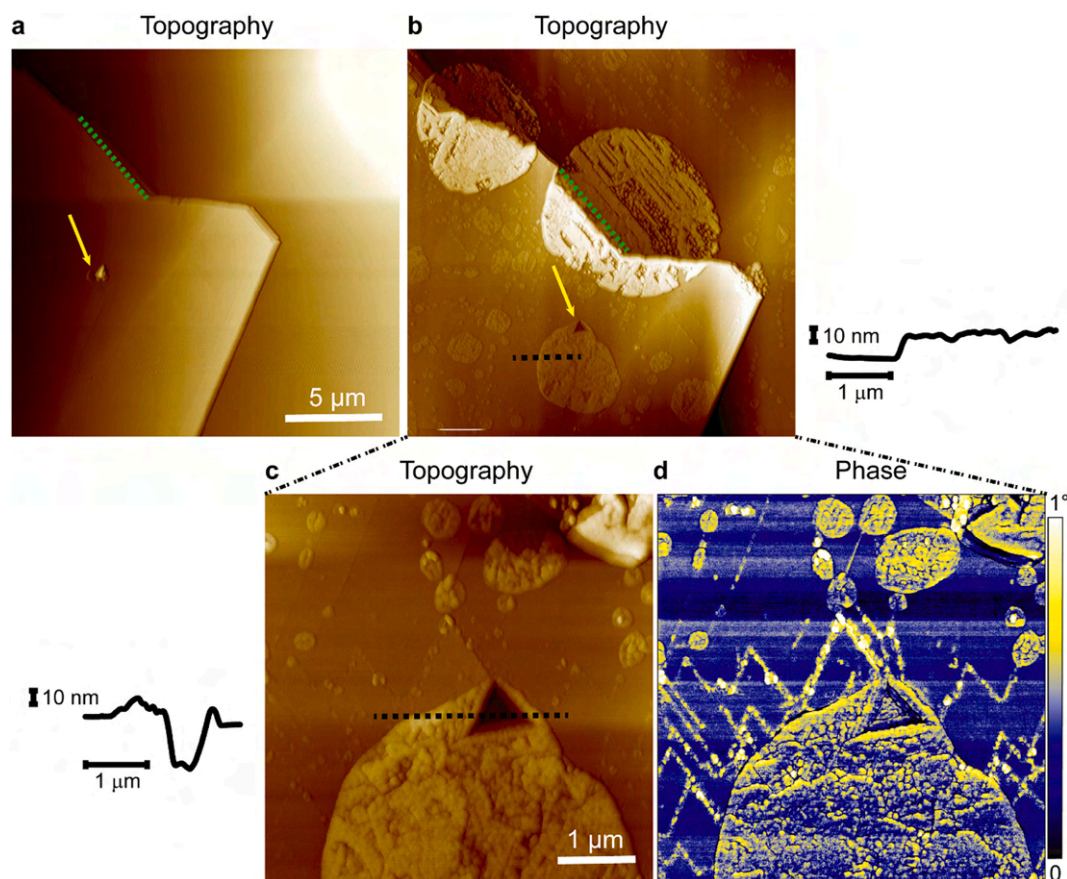


Fig. 2. Brucite surface under hydrothermal conditions and partial pressure of N_2 and CO_2 . (a) AFM image of a region of the (001) surface of a freshly-exfoliated single crystal of brucite; the yellow arrow indicates a hole formed by nanoindentation, marking the surface region for its retrieval after *ex situ* treatments. The green dotted segment marks one step edge. (b) Same region as panel (a) after a 10 min-treatment at 80 °C under $p\text{-}CO_2 = 5$ bar + $p\text{-}N_2 = 5$ bar; the inset on the right shows a cross-sectional profile as taken along the black dotted segment. The yellow arrow indicates the triangular-shape evolved indentation hole. (c) Zoomed image of an area nearby the indentation spot, with a cross-sectional profile as taken along the black dotted segment. (d) Phase contrast image of the region in panel (c), highlighting round-shaped islands decorating the surface step-edges and terraces. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.4. AFM measurements and images analysis

AFM measurements were performed by using a Keysight 5500 scanning probe microscope (SPM). For all the measurements, tapping mode (amplitude modulation imaging) was used to preserve the sample surface from damages, adopting a setpoint of ca. 93% of the free oscillation amplitude. Single beam silicon tips from NanoSensors™, with cantilever of nominal elastic constant k of about 40 N/m and resonance frequency around 310 kHz, were adopted. The tapping acquisition mode offers also the possibility to acquire phase-contrast signals, in which oscillation phase-lag changes due to different visco-elastic properties are recorded.

On each freshly-cleaved and exfoliated brucite (001) surface, by forcing the AFM tip on it, an indentation was deliberately performed for marking a specific position on the crystal, enabling easier retrieval of the same investigation area in the case of drastic transformation induced by the occurrence of chemical reactions. Images by an optical microscope, integrated in the Keysight 5500 SPM, have been also acquired to allow a fine positioning of the AFM tip on the same area of the sample surface, in pre- and post-carbonation *ex situ* measurements.

AFM measurements of the dissolution of carbonation islands on the brucite surface were performed *in situ*, with the sample horizontally immersed in a liquid cell filled by ultra-pure water ($> 18\text{ M}\Omega\text{ cm}$). The layout of the liquid cell allows the full insertion of the AFM tip holder from the top. Working oscillation frequency of the cantilever was reduced to ca. 100 kHz.

AFM images were analyzed using WSxM software [23]. For the statistical analysis, more than 500 images were acquired and processed, obtained by probing at least 5 different areas of each crystal surface undergoing each hydrothermal treatment.

Quantitative evaluation of the material eroded from steps on the brucite surface was carried out by comparing identical areas in pre- and post-carbonation topography images and marking morphological differences. Cross-sectional profiles were extracted to determine height, area, and volume variations.

To estimate the relative height of islands formed on the brucite surface after carbonation, a baseline was defined around each island as observed in the topography images. With respect to this baseline, the mean island height was calculated by binarizing the distinct islands in the image, by using an appropriate colored mask (see the example in Fig. 3a-ii). Binarization was also employed to determine the island area, while the island volume was estimated by multiplying its mean height by its area.

Error bars in graphs of Figs. 3 and 4 arise from the estimation of the variability of binarization procedure.

3. Results and discussion

3.1. Morphology and stability of pristine brucite surfaces under hydrothermal conditions

Brucite crystallizes in the trigonal crystal system with unit cell

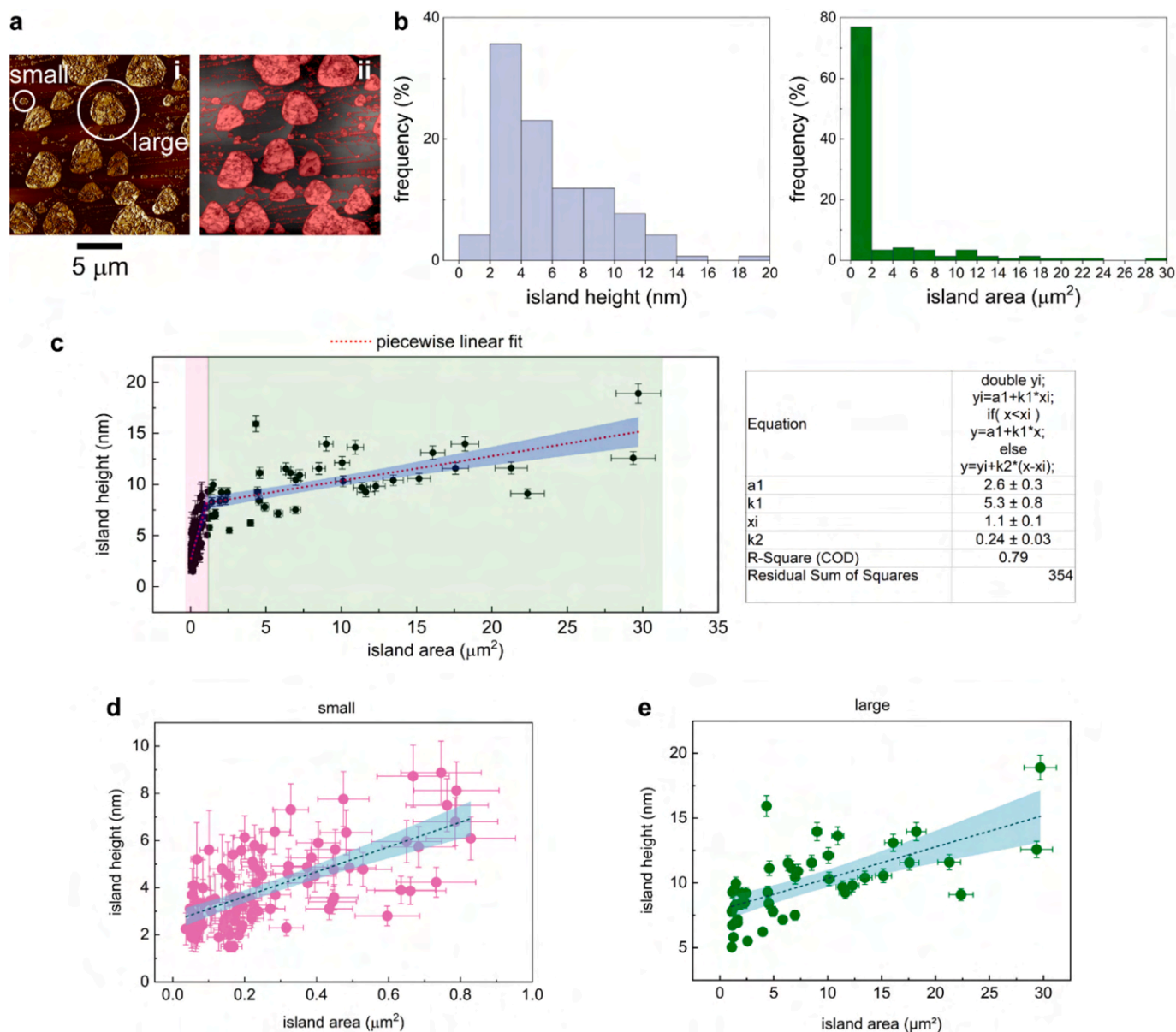


Fig. 3. Statistics and scaling of island size. (a-i) AFM topography of a representative region of the brucite sample surface, after a 10 min-treatment at 80 °C under $p\text{-CO}_2 = 5$ bar and $p\text{-N}_2 = 5$ bar. White circles enclose islands of different sizes (*small* and *large*). The scale bar is reported at the bottom of the image. (a-ii) In red, an example of binarization of the topography image (panel (a-i)) for quantitative statistical analysis of the geometrical parameters of islands. (b) Histograms for height and area distributions evaluated on a statistical group of both small and large islands. (c) Overall graphical distribution of height (nm) vs area (μm^2) evaluated on a statistical group of islands. The piecewise linear fit with two segments (dash red lines) shows two growth regimes, with different linear regressions, from which small and large islands, respectively in light pink and light green layer areas, can be clearly distinguished; the 95% confidence bands are highlighted in blue. In the table, equations and fit parameters are reported, where the “xi” value represents the breakout point between the two segments. (d,e) Graphical distribution of height (nm) vs area (μm^2) evaluated on a statistical group of small (pink symbol) and large (green symbol) islands. The best linear fit is shown by the dash black lines, and the 95% confidence band is highlighted in light blue. The linear regressions show the following parameters: for small islands, $\text{slope} = (5.3 \pm 0.6) \text{ nm } \mu\text{m}^{-2}$, r (Pearson's) = 0.65 ($p\text{-value} = 2.6 \times 10^{-13}$); for large islands, $\text{slope} = (0.24 \pm 0.04) \text{ nm } \mu\text{m}^{-2}$, $r = 0.65$ ($p\text{-value} = 1.5 \times 10^{-6}$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

parameters $a = b = 3.15 \text{ \AA}$, $c = 4.77 \text{ \AA}$, $\gamma = 120^\circ$ [24]. The crystal possesses a natural cleavage surface parallel to the (001) plane. {001} planes enclose single octahedral $\text{Mg}(\text{OH})_6^{4-}$ units with spacing $d_{001} = c = 4.77 \text{ \AA}$ (inset Fig. 1a, see Fig. S2 for more details). The surface topography as measured by AFM of a freshly-exfoliated brucite crystal is displayed in Fig. 1a.

The freshly cleaved surface exhibits atomically flat terraces separated by monolayer steps with height multiple of $d_{001} = c = 0.477 \text{ nm}$, having step edges oriented azimuthally at integer multiples of 60° one another, reflecting the hexagonal symmetry of the crystal [6]. This

morphology provides a well-defined platform to track interfacial transformations with nanometric resolution.

Fig. 1b reveals that hydrothermal treatment of the crystal in a pure nitrogen atmosphere ($p\text{-N}_2 = 10$ bar) at 80 °C for 10 min results in the formation of nanometric bulges decorating the step-edges; their presence is better indicated by the phase-contrast image in Fig. 1c.

Defects on the basal surface of brucite represent a primary driver of its reactivity. Step-edges represent sites of undercoordinated Mg-ions (Fig. S2) which can be attacked by both water and CO_2 molecules if present in the environment. The results of hydrothermal treatment in

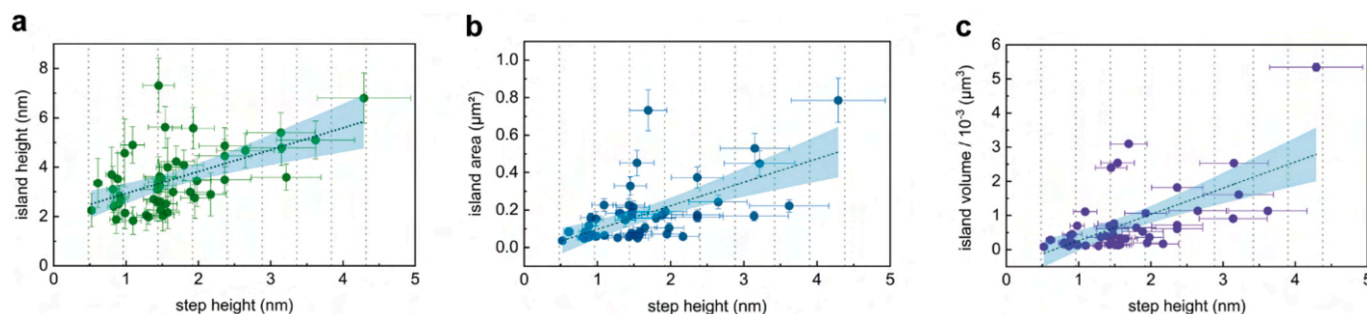


Fig. 4. Dependence of island size on the height of the brucite (001) step-edges. Distribution of height (panel (a)), area (panel (b)) and volume (panel (c)) of small islands vs the height of the brucite (001) step-edge across which they grow. In each graph, the best linear fit is shown by the dash black line, and the 95% confidence band is highlighted in light blue. The best linear fits have the following parameters: in (a), $\text{slope} = 0.9 \pm 0.2$, $r = 0.55$ ($p\text{-value} = 4.2 \times 10^{-5}$); in (b), $\text{slope} = (0.13 \pm 0.02) \mu\text{m}^2 \text{nm}^{-1}$, $r = 0.60$ ($p\text{-value} = 5.3 \times 10^{-6}$); in (c), $\text{slope} = (8 \pm 1) \times 10^{-4} \mu\text{m}^3 \text{nm}^{-1}$, $r = 0.63$ ($p\text{-value} = 2.0 \times 10^{-6}$). Vertical dotted lines correspond to single and multiple-layer steps. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

absence of CO_2 reported in Fig. 1 demonstrate that water molecules (at specific humidity as low as $\sim 2\text{--}3\%$) can modify the morphology of brucite crystals as step-edges are observed to act as preferential sites for particle nucleation. Due to the presence of only H_2O and N_2 in the environment, we interpret this result as due to a mobilization of hydrated Mg^{2+} and OH^- ions just along the step-edges and recrystallisation in the form of nanoparticles or clusters along the same step-edges. In this respect, although the hydrothermal treatments were conducted under nominally water-lean conditions, an interfacial liquid water on the brucite basal surface can be likely assumed. A growing body of experimental and theoretical work demonstrates that strongly hydrophilic and hydroxylated mineral surfaces can stabilize sub-nanometer to nanometer-scale adsorbed water films at very low water activities, well below the threshold required for bulk condensation. Indeed, even at relative humidity as low as $\text{RH} \sim 5\%$, mineral surfaces are coated by this confined water films, typically limited to a few molecular layers and preferentially localized at surface defects such as step edges [25]. Recent surface-science studies have further shown that even sub-nanometric hydration layers can directly promote CO_2 activation and carbonate formation at mineral surfaces, enabling water-assisted solid-gas carbonation pathways with negligible kinetic barriers [26]. Importantly, brucite exposes a fully hydroxylated (001) basal surface, which is expected to exhibit particularly strong affinity for water adsorption, as supported by *ab initio* surface studies and nanoscale observations of brucite-fluid interfaces [2,7,27]. Consequently, even under the low specific humidity conditions adopted here, the presence of interfacial few molecular water layers on brucite surfaces cannot be excluded and likely contributes to the observed surface reactivity. It is remarkable that the size of the recrystallized particles is correlated with the thickness of the attacked step-edge, suggesting that the higher the step-edge, the larger the amount of recrystallized brucite. The clear contrast difference in phase-lag AFM images (Fig. 1c) between the basal surface and the particles is indicative of phases with substantially different visco-elastic properties arising from the disordered nature of the latter domains.

3.2. Defect-mediated nucleation of a poorly crystalline carbonate nanophases

With presence of CO_2 in the reactor environment, the surface evolution drastically changes. Fig. 2a shows the freshly-exfoliated brucite (001) surface of another sample, over which the indentation performed by the AFM tip is indicated by the yellow arrow. The indentation created a *ca.* 25 nm-deep hole and the accumulation of displaced material on the right side of the hole edge (see Fig. 2a and Fig. S3). Fig. 2b shows that with $p\text{-CO}_2 = 5$ bar, step-edge erosion (retreat) is visible (e.g., compare the position of green dotted segments in panels a,b), corresponding to an eroded volume of $(0.37 \pm 0.03) \mu\text{m}^3$, together with the formation of structured round-shaped islands and the disappearance of the material

accumulated nearby the indented hole, which assumes a sharp triangular shape.

The formed islands, though exhibiting a peculiar texture, have a rather uniform height, as shown by the cross-sectional profile reported in Fig. 2b. The two islands dominating the contrast of Fig. 2b clearly develop across an eroded step-edge, with a portion covering the terrace above, occupying a volume of $(1.10 \pm 0.08) \mu\text{m}^3$, and another portion covering the terrace below, occupying a volume of $(1.1 \pm 0.1) \mu\text{m}^3$. This motive holds for all islands, even though less evident for smaller ones. Different islands have different sizes and heights, both depending on the height of the step-edge across which they grow (see below). In Fig. 2c, a zoomed image of the area near the indentation hole shows that, after the reaction, the hole evolved in a *ca.* 33 nm-deep triangular-shaped one (see cross sectional profile). In the phase contrast image reported in Fig. 2d, the triangular-shaped hole and all islands appear with a bright contrast, differentiating substantially from the background, indicating a different chemical composition. Whereas, within the triangular hole, the same texture and bright contrast of the islands are shown, indicating that the islands and the area inside the deep hole have similar chemical composition. A more detailed zoomed image on the area inside another triangular-shaped indentation spot, created on a different region of the same sample, showed the same behavior (see Fig. S4).

A deeper insight into the morphological and scaling aspects of the islands is provided by the results reported in Fig. 3. Fig. 3a reports a representative area of a brucite crystal subjected to carbonation with $p\text{-CO}_2 = 5$ bar at 80°C . To evaluate the size distribution of islands, the image contrast was binarized with respect to the best plane identifying the bare substrate level (see Table S1 for more details). Fig. 3b shows the area and height distribution of a group of almost 200 islands identified after image binarization. It is evident that islands distribute in accordance with two main groups: a large fraction ($\sim 80\%$) has an area lower than $2 \mu\text{m}^2$, whereas the rest of islands have a larger area. Islands pertaining to the former group are referred to as *small* islands, whereas islands pertaining to the latter group are referred to as *large* islands (Fig. 3a). The height distribution of islands shows one population centered at about 4 nm and a population centered at about 8 nm. As illustrated by the segmented model used to fit data points reported in the graph of Fig. 3c, the island height as a function of the island area is characterized by a rapid increase with size for small islands, followed by a substantially slower increase for large islands. The breakout point has best-fit coordinates $(1.1 \pm 0.1) \mu\text{m}^2$ and $(8.4 \pm 1.0) \text{nm}$. The piecewise fit is superior to a continuous single linear fit (Fig. S5), as demonstrated by comparing the R-square and residual sum of squares in Fig. 3c and Fig. S5, and indicates that island growth occurs in accordance with two regimes: an initial regime in which the islands develop preferentially in height, and a late regime in which islands increment preferentially their lateral size, forming a uniform layer with thickness ~ 8 nm. Fig. 3d quantifies these aspects, by showing that the linear regression performed

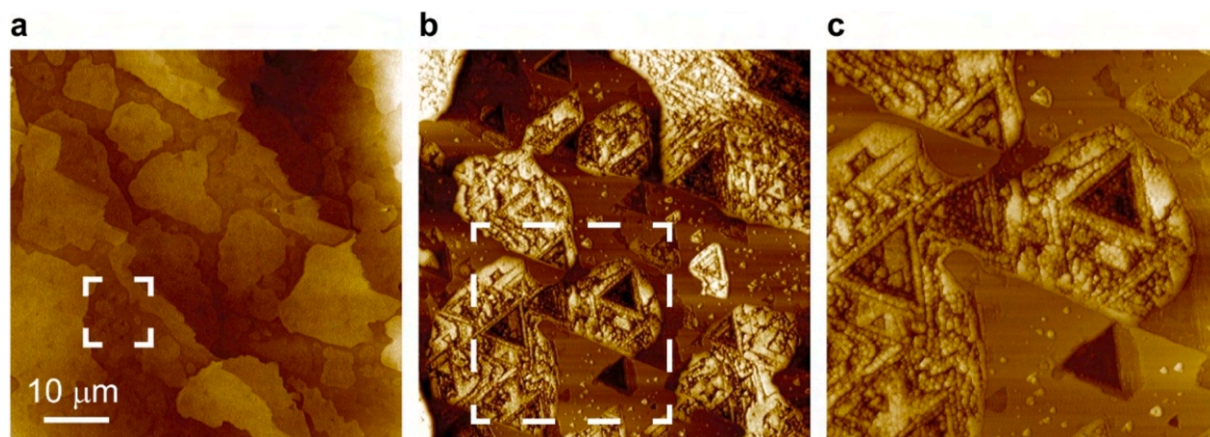


Fig. 5. Brucite surface under hydrothermal conditions and partial pressure of CO₂. (a) AFM image of the (001) surface after a 10 min-treatment at 80 °C under $p\text{-CO}_2 = 10$ bar; the white dashed square highlights the area of subsequent zoomed images. (b) $(10 \times 10) \mu\text{m}^2$ zoomed image of the area enclosed by the white dashed square in panel (a); coalescence between islands to form multilayers and triangular etch-pits are well discernible. (c) $(5 \times 5) \mu\text{m}^2$ zoom on a surface region showing the coalescence between two islands and the multilayer structure of the area enclosed by the white dashed square in panel (b).

with the datasets pertaining to *small* [$\text{size} < (1.1 \pm 0.1) \mu\text{m}^2$] and *large* [$\text{size} > (1.1 \pm 0.1) \mu\text{m}^2$] islands gives a height increment with area of

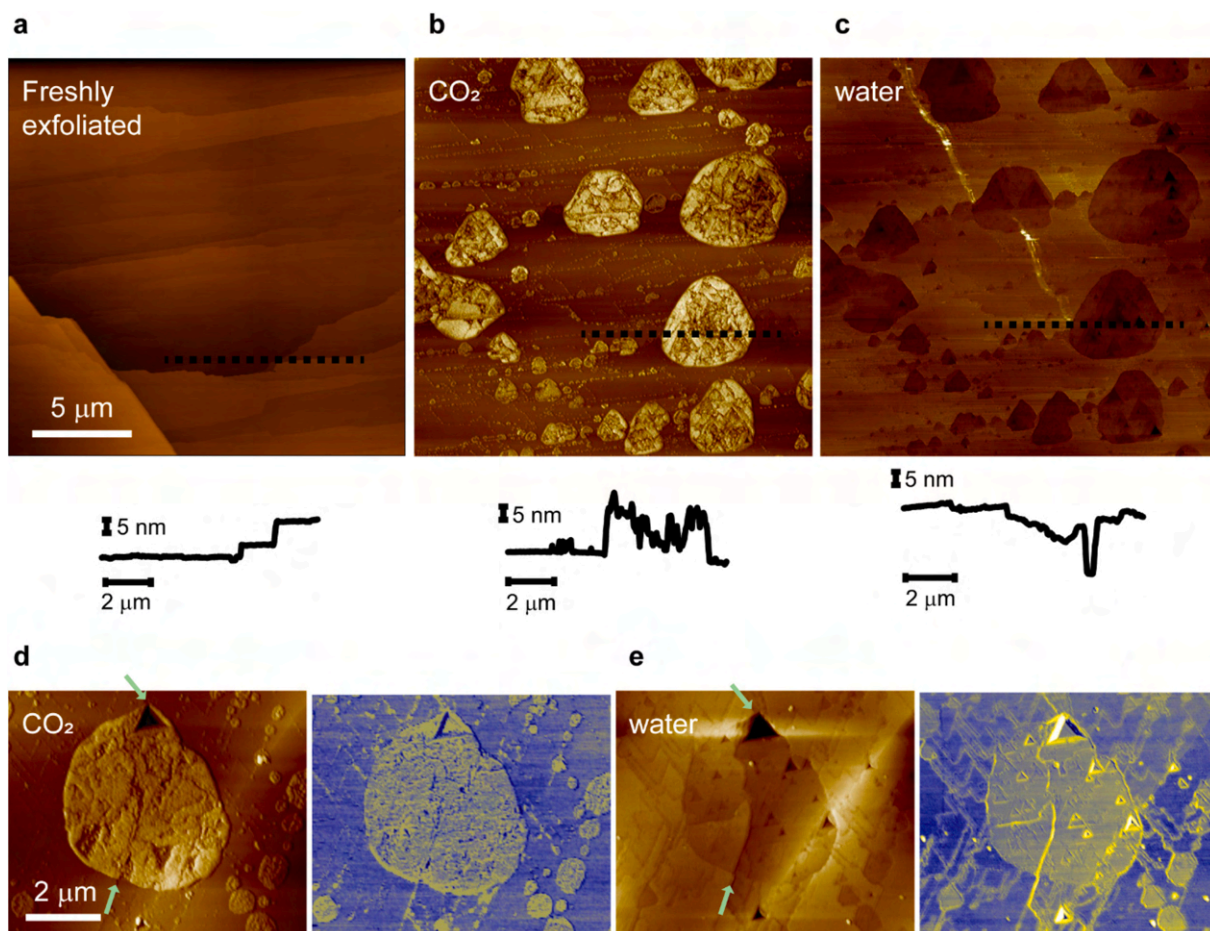


Fig. 6. Dissolution of islands in water. (a) AFM image of a region of the (001) surface of a freshly-exfoliated single crystal of brucite; the inset at the bottom of the image shows a cross-sectional profile as taken along the dotted black line. (b) Same region as panel (a) after a 10 min-treatment at 80 °C under $p\text{-CO}_2 = 5$ bar + $p\text{-N}_2 = 5$ bar; the inset at the bottom of the image shows a cross-sectional profile as taken along the dotted black segment. (c) *In situ* AFM image of the same region as panels (a,b) during immersion in ultra-pure water. Depressed areas (darker colour) created by dissolution of the islands clearly match island positions shown in panel (b). At the bottom of the image, a cross-sectional profile as taken on a depressed area, along the black dotted segment, is reported. (d) Zoomed image of an island created by the hydrothermal + CO₂ conditions; green arrows mark step-edges. On the right, the phase signal image highlights the different contrast between the island and substrate. (e) *In situ* AFM image of the same region as panel (d) during immersion in ultra-pure water; green arrows mark step-edges. On the right, the phase signal image highlights the different contrast between the depressed area and substrate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

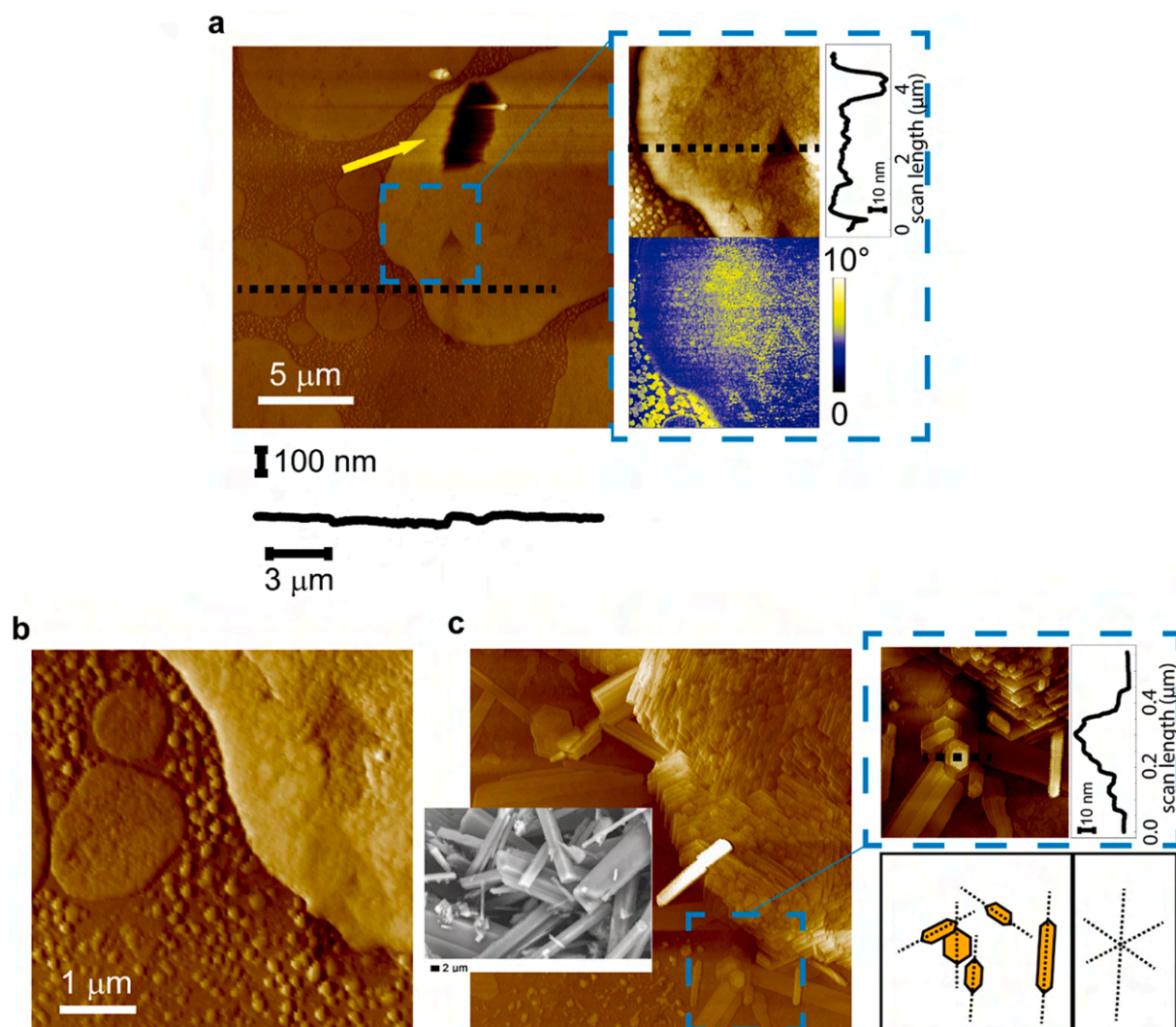


Fig. 7. (a) AFM image of a region of the (001) surface after a 10 min-treatment at 80 °C under $p\text{-CO}_2 = 5$ bar and $p\text{-N}_2 = 5$ bar; the inset at the bottom shows a cross-sectional profile as taken along the dotted black line. As described in Fig. 2, the yellow arrow indicates the evolution of a hole created on the freshly-exfoliated surface by nanoindentation, before the exposure of the sample to CO_2 . The dashed square box, with light blue borders, shows the topography of a zoomed area $[(5 \times 5) \mu\text{m}^2]$ nearby a wide round-shaped island. On the right of the topography image, a cross-sectional profile, as taken along the black dotted segment, is reported. At the bottom of the topography image, the related phase contrast image is shown. (b) Zoomed image $[(5 \times 5) \mu\text{m}^2]$ on some islands in the same region as panel (a). (c) Same region as panel (b), after about 1 month of aging in atmospheric conditions. Needle-like crystallites, resembling those showed in the inset (SEM image of nesquehonite from ref. [30]) are clearly visible. The dashed square box, with light blue borders, shows the topography of a zoomed area $[(1.5 \times 1.5) \mu\text{m}^2]$ nearby a wide round-shaped island. On the right of the topography image, a cross-sectional profile, as taken along the white dotted segment, is reported. At the bottom of the same image, a sketch reproduces the habit of some oriented needle-like crystallites, elongated along three directions (translated into a single scheme on the right panel) rotated 60° relative to each other. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$(5.3 \pm 0.6) \text{ nm } \mu\text{m}^{-2}$ and $(0.24 \pm 0.04) \text{ nm } \mu\text{m}^{-2}$, respectively.

These observations indicate that step edges act as localized sources of interfacial mass flux, spatially coupling brucite dissolution and carbonate growth, likely within confined water films. The identification of step-edges of the brucite substrate as preferential nucleation sites for islands (Figs. 1 and 2) therefore motivates an evaluation of the influence of step-edge morphology on the geometrical characteristics of the carbonate islands developing across them. This holds particularly for islands at their initial growth stage, due to the dramatic dependence on area of their height while maintaining constant the height-to-area ratio (Fig. 3c). In fact, Fig. 4 shows the linear correlation (Pearson's $r > 0.5$ and $p\text{-value} \ll 0.05$) between the island height, area, and volume, and the height of the underlying substrate step-edge (see Table S1 for more data). This correlation substantiates the role played by step-edges in providing the required feedstock for the development of the islands.

This change in aspect ratio is indicative of the affinity of the

carbonate layer toward the underlying brucite surface. This affinity is supported by structural arguments that will follow. The prevalence of small islands is clearly driven by the dominance of elemental steps against multiple steps, the former providing the least possible amount of reactant to form the carbonate island.

The tendency of islands to maintain a uniform thickness is also verified at advanced stages of carbonation, by performing treatments with $p\text{-CO}_2 = 10$ bar. Fig. 5 displays a progressive zoom on a representative region on a brucite crystal subjected to such a treatment. Despite the occurrence of substantial roughening of the surface, islands are still recognizable, undergoing coalescence with formation of a multilayer structure (see Fig. S6d for further examples).

This represents the first direct evidence of the formation of a smooth conformal layer of carbonates, previously inferred by X-ray and neutron scattering analyses [21]. This conformal layer was believed to be the primary impediment of effective reaction progression; however, in our

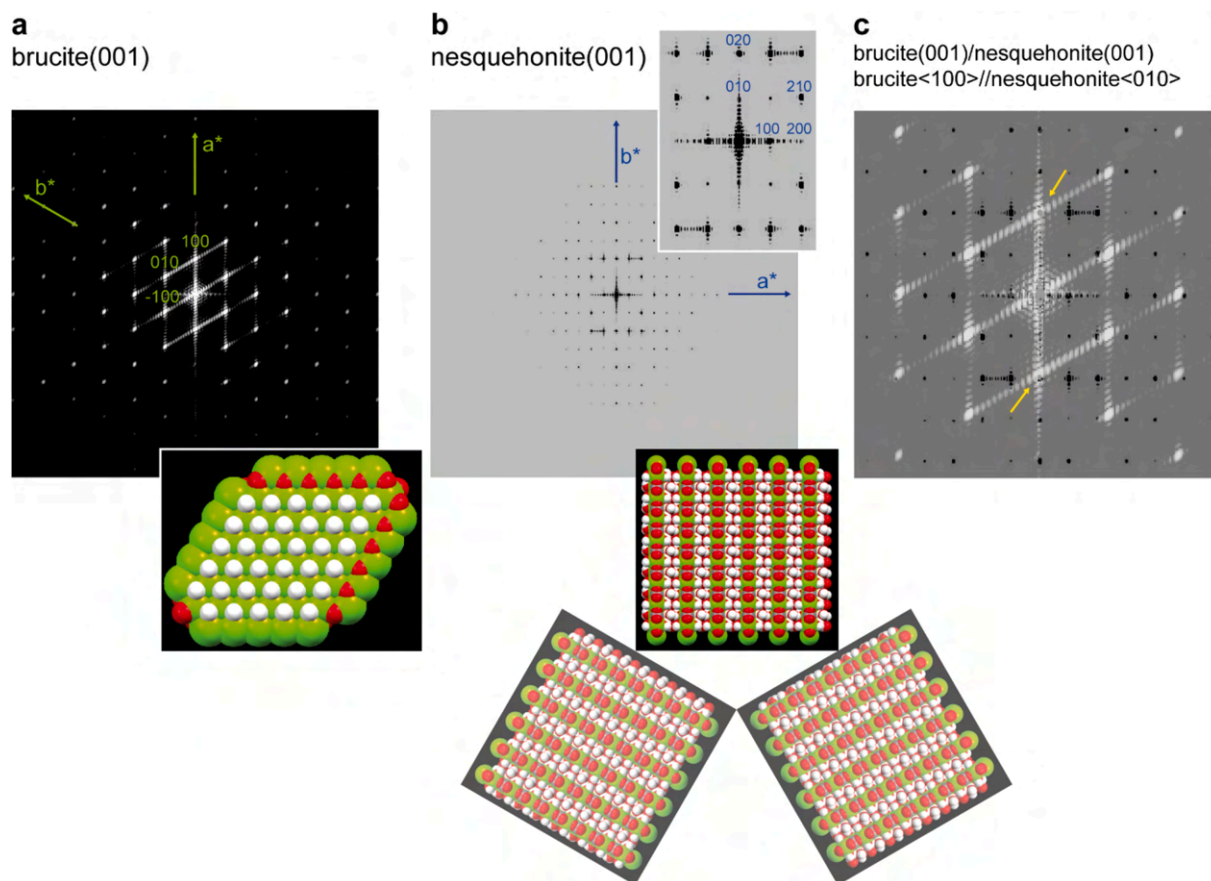


Fig. 8. Epitaxial relationship of nesquehonite on the basal plane of brucite. (a) FFT of a false-colour structural model of the brucite (001) surface (inset: green: Mg-atoms; red: O-atoms; white: H-atoms) and indexation of reciprocal lattice points. (b) FFT of a false-colour structural model of the nesquehonite (001) surface (lower inset: green: Mg-atoms; red: O-atoms; grey: C-atoms; white: H-atoms) and indexation of reciprocal lattice points (upper inset). (c) Superimposition of the reciprocal lattices in (a) and (b) evidencing the coincidence between brucite {100} and nesquehonite {020} (yellow arrows), giving rise to three symmetrically equivalent azimuthal orientations of nesquehonite (001) on brucite (001), rotated 60° relative to each other, with nesquehonite <010> parallel to brucite <100>. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

images it is visible that triangular-shaped depressions, with lateral size of the order of few micrometers, are present all over the film surface. These depressions are indicative of an etching process of the brucite surface underneath, which is in progress during the carbonate layer growth, since at the solid-vapor interface, spatial coupling between dissolution (etching) and precipitation is preserved. This contrasts with the critical shielding role attributed to the carbonate layer, as further demonstrated by the results discussed in the following section.

3.3. Interfacial transport through the carbonate layer

The comparison of the same crystal area before and after a treatment with the presence of CO₂ in the environment (Fig. 2) allows from the one hand to substantiate the role of step-edges as preferential sites for the transformation of the brucite crystal and, from the other hand, to identify both an erosion process of the crystal (step retreat) and the formation of a new phase having island-like morphology. The additional volume due to the formation of the new phase is almost six times the eroded volume observed at the step-edge, suggesting that the solid system after the treatment undergoes a net volumetric expansion. Hence, the new phase is fed by brucite which spontaneously tends to mobilize at step edges and react with CO₂ to form a Mg-carbonate layer. This layer, based on its observed morphological characteristics and recent results of direct and indirect monitoring of brucite crystal reactivity at the solid-liquid interface [21], is probably amorphous and can develop by maintaining a certain degree of hydration. In this respect,

entrapped water molecules would influence the volume expansion, which can be evaluated by the comparison of the molar volume of brucite and that of model structures of Mg-carbonates. While the molar volume of brucite is $\sim 24 \text{ cm}^3 \text{ mol}^{-1}$ [24], that of known crystalline Mg-carbonates varies from a minimum corresponding to that of the anhydrous magnesite phase (MgCO₃), $\sim 28 \text{ cm}^3 \text{ mol}^{-1}$ [28], to that of the most hydrated phase of nesquehonite (MgCO₃·3H₂O), $\sim 77 \text{ cm}^3 \text{ mol}^{-1}$ [29], passing through an intermediate hydrated phase of hydromagnesite [30], Mg₅(CO₃)₄(OH)₂·4H₂O, which is the one expected at 80 °C [30], having a volume per mole of Mg of $\sim 42 \text{ cm}^3 \text{ mol}^{-1}$ [31].

To have an insight into interfacial transport and to assess mass conservation, we exploited the observation that, just after *in situ* immersion in ultra-pure water at room temperature, islands promptly dissolve. This was already observed by Yang et al. [18], who describe the carbonate phase arising from carbonation of MgO as easily removed by deionized water. However, as illustrated in Fig. 6b and c, we additionally realized that the volume of dissolved material is not limited to the portion of island protruding above the substrate plane; rather, its dissolution leaves a substantial depression on the substrate surface, involving a volume below the substrate plane. The persistence of etching beneath the carbonate overlayer demonstrates that the incipient phase does not behave as an impermeable passivating barrier. We estimated through before-and-after imaging within the same area of ca. 400 μm² the total volume of islands protruding from the substrate plane (V_e) and the total volume of dissolved brucite (V_b , volume of the void below the substrate plane left by dissolved islands). These volumes are $(0.16 \pm$

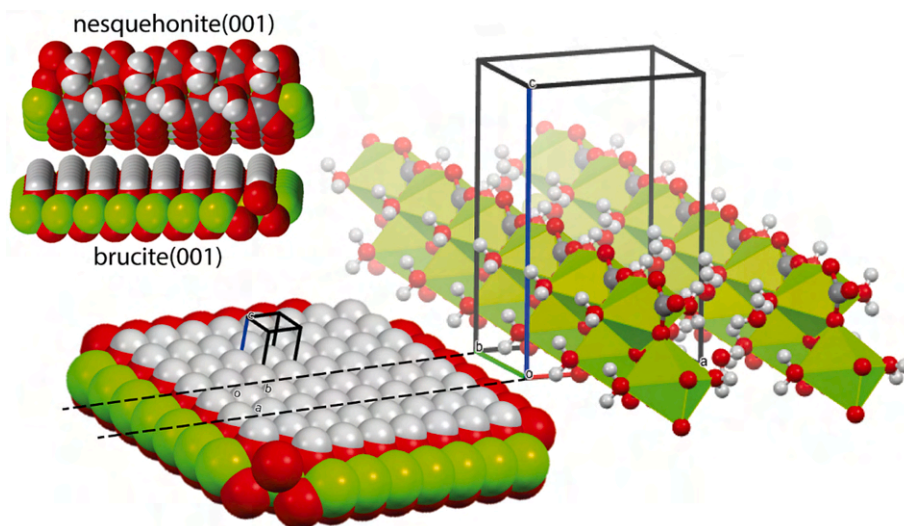


Fig. 9. Structural model of the epitaxial interface between nesquehonite and brucite. When nesquehonite (001) is in contact with brucite (001) and under the epitaxial relationship nesquehonite $\langle 010 \rangle //$ brucite $\langle 100 \rangle$, the spacing of (020) planes of nesquehonite coincides with that of (100) layers of brucite (2.68 Å vs 2.73 Å). Under these three symmetrically equivalent reciprocal orientations, twice the spacing among rows of prominent H-atoms of the brucite surface (5.46 Å) matches within 1.6% with the length of the b -axis of nesquehonite (5.36 Å), bringing to an energetical favourable geometrical registry between the two contacting crystalline surfaces.

$0.08 \mu\text{m}^3$ and $(0.05 \pm 0.02) \mu\text{m}^3$, respectively. The sum $V_e + V_b$ represents the total volume of the carbonate layer formed, $V_c = (0.21 \pm 0.08) \mu\text{m}^3$. The ratio $V_c/V_b = (4.2 \pm 2.3)$, corresponding to the ratio between the volume of the carbonate layer formed and that of dissolved brucite. This ratio can be regarded as our best estimate of the molar-volume ratio between the observed carbonate layer and brucite. This suggests that the hydration level of the carbonate layer more closely approaches that of nesquehonite (molar-volume ratio nesquehonite/brucite = 3.2) than that of hydromagnesite (molar-volume ratio = 1.8). This carbonate layer remains dynamically permeable to interfacial transport during early-stage growth. Additionally, the surface beneath the removed island is rich in etch-pits with triangular shape, extending in depth down to some tens of nanometers (Fig. 6c and Fig. S7), and gives rise to a different phase contrast relative to the background (Fig. 6d,e), pointing to a permanent modification of the brucite/island interface, as better described in the next section.

3.4. Epitaxial crystallization and evolution of the carbonate interface

As discussed above, the round-shaped islands observed immediately following hydrothermal and CO_2 treatment exhibit a structured morphology, marked by features consistent with a substantially amorphous phase, yet already indicating an incipient propensity for textural ordering. Although the island surface is grainy in appearance (Fig. 2b–d), these grains are not randomly distributed; rather, they tend to arrange along crystallographic directions that reflect the symmetry of the underlying hexagonal lattice (see also Fig. 3a and Fig. 6b). Subsequent aging under atmospheric conditions promotes extensive mass redistribution, through which the islands acquire morphological patterns that are representative of crystalline phases. This can be observed in the area illustrated in Fig. 7, where an initial grainy island (Fig. 7b) is observed to develop well-defined and oriented needle-like crystallites with pseudo-hexagonal shape after 1-month aging (Fig. 7c).

This crystal habit, together with recent observations of evolution of an amorphous Mg-carbonate layer [16], points to the formation of nesquehonite (compare the AFM images showed in Fig. 7c with the SEM image reported as an inset of the same figure). This transition may also be favoured by the molar-volume (*i.e.*, hydration level) of the native carbonate layer, which was estimated to be comparable to that of nesquehonite (Sec. 3.3). This mineral is characterized by 1D chains of

octahedrally coordinated Mg^{2+} ions developing along the b -axis, interacting one another by H-bonds through bridging of water molecules [29]. This structural motive driven by high hydration levels gives rise to needle-like crystals elongated parallel to the b -axis and with a perfect cleavage along (001). On this basis, we checked the occurrence of epitaxial coincidence between brucite (001) and nesquehonite (001). To allow for the most general analysis, we report the comparison between the reciprocal lattices involved [32,33]. Fig. 8a reports the reciprocal lattice obtained by applying a fast Fourier transform (FFT) algorithm to the contrast generated by a real-space structural model of the brucite (001) surface. By applying the same procedure, the reciprocal lattice of the nesquehonite (001) surface was obtained and is presented in Fig. 8b. Superposition of this lattice with that of brucite, together with systematic relative rotation, enables the identification of reciprocal-lattice coincidences and thus of plausible orientational relationships between the two phases. This analysis unambiguously shows that nesquehonite {020} coincides with brucite {100}. In real space, this coincidence translates into three symmetrically equivalent orientations, rotated 60° relative to each other, in which nesquehonite $\langle 010 \rangle$ is parallel to brucite $\langle 100 \rangle$ (Fig. 8c).

Fig. 9 illustrates with real-space models that, under the illustrated epitaxial coincidence, the surface corrugation of nesquehonite (001) with spacing equal to b (5.37 Å) matches within 1.6% with twice the main surface corrugation of brucite (001) with spacing equal to (100) (5.46 Å).

Epitaxial coincidences are at the basis of interactions among crystal phases favoring nucleation, growth in a layer-by-layer fashion, and following preferential orientations. In the present framework, the emergence of epitaxial registry suggests that late-stage crystallization is governed by interfacial structural matching with the underlying brucite lattice. Actually, in accordance with this occurrence, needle-like crystallites are observed to align along three preferential directions rotated 60° relative to each other (Fig. 7c). The nesquehonite growth slowly propagates through the early carbonate layer up to its top surface. This picture is consistent with the observation of a foreign bottom layer after *in situ* carbonate dissolution (Fig. 6d,e), being attributable to the early, less soluble nesquehonite layer nucleated at the brucite/island interface.

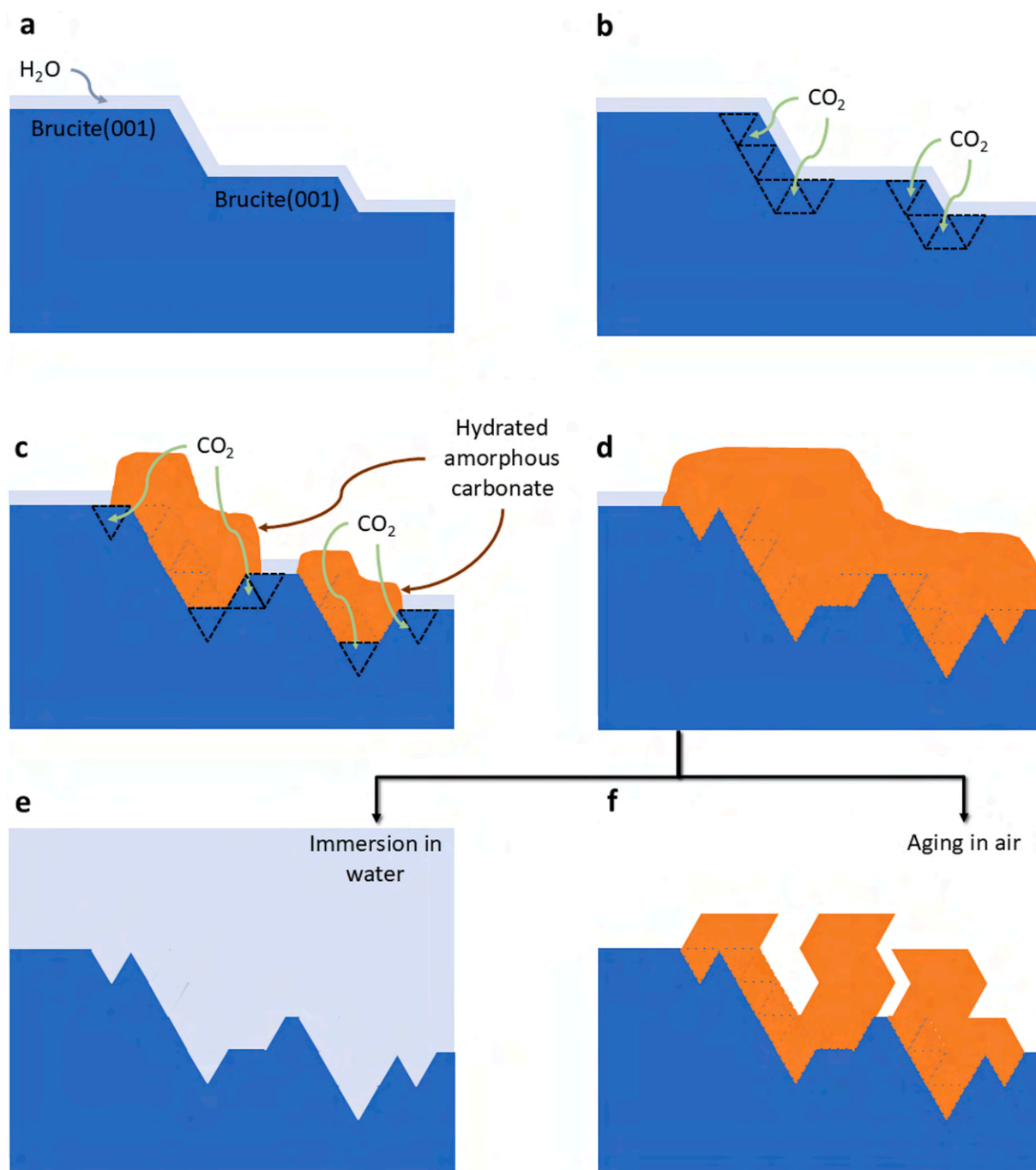


Fig. 10. Schematic of the carbonation pathway of brucite (001) at the solid-gas interface. (a) The pristine brucite (001) terraced surface (blue) covered by a water layer (light blue). (b) Dissolution of CO₂ in the water layer with formation of carbonic acid ready to attack the brucite layers nearby the step-edges. (c) Formation of carbonate islands (orange) with a volume roughly twice that of the attacked brucite. CO₂ can diffuse through the carbonate layer. (d) Further growth of the carbonate layer with coalescence of the two adjacent islands. (e) Total removal of the carbonate layer by immersion in pure water. (f) Crystallization of the carbonate layer by aging in air. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.5. Overall mechanism of carbonation

Overall, the AFM observations indicate that brucite carbonation at the solid-gas interface proceeds through a localized dissolution-precipitation pathway confined to the interfacial water film, as depicted in Fig. 10. CO₂ uptake in this film promotes brucite dissolution preferentially at step edges, where Mg-rich and carbonate-bearing species locally accumulate and nucleate hydrated poorly crystalline Mg-carbonate. This phase first bridges the step-edge and grows rapidly in height, then reaches a geometry-controlled thickness and spreads

laterally over both terraces. Because triangular etch pits continue to develop beneath the carbonate layer, the nascent phase is not fully passivating but remains permeable to interfacial mass transport. Subsequent exposure to liquid water dissolves the amorphous carbonate and reveals the etched substrate, whereas aging in air converts the carbonate layer into oriented acicular crystalline domains. This mechanism links defect-controlled flux localization, precursor formation, sustained underlayer dissolution, and post-reaction crystallization into a single pathway for brucite carbonation at solid-gas interfaces.

Table 1

Comparison of interfacial carbonation pathways reported for Mg-bearing systems under different hydration regimes.

Study	Reactive system	Water environment	Dominant interfacial pathway	Carbonate precursor/product	Morphological evolution	Passivation behavior	Direct nanoscale imaging	Main conceptual contribution
Hövelmann et al., 2012 [7]	Brucite + dissolved inorganic carbon	Bulk aqueous solution	Dissolution–precipitation at solid–liquid interface	Hydrated Mg-carbonates (likely dypingite)	Etch pits followed by particulate precipitates	Not explicitly resolved	Yes (AFM)	Established coupling between brucite dissolution and carbonate precipitation in aqueous environments
Zhang et al., 2022 [16]	Brucite + wet supercritical CO ₂ (scCO ₂)	Water-saturated scCO ₂	Water-mediated carbonation through confined interfacial films	AMC to nesquehonite	Dissolution pits, AMC nanoparticles, crystalline overgrowth	Intermediate AMC phase observed but transport permeability unresolved	Yes (high-pressure AFM)	Demonstrated amorphous precursor-mediated carbonation pathway under scCO ₂
Luong et al., 2023 [17]	MgO nanocubes + CO ₂	Nanometric water films	Humidity-dependent carbonation in adsorbed water layers	AMC (MgCO ₃ ·2.3–2.5H ₂ O)	Progressive nanocoating growth	Strong dynamic passivation by AMC coatings	No direct AFM imaging of evolving interface	Linked carbonation kinetics to nanometric water film thickness and humidity
Weber et al., 2023 [20]	MgO single crystals + atmospheric CO ₂	Ambient humidity air	Hydroxylation followed by hydrated carbonate formation	Hydrated Mg-carbonates	Surface armoring and conformal reacted layer	Strong long-term passivation	Partial nanoscale characterization	Demonstrated that surface armoring severely limits MgO direct air capture efficiency
King et al., 2025 [21]	Mg(OH) ₂ and ca(OH) ₂	Controlled humidity atmosphere	Humidity-mediated carbonation	Hydrated Mg-carbonates	Smooth conformal coatings on Mg (OH) ₂	Progressive interfacial blocking inferred	No direct <i>in situ</i> AFM tracking	Distinguished fractal ca-carbonation from conformal Mg-carbonation behavior
This work	Brucite single crystal + CO ₂	Water-lean solid–gas interface (RH ~ 5%)	Defect-mediated confined interfacial carbonation	Amorphous precursor to epitaxial nesquehonite	Step-edge nucleation, subsurface growth beneath terraces, epitaxial crystallization	Initial carbonate layer remains permeable to mass transport	Yes (<i>ex situ</i> AFM tracking of identical surface regions)	Direct visualization of defect-controlled flux localization and non-classical carbonate growth through confined water films

3.6. Implications for confined interfacial carbonation pathways

The present observations provide direct evidence that carbonation under water-lean conditions proceeds through a confined interfacial pathway fundamentally different from that operating in bulk aqueous systems. In conventional aqueous environments, dissolution, transport, and precipitation occur in spatially separated domains, obscuring the direct coupling between surface reactivity and carbonate growth. Here, by restricting the reaction to nanometric water films adsorbed at the solid–gas interface, dissolution and precipitation remain spatially coupled within the same interfacial region. Under these conditions, step edges act as localized sources of interfacial mass flux, driving the redistribution of Mg-bearing species and controlling the nucleation of carbonate nanophases. The observed scaling between step height and island size further indicates that defect morphology directly regulates the amount of material involved in the reaction pathway.

Although the present study focuses on brucite as a model Mg-hydroxide surface, the mechanism emerging from same-region AFM tracking is relevant to a broader class of water-mediated mineral reactions. In many natural and technological environments, including atmospheric weathering, mineral dust reactivity, unsaturated porous media, and solid–gas mineralization processes, water is not present as a bulk liquid reservoir but as adsorbed films, capillary condensates, or

locally confined interfacial domains. Previous nanoscale studies have shown that such water films are spatially heterogeneous and can nucleate preferentially at mineral edges, steps, and other defect sites, where enhanced hydrophilicity and capillary effects promote localized water accumulation [25]. Water uptake is also strongly affected by particle size and surface morphology, with adsorption and condensation regimes controlling whether mineral surfaces host only a few molecular layers or much thicker water films [34]. In this context, our observations indicate that the same nanoscale heterogeneity that controls water-film formation can also regulate where dissolution, ion transport, and carbonate nucleation occur. This coupling is important for atmospheric and near-surface weathering of alkaline minerals, but also for engineered CO₂ mineralization strategies based on Mg-bearing oxides, hydroxides, mine tailings, and magnesia-based binders, where carbonation efficiency is often limited by the balance between reactive interfacial transport and surface passivation. The defect-mediated pathway resolved here therefore identifies surface morphology, possible water-film presence, and product-layer permeability as key design variables for controlling solid–gas carbonation beyond the specific case of brucite.

The results additionally demonstrate that the early poorly crystalline carbonate layer does not behave as an impermeable passivating barrier. In contrast with classical armoring models proposed for MgO-based carbonation systems [17–19], etching of the underlying brucite

surface continues beneath the carbonate overlayer, indicating that interfacial transport remains active during the early stages of growth. The carbonate phase therefore behaves as a dynamically permeable interfacial medium, enabling simultaneous dissolution and precipitation within confined water films. Only at later stages, the progressive crystallization of the interface, driven here by epitaxial nesquehonite formation, appears to introduce a more stable structural configuration that may hinder further reaction progression. These observations support a mechanistic picture in which carbonation evolves through successive interfacial regimes, from defect-mediated transport and amorphous growth to structurally organized crystalline interfaces.

4. Conclusions

This work provides a direct nanoscale description of brucite carbonation at water-lean solid-gas interfaces, revealing how defect structure, confined interfacial transport, and phase evolution jointly govern carbonate growth. By tracking identical surface regions through AFM observations, carbonation was shown to initiate preferentially at step edges, where localized dissolution promotes the nucleation of hydrated poorly crystalline carbonate islands. The size and volume of these islands scale with the height of the underlying substrate steps, demonstrating that surface defects act as localized sources of interfacial mass flux. The carbonate phase subsequently propagates beneath surface terraces while maintaining a nearly uniform thickness, ultimately evolving toward epitaxially oriented nesquehonite crystallites.

Compared with carbonation studies performed in bulk aqueous environments [7,15,16], the present water-lean configuration preserves the spatial coupling between dissolution, transport, and precipitation at the reactive interface. This enables direct identification of redistributed and newly formed interfacial volumes during reaction evolution. As summarized in Table 1, previous investigations on Mg-bearing carbonation systems reported either bulk-mediated dissolution-precipitation pathways [7], humidity-dependent amorphous carbonate growth [17], or progressive surface armoring and passivation phenomena [18–21]. In contrast, the present results demonstrate that the incipient carbonate overlayer remains permeable to interfacial transport, allowing continued etching of the underlying brucite surface. The observations therefore identify a dynamically permeable poorly crystalline phase as a transient regime preceding late-stage crystallization and possible interfacial stabilization.

These findings establish a mechanistic framework for mineral carbonation likely mediated by confined water films, in which nanoscale transport is governed by the interplay between surface defects, hydration, and evolving interfacial structure. More broadly, the results highlight how nanometric water films can sustain localized dissolution-precipitation reactions even under water-limited conditions, supporting the view of confined interfacial water as an active reactive medium rather than a passive adsorbed phase [8–14,25,26]. In this framework, carbonation proceeds through non-classical pathways involving localized mass redistribution, transient amorphous intermediates, and delayed passivation dynamics.

Beyond the specific case of brucite, these mechanisms may extend to a broader class of solid-gas reactions occurring in confined aqueous environments, including mineral weathering, corrosion, and interfacial catalytic transformations. Future work combining nanoscale imaging, interfacial spectroscopy, and atomistic simulations may further clarify how water-film thickness, defect chemistry, and crystallographic matching collectively regulate reactive transport and phase evolution at mineral interfaces.

CRedit authorship contribution statement

Rossella Yivlialin: Writing – review & editing, Writing – original draft, Supervision, Software, Methodology, Investigation, Formal analysis, Data curation. **Barbara Menno di Bucchianico:** Software,

Investigation, Data curation. **Mattia Corti:** Methodology, Investigation. **Lamberto Duò:** Writing – review & editing, Validation, Resources. **Marcello Campione:** Writing – review & editing, Writing – original draft, Methodology, Funding acquisition, Formal analysis, Conceptualization. **Nadia Malaspina:** Validation, Resources, Project administration, Funding acquisition. **Gianlorenzo Bussetti:** Writing – review & editing, Validation, Resources, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors gratefully acknowledge Prof. D. Belmonte, University of Genova, and Dr. P. Gentile, University of Milano – Bicocca, for providing the natural brucite specimens from which the single-crystal lamellae were cleaved; Dr. C. Recalcati and Prof. A. Guadagnini, Politecnico di Milano, for useful discussions on mineral carbonation processes.

The AFM measurements were performed at the Solid-LiquidInterface Nanomicroscopy and Spectroscopy laboratory (SoLiNano-Σ LAB, <https://www.polimi.it/en/research/laboratories/interdepartmental-l-laboratories/solinano-s-lab-solid-liquid-interface-nanomicroscopy-and-spectroscopy-lab>) which is an interdepartmental facility at Politecnico di Milano.

We acknowledge funding by Cariplo Foundation “ANTICARB - Quarrywaste ANTigorite CARBonation: a zero emission platform for remanufacturing with the benefit of CO₂ sequestration” (Grant no.2020-0977); Italian Ministry of University and Research “Competing geological and biological processes in underground carbon and hydrogen storage” (Grant no. 20224YR3AZ); University of Milano - Bicocca “A nano-technological approach for implementing circularity and carbon-neutrality in antigorite quarry industry” (Grant n. 2024-ATEQC-0017). Part of the work was performed with the support of Project MIUR – Dipartimenti di Eccellenza TECLA, Department of Earth and Environmental Sciences, University of Milano-Bicocca. This work has also been funded within the framework of the Regional Programme of the European Regional Development Fund 2021–2027 of Regione Lombardia (PR FESR 2021-2027, Action 1.1.3, in compliance with European Regulation No. 1060/2021), following the public call “Collabora&Innova”. Project “CO₂: from a global problem to a tool to implement circularity – CO-Tool” (Project ID 6144755).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2026.141596>.

Data availability

The data that has been used is confidential.

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