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Iceland spar calcite: Humidity and time effects on surface properties and their reversibility

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Abstract

Understanding the complex and dynamic nature of calcite surfaces under ambient conditions is important for optimizing industrial applications. It is essential to identify processes, their reversibility, and the relevant properties of CaCO3 solid-liquid and solid-gas interfaces under different environmental conditions, such as at increased relative humidity (RH). This work elucidates changes in surface properties on freshly cleaved calcite (topography, wettability and surface forces) as a function of time (≤28 h) at controlled humidity (≤3–95 %RH) and temperature (25.5 °C), evaluated with atomic force microscopy (AFM) and contact angle techniques. In the presence of humidity, the wettability decreased, liquid water capillary forces dominated over van der Waals forces, and surface domains, such as hillocks, height about 7.0 Å, and trenches, depth about –3.5 Å, appeared and grew primarily in lateral dimensions. Hillocks demonstrated lower adhesion and higher deformation in AFM experiments. We propose that the growing surface domains were formed by ion dissolution and diffusion followed by formation of hydrated salt of CaCO3. Upon drying, the height of the hillocks decreased by about 50% suggesting their alteration into...
1. Introduction

Calcium carbonate (CaCO₃) is present in rocks such as limestone, chalk and marble, and is crucial in many biological processes, as well as widely used in industrial processes and products. It contributes to a positive global carbon dioxide balance, is a buffer for acid rains, takes up toxic compounds (such as heavy metals), and reduces bacterial activity in water [1]. CaCO₃ minerals are essential for the growth and degradation of shells, bones and teeth [1,2]. From an industrial perspective, CaCO₃ is used as a powder, granulate or aqueous dispersed filler or pigment in a broad range of applications, such as paper, packaging, paint, plastics, food, pharmacy, water treatment, and many others [2]. However, the nature of the calcium carbonate surface changes under ambient conditions, and its functionality for possible applications can be disturbed or enhanced by evolving heterogeneous surface properties, such as varied morphology and growth of polymorphs [1,3,4]. This issue, despite several studies, is not fully understood, but it could be the key to improve understanding of biomineralisation and to develop more efficient industrial processes, as well as new or improved applications.

Among the crystalline forms of calcium carbonate minerals, such as calcite, aragonite and vaterite, calcite is the most stable polymorph; therefore, it is commonly used in laboratory studies as a model of CaCO₃ minerals [4,5]. The properties of calcite crystal surfaces in liquid and gaseous environments have drawn scientific interest for at least the last two decades, and to this end it has been studied using a variety of techniques, e.g., atomic force microscopy [1,3,6–15], surface force apparatus [16], liquid-solid contact angle [17–20], X-ray photoelectron spectroscopy [1,7,21,22], time-of-flight secondary ion mass spectrometry [1,7], atomic absorption spectroscopy [13], X-ray reflectivity [6], Fourier transform infrared spectroscopy [23], diffuse reflectance infrared Fourier transform spectroscopy [24], thermogravimetric analysis [24], as well as computer modelling [10–12,14,25–28]. According to Stipp et al. [7], the dynamic nature of calcite becomes evident already at the instance of its fracture, which disrupts the atomic structure in the outermost atomic layer and leads to bond relaxation. The surface atomic structure re-arranges to expose dangling bonds (CO₃²⁻) on each side of the crystal [12]; hence, along the dominant cleavage plane (1014) present in all three crystal directions [17,26,30]. Compared to other vicinal faces, a smoother cleavage can be obtained at (1014) as a result of weak ionic bonds between such atomic planes (therefore, the lowest induced interfacial energy within the crystal) [12] leading to fracture with minimum energy cost (0.59 J m⁻²) [26]. As mentioned in the previous section, the surface termination reconstructs just after the cleavage; notwithstanding, the rhombohedral symmetry remains [11]. Prior to humidity experiments, samples of about 8 × 8 × 2 mm³ (for AFM) and about 35 × 10 × 5 mm³ (for SCA), were fractured with a fine chisel and hammer in ambient air. Each sample was purged with pressurized nitrogen (industrial quality: nitrogen ≥ 99.9 vol%, oxygen ≤ 20 ppm, water ≤ 10 ppm) to clean the surface from small debris remaining from the fracturing, and then immediately transferred for analyses. The samples were subsequently kept in a closed environmental chamber under streaming nitrogen in order to minimize uptake of airborne molecules [21]. Areas showing no evidence of micro-sized cracks and surface steps in optical microscope images were selected for further studies (Fig. 1). To limit the influence of foreign molecules, MilliQ water was used for wettability studies and humidity generation (water type 1, ASTM D1193-91). In atomic force microscopy measurements two model samples were used for tip radius determination: a titanium roughness sample (RS-12M, Bruker) and a polydimethylsiloxane sample (PDMS-SOFT-2–12M, Bruker).

2. Materials and methods

2.1. Materials

The material analyzed was optical quality Iceland spar calcite, obtained from Omya International AG, Switzerland, with the average rhombohedral dimensions of approximately 35 × 35 × 35 mm³. The crystal was fractured in ambient air following the natural crystal angles of the rhombohedron (two obtuse 101° 6’ and two acute 78° 4’ on each side of the crystal [12]); hence, along the dominant cleavage plane (1014) present in all three crystal directions [17,26,30]. Compared to other vicinal faces, a smoother cleavage can be obtained at (1014) as a result of weak ionic bonds between such atomic planes (therefore, the lowest induced interfacial energy within the crystal) [12] leading to fracture with minimum energy cost (0.59 J m⁻²) [26]. As mentioned in the previous section, the surface termination reconstructs just after the cleavage; notwithstanding, the rhombohedral symmetry remains [11]. Prior to humidity experiments, samples of about 8 × 8 × 2 mm³ (for AFM) and about 35 × 10 × 5 mm³ (for SCA), were fractured with a fine chisel and hammer in ambient air. Each sample was purged with pressurized nitrogen (industrial quality: nitrogen ≥ 99.9 vol%, oxygen ≤ 20 ppm, water ≤ 10 ppm) to clean the surface from small debris remaining from the fracturing, and then immediately transferred for analyses. The samples were subsequently kept in a closed environmental chamber under streaming nitrogen in order to minimize uptake of airborne molecules [21]. Areas showing no evidence of micro-sized cracks and surface steps in optical microscope images were selected for further studies (Fig. 1). To limit the influence of foreign molecules, MilliQ water was used for wettability studies and humidity generation (water type 1, ASTM D1193-91). In atomic force microscopy measurements two model samples were used for tip radius determination: a titanium roughness sample (RS-12M, Bruker) and a polydimethylsiloxane sample (PDMS-SOFT-2–12M, Bruker).

2.2. Methods

2.2.1. Surface wettability

In order to determine the calcite surface wettability, an optical contact angle device (OCA40, Data Physics Instruments GmbH) was used. Freshly cleaved calcite samples in air were immediately transferred into the Petter temperature-controlled chamber (allowing measurements under protective atmospheres under controlled temperature) with already established conditions of temperature and humidity. A minimum of 7 samples were analyzed.
in parallel (each capable to fit about 3 independent water droplets within the desired area of 100 mm² per droplet). Controlled relative humidity (RH) in the range between 1 ± 0.5 %RH to 95 ± 2 %RH, and flow rate of 3 ± 0.2 L/min were achieved by connecting the pressurized nitrogen (overpressure of 13.8 ± 3.5 kPa) to a P-50 membrane flow humidifier (Cellkraft AB) and fitted with a heated tube into the SCA chamber equipped with a temperature controller (TPC-150, Data Physics Instruments GmbH). The temperature of the heating table inside the chamber was set at 25.5 ± 0.2 °C, which was preferably the same or slightly higher than the temperature of both the heated tube and incoming gas inside the chamber to avoid moisture condensation on the calcite samples. An external sensor (HMT317, Vaisala) inside the SCA chamber, placed close to the calcite samples, controlled the incoming gas temperature and humidity.

Contact angles were measured using MilliQ water placed in an automated micro-pipette that allowed application of 1 μL water droplets on the samples. The droplets were dispensed on the flat areas with no visible steps or cracks inside the environmental chamber after 7 h of exposure at the set humidity. For reversibility studies, the droplets were applied in separate experiments after 21 and 28 h from sample cleavage (the process included humidity exposure for 7 h, drying for 14 h, followed again by humidity exposure for 7 h). The droplet image was captured by a camera at a rate of 8 frames/s. The average of the droplet angles (for both right and left side) was calculated using the SCA20 software (DataPhysics Instruments GmbH) using the ellipse fitting method. Other fitting procedures appeared to be less reliable; tangent fitting was difficult to apply to such low angles, while the Young-Laplace method demonstrated values slightly lower comparing to the ellipse method, by maximum 5°. The contact angles were recorded as a function of time, but the reported static contact angle was captured at 1.2 s, which was sufficient to reach a stable value on the calcite surface (details in supplementary information, Fig. S1).

2.2.2. Surface topography and nanomechanical properties

An atomic force microscope instrument (MultiMode 8 with heater/cooler) equipped with a glass probe holder (MTFML-V2, Bruker) was used for in situ measurements of morphology, surface structure, adhesion, deformation, and surface forces. The cleaved calcite sample was put directly on the heated AFM stage covered with thermal joint compound (Wakefield Solutions). A scanner with a heating stage (S/N: 9763/HVC, Bruker) and cooling pump was used as in wettability studies, to keep the temperature constant at 25.5 ± 0.3 °C. A white-light microscope was used to locate a smooth area for further studies. A humidifier (Gen-RH, Surface Measurement Systems) connected to pressurized nitrogen (13.8 ± 3.5 kPa of overpressure) with already stabilized humidity conditions was fitted with a heated tube into a glass probe holder giving a final flow rate of 0.1 to 0.2 L/min. The inlet sensor (EK-H4, Sensirion) controlled the temperature and RH before reaching the glass probe, while the outlet one (EK-H4, Sensirion) monitored the same, in order to calculate the average values inside the cell (the difference could reach up to 5 %RH at high humidity). The conditions followed those used during the water contact angle measurement, although Gen-RH humidifier reached slightly different humidity levels from about 2 ± 1 %RH to 95 ± 3 %RH. The lowest stable humidity that was achieved at 1–3 %RH, so consequently, traces of water vapor were present also at the lowest humidity. We used triangular cantilevers with Si3N4 tips having a nominal tip diameter of 2 nm, according to the manufacturer (ScanAsyst Air, Bruker). The spring constant of the cantilevers was calculated using the thermal tuning method [31], and varied between 0.38 and 0.45 N/m. Peak Force Quantitative Nanoscale Mechanical Characterization (QNM) mode was used for the study of topography and nanomechanical properties, where the maximum force applied can be selected [32]. The Peak-Force frequency was set at 2.0 kHz, the setpoint at 2.0 nN (approach amplitude of 50–200 nm and speed of 10–40 nm/s), and the lateral scanning rate of the 512 x 512 pixel images was set at 0.375 Hz. To investigate rapid changes on the calcite surface, the scanning speed was increased to 0.975 Hz, decreasing often the image quality. Higher and lower resolution scans were performed alternately. Sample scanning continued incessantly from 7 to 28 h. Optimization of the scan angle (rotation from 90° to 0°) and scan size (from 10 x 10 μm² to 0.5 x 0.5 μm²) was performed in order to exclude possible imaging artifacts. Height images were flattened (1st order) with no further image enhancement. Image processing (with color level thresholding) of adhesion scans was performed in order to calculate surface coverage by domains in different environments. The adhesion and deformation images were extracted from the retraction force curves, as described previously [32].

2.2.2.1. Surface forces

The surface forces were studied in a ramping mode with at least 1 024 data points for each force curve, while when performing nanomechanical mapping studies they consisted of 128 points for each force curve. The resulting data sets were analyzed using a Matlab script in the software (ForceITl). To determine the interactions between the calcite surface and the Si3N4 tip in air of different humidity, the average force curve (above one hundred measurements were performed for each condition) was then selected and compared to the calculated van der Waals force curve. Assuming that the cantilever tip has a spherical termination as in Fig. 2 (with effective tip radius larger than the surface separation), the theoretical non-retarded van der Waals (vdW) force F can be calculated from [33]:

\[
F = -\frac{A \cdot R_{\text{eff}}}{6D^2}
\]

(1)

where \(R_{\text{eff}}\) represents the effective radius (m), D the surface separation (m) and A the Hamaker constant (J). The Hamaker constant was calculated from the non-retarded three-media Lifshitz’ formula for material 1 (calcite) interacting with material 2 (silicon nitride) across medium 3 (air / nitrogen) [33]:
3.1. Humidity effects on calcite surfaces

Humidity effects on calcite surface properties were investigated as a function of time. These studies included measurements of water contact angles, nanomechanical mapping by AFM, as well as force measurements between an AFM tip and a calcite surface.

3.1.1. Surface wettability

The static water contact angles determined on freshly cleaved calcite surfaces exposed to different humidities for 7 h are presented in Fig. 3. A set of freshly cleaved surfaces was also examined directly after cleavage. A water droplet size of 1 μL resulted in an average contact angle of below 5° on the freshly cleaved surface, and it increased to 11 ± 5° after 7 h exposure at ≤1.5 %RH and 25.5 °C. Similar time dependence was also observed at higher humidity, where after 7 h of exposure the average contact angle increased to the peak value of 22 ± 8° at 75 %RH (Fig. 3). However, both the standard deviation and distribution were relatively large (for instance, for 7 h exposure at 75 %RH: minimum 10° and maximum 44°, see supplementary material – Fig. S2).

3.1.2. Surface topography and nanomechanical properties

The typical calcite surface is not atomically flat. In our AFM studies the examined surface was relatively smooth, with a roughness (R\text{\textsubscript{rms}}, geometric average roughness, and R\text{\textsubscript{a}}, arithmetic average roughness) of up to 1.1 Å (R\text{\textsubscript{rms}}) and 0.9 Å (R\text{\textsubscript{a}}). Such roughness is achievable only in the areas free from surface defects or steps, that is, on terraces. However, the step height between terraces differed between samples from a few Å up to a few nm (summary provided in Table 2), which is due to imperfect cleavage.

At increased humidity, new surface domains with increased height, here called hillocks, and with reduced height, called trenches, started to appear on the calcite surface within the first hour of humidity exposure. The height of the domains was found to be only slightly dependent on time and relative humidity, as shown in Fig. 4. The details about each humidity results follow below. All the domain height values were calculated in relation to the average height of the terraces on which they appeared. The time denoted in Fig. 4 is when the scan was complete; the new surface features started to appear before 30 min had elapsed. However, the changes could be observed already within the first hour, when the scanning rate was increased to 0.975 Hz (see sample at 50 %RH in Fig. 4).

At 95 %RH, hillock-like domains grew primarily in lateral dimensions with time, while their height remained constant. The lateral dimension was mostly limited by surface features, such as steps and cleavage direction, as demonstrated in Fig. 5. After image processing of the adhesion images, where the domains are distinguished by lower adhesion, we can assess that the domains covered around 24% of the studied surface area after 7 h. The average adhesion value for the initial surface was relatively stable at approximately 2 nN. The adhesion values found on the hillocks were 80–85% of that on areas without hillocks. After 7 h, the hillocks appeared with an average lateral size of 3.96 ± 0.31 μm\textsuperscript{2} (Table 2) and height of 7.4 Å. Other calcite samples exposed to the same condition demonstrated also trench-like domains, with average height of −3.8 Å, lateral size 0.31 × 0.12 μm\textsuperscript{2}, and adhesion

![Graphical visualization of the tip termination of the triangular cantilevers](image)

Fig. 2. Graphical visualization of the tip termination of the triangular cantilevers, where R\text{\textsubscript{eff}} is the effective radius. The termination in reality is not perfectly spherical, as seen in the absolute calibration method, and the effective radius is defined as the radius that gives agreement between measured and calculated vdW forces at low RH values (≤3 %RH).

### Table 1

Static dielectric constant ε\text{\textsubscript{i}} and refractive index n\text{\textsubscript{i}} used for calculating the non-retarded Hamaker constant. Decimal accuracy differs due to different literature sources, as stated in the table. Due to birefringence of calcite, two values are displayed regarding (*) the ordinary and (**) the extraordinary rays. The average value of (*) and (**) was used for further calculations.

| Parameter | Media i = 1, 2, 3 | \( \varepsilon_1 \) | \( \varepsilon_2 \) | \( n_1 \) | \( n_2 \) | \( n_3 \) | \( n_4 \) |
|-----------|------------------|----------------|-----------------|----------------|----------------|----------------|----------------|
| Si\text{\textsubscript{3}}N\text{\textsubscript{4}} [52] | \( i = 1 \) | 7.4 | 1.98 | | | | |
| CaCO\text{\textsubscript{3}} [52] | \( i = 2 \) | 8.0* | 8.5** | | | | |
| | | 8.5** | 1.658* | 1.477** | | | |
| H\text{\textsubscript{2}}O [53] | \( i = 2 \) | 78.36 | 1.333 | | | | |
| | | | | | | | |
| nitrogen/air [53] | \( i = 3 \) | | | | | | 1.0003 |

where \( k \) is the Boltzmann's constant, \( T \) the absolute temperature (298.65 K), \( h \) the Planck's constant, \( \nu \) the frequency of the electronic absorptions in the UV region [34], assumed to be the same in each media (3 × 10\textsuperscript{15} s\textsuperscript{−1}), \( \varepsilon_1 \) the static dielectric constant for medium \( i \), and \( n_1 \) the refractive index of medium \( i \). The values of \( \varepsilon_1 \) and \( n_1 \) are provided in Table 1, and used under the assumption that the dielectric properties of the Si\text{\textsubscript{3}}N\text{\textsubscript{4}} tip are the same as for the bulk material. This may not be entirely correct, but we note that the effective radius determined from force curves are similar to those obtained by tip imaging, see Table 3. The calculated Hamaker constant was found to be 13.4 ± 10\textsuperscript{−20} J.

In this work the tip radius was calculated in order to apply Eq. (1). Three methods were used: absolute (direct), relative (indirect), and from fitting of force curves (effective tip radius). The first method allowed tip imaging by using a titanium sample (RS-12M) with sharp features on the surface [34]. In the second indirect method, a soft PDMS sample (PDMS-SOFT-2-12M) with a known elastic modulus (3.5 MPa) was used to adjust the tip radius until the resulting elastic modulus was in agreement with the known value [34]. The effective radius of the tip (Fig. 2) was calculated by adjusting the radius value until the theoretically calculated vdW force curve agreed with the measured one at low humidity conditions (≤3 %RH).

3. Results and discussion

### 3.1. Humidity effects on calcite surfaces

H...
within the same range as the terraces. We suggest such differences in the lateral dimension to be due to variations in the surface features on the original sample, where small trenches can be difficult to detect even in higher resolution images. This is consistent with that even on the sample shown in Fig. 5 relatively vast trenches were observed after overnight exposure at high humidity.

At 75 %RH, the trenches and hillocks were found to be in comparable size range (Table 2). However, after 7 h of humidity exposure they occupied only about 7% of the studied area (Fig. 9). Repeated experiments demonstrated that hillocks may cover up to 25% of surfaces with similar microstructure. Even surface areas opulent with steps, from below 1 nm to around 4 nm in height (see supplementary material: Fig. S3, Table S1), develop surface hillock-like and trench-like domains. That sample was exposed to 75 %RH for 7 h, which resulted in a surface coverage by hillock-like domains of up to 15% (average size 0.16 \( \pm \) 0.06 \( \mu \text{m}^2 \) and height 6.3 Å) (Table 2).

The domains also appeared at 50 %RH, where the surface presented in Fig. 6 was covered by hillocks by 7% already within the first hour, and up to about 17% after 7 h. The average size of the domains decreased by half compared to those at higher relative humidity. However, the adhesion was also at 50 %RH about 85% of that found on unaffected terraces. Fig. 7 represents the surface topography under drier conditions (25 %RH). Here, small hillock-like domains (10% of the size obtained at higher humidity) with height of 6.4 \( \pm \) 0.9 Å appeared after three hours of exposure (Fig. 4) and covered no more than 3% of the studied area 7 h into the experiment. The adhesion force on the hillock area was, again, found to be about 80% of that on unaffected terraces. In contrast, no similar hillock-like domains were observed to form on samples exposed for 7 h at \(< 3 \%\text{RH} \) (Table 2), not even after 21 h of exposure, only small trench-like features could be observed on few samples.

In summary, hillocks and trenches appeared on all samples exposed to humid air of RH \( \geq 25\% \), hillock-like domains demonstrated decreased adhesion in relation to surface terraces. The domain growth rate increased with rising RH, and the height of the hillocks and the depth of the trenches were reproducible between samples studied under similar conditions. In contrast, the lateral size and surface coverage varied between samples exposed to the same humidity for the same length of time, which likely was due to variations in the surface structure.

3.1.3. Surface forces

Besides imaging and nanomechanical mapping, atomic force microscopy provided information on surface forces between calcite and the Si\( _3 \)N\( _4 \) tip of the cantilever in the different environments. In order to compare measured forces with theoretical predictions of van der Waals forces, one needs to know the tip radius. To this end, the tip radius was quantified using two different methods and compared with the tip’s end radius value of 2 nm reported by the manufacturer (Table 3). From imaging the roughness sample, we obtained a tip end radius in the range 4–10 nm, and by fitting experimental data to the known value of the elastic modulus of the PDMS sample, we obtained a tip radius of 20–40 nm (at deformation depth 1.4–3.4 nm). Thus, a significant ambiguity remained. For this reason we adopted a third approach. Under dry conditions one would expect the attractive van der Waals force to dominate the interaction between the tip and the surface, and indeed the shape of the measured force curve at RH \(< 3\% \) appears similar to that of a vdW force. We could then use Eq. (1) and treat the tip radius as a fitting parameter. This approach gives a value of the effective radius in the range 8–18 nm, which is close to the value obtained from the roughness sample. For the calculated vdW force shown in Fig. 8 we used a value for tip radius of 10 nm. We note that the effective radius determined from force measurements was found to be constant within the range given for the different cantilevers and samples used, and it did not vary with the number of measurements. The latter implies that there was no significant change in the tip radius during the experiment.

Force measurements were performed at the same conditions as above. Under the action of attractive forces, when the force gradi-

Table 2

| Relative humidity [%RH] | Initial surface | Domain size after 7 h exposure |
|-------------------------|-----------------|-------------------------------|
|                         | Terraces roughness | Step height [Å] | | | Hillocks | Trenches |
|                         | \( R_\text{g} \) [Å] | \( R_\text{s} \) [Å] | \( L \) [Å] | \( W \) [μm] | \( H \) [Å] | \( L \) [μm] | \( W \) [μm] | \( H \) [Å] |
| \(< 3\% \)              | 0.9 | 0.7 | 3.3 ± 0.5 | — | — | — | — | — |
| 25                      | 0.9 | 0.8 | 4.1 ± 0.8 | 0.07 ± 0.02 | 0.06 ± 0.02 | 6.4 ± 0.9 | 0.06 ± 0.04 | 0.02 ± 0.01 | 3.6 ± 0.7 |
| 50                      | 0.9 | 0.7 | 5.3 ± 2.3 | 0.58 ± 0.41 | 0.28 ± 0.16 | 7.6 ± 1.9 | 0.07 ± 0.03 | 0.03 ± 0.01 | 3.3 ± 0.6 |
| 75                      | 0.8 | 0.6 | 4.0 ± 0.7 | 1.09 ± 0.50 | 0.75 ± 0.29 | 7.0 ± 1.2 | 0.23 ± 0.36 | 0.06 ± 0.02 | 3.9 ± 1.2 |
| 95                      | 1.1 | 0.9 | 4.2 ± 2.5 | 3.96 ± 0.78 | 0.74 ± 0.45 | 7.4 ± 1.2 | 0.31 ± 0.16 | 0.12 ± 0.02 | 3.8 ± 0.8 |

* Small trench-like features observed on some samples.

\( ^a \) No trenches observed after 7 h, but clearly visible after overnight exposure; here values obtained after 7 h of exposure of another sample is provided.
ent, \( \text{d}f/\text{d}D \), becomes larger than the spring constant, a jump into contact with the surface, at a distance \( D_j \) occurs due to a mechanical spring instability. At low humidity, \( \text{RH} \leq 3\% \), \( D_j \) was found to be at a separation of 2.8 nm independent of time (Fig. 8). The adhesion force, measured on the retraction curve, was also found to be close to constant with time. Notably, the attractive force observed on approach and distances above \( D_j \) is consistent with the theoretical vDW curve calculated by Eqs. (1) and (2). This implies that the observed forces indeed were due to vDW interactions. The forces measured at 25, 50 and 75 \%RH were similar to those reported

Fig. 4. Height changes (average with a standard deviation) as a function of time for (a) hillock-like domains, and (b) trench-like domains, calculated from AFM images. The x-axis represents time of a finished scan; it is expected that changes could appear faster, which was proved by experiments with a higher scan rate for the sample at 50 \%RH (the first data point for hillocks). Open triangles for 95 \%RH in figure (b), for example, represent data obtained at this condition on another sample than that shown in Fig. 5. The error bars were estimated based on about 10 measurements on different surface areas (the number of measurements could increase due to potential surface heterogeneity).

Fig. 5. AFM height and adhesion scans with adhesion distribution histograms measured on a freshly cleaved calcite surface within (a) 2 h, and (b) 7 h of exposure to nitrogen gas at 95 \%RH. Scan size 10 \times 10 \mu m^2.
for ≤ 3 %RH, except that some force measurements performed at 75 %RH showed indications of a capillary attraction (see discussion below).

At 95% RH the larger amount of water present on the surface gave rise to larger attractive forces and $D_I$ was found at 3.7 nm, i.e. 1.1 nm further away from the surface compared to under dry conditions (RH ≤ 3%), see Fig. 8. With increasing exposure time to 95% RH it was observed that during retraction, the tip did not jump out of the contact directly (as observed and expected for a vdW force), but after a gradual decrease of the attractive force down to about 1.0 nN. These effects are the signs of a capillary water bridge connecting the tip and the surface.

In summary, at low humidity conditions, typical van der Waals forces could be observed, while at high humidity, close to 95 %RH, water adsorption capillary forces were detected.

3.2. Reversibility studies

The reversibility of the aging processes was investigated in a set of experiments using SCA and AFM instrumentation. Fig. 9 displays wettability changes on the calcite surface first aged at 75 %RH for 7 h and then exposed to dryer conditions at RH ≤ 1.5%. As presented in Fig. 9a, the contact angle was continuously increasing also during drying at ≤ 1.5 %RH and the subsequent exposure for 7 h at 75 %RH, reaching the final value of 45 ± 22° (see distribution histograms in supplementary material – Fig. S4). Thus, the decreasing wettability was not reversible when the humidity was changed from 75 %RH to ≤3 %RH and then back again to 75 %RH.

In contrast, the topography images in Fig. 9b demonstrate that as the humidity was decreased from 75 %RH to ≤3 %RH, the height of the hillocks decreased by about 50% (down to 3.7 Å), while their lateral size and the depth of the trenches were hardly affected (difference much less than 1 Å). Furthermore, new small hillocks (lateral dimension ≤ 0.05 μm) with average height of 3.7 ± 0.8 Å appeared as the water was removed from the surface. The adhesion force also decreased upon drying, and the adhesion difference between terraces and hillocks decreased (Fig. 9b). Interestingly, the deformation increased further upon drying, and the deformation difference between hillocks and terraces disappeared (Fig. 9b).

In the next step, the humidity was increased to 75 %RH again, which resulted in disappearance of the newly appearing hillocks. However, the older, larger, hillocks started to grow again, and a

Fig. 6. AFM height images with height profile (through the same area of the step adhesion images with distribution histograms measured on freshly cleaved calcite surface within (a) 2 h and (b) 7 h of exposure to nitrogen gas at 50 %RH. Scan size 10 × 10 μm². All the height profiles were taken at the same surface area, despite the visible scanning shift.
few new ones appeared. The height of the hillocks also returned to the values they had prior to drying (Fig. 9a). The adhesion force on the hillocks and the adhesion contrast between hillocks and terraces again became clearer, but the new values remained lower than prior to drying (Fig. 9b). This suggests that some of the compounds that were deposited upon drying remained on the surface after rehydration. Similar observations were made when drying surfaces previously exposed to 25 or 95 %RH, while exposing them to 25 or 95 %RH again.

In summary, we observe that the height of the hillocks changed reversibly by 50% when the RH was decreased from a high value (25–95 %RH) to low (≤3%) and then increased again to the high value. Dry conditions do not entirely terminate domain growth, but decrease their growth rate. The growth of small hillocks, which occurred upon drying, was also reversible, as the humidity was increased, these features disappeared. In contrast, reduced adhesion force, increased surface deformation under a given tip load, and decreased wettability were not reversible.

3.3. Implications of the SCA and AFM data

In the absence of any foreign adsorbed molecules in nitrogen atmosphere, one would expect that the water contact angle would remain low [35] (≤5° was observed on flat surfaces) as a function of time at any humidity. In contrast, we saw an increase in contact angle with time, with relatively large variations, suggesting a non-uniform adsorption of non-polar gas-stream borne molecules from the nitrogen atmosphere, which continued even upon continuous and relatively long drying at ≤3 %RH. However, as presented further in the AFM section, the surface morphology and chemistry also undergoes changes with time, and this may also have an effect on the contact angles. One of the reasons for the broad distribution of water contact angles is surface roughness (originating from steps and molecules on the surface), which affects the shape of the contact line of the droplet on the surface. Interestingly, the increase in contact angle is highest at intermediate relative humidity (50–75%), which suggests that a small amount of adsorbed water facilitates adsorption of the gas-stream borne substances, while at higher, 95 %RH, this tendency is reversed as a thicker water layer is formed, presumably due to dissolution of these gas-stream borne molecules in the aqueous layer.
Concerning the AFM studies, we note that investigations on different surface areas at 25–95 %RH demonstrate variations in the average lateral size of the domains due to surfaces features and roughness. Notwithstanding, the height of the hillocks are consistently found in the range 6–9 Å, and at approximately 3.5 Å for the trenches. A hillock height of 6–9 Å corresponds to 2–3 monolayers of CaCO₃ and water (the thickness of one monolayer of water is about 3–3.5 Å [36,37], and for CaCO₃ it is 3.036 Å [12]). The depths of the trenches was thus within 1–2 monolayers. For relatively dry conditions, ≤ 3 %RH, the hillock-like domains did not emerge within the first 24 h, although some changes were indicated in earlier studies [3].

The domain size was much greater in the horizontal than in the vertical direction, which was due to the presence of the thin water layer that allows motion along the surface but restricts motion perpendicular to it [38]. Differences in Ca²⁺ and CO₃²⁻ ion activities in the water layer at different positions could be a driving force for ion mobility along the surface and influence the domain shapes together with the number of step edges with acute and obtuse sites [11,12]. Further, potential occurrence of adsorbed organic airborne molecules with low surface energy, surface roughness and nanostructure may block further ion diffusion by disrupting the water layer resulting in varied lateral shapes of the domains.

Concerning surface forces at higher humidity, the effect of capillary water bridging between the tip and the surface has been reported before, for hydrophilic surfaces in air, and also for hydrophobic surfaces in water where the capillary instead contains gas/vapor [39]. Over longer exposure at high humidity conditions, both decreasing adhesion force between the surface and the silicon nitride AFM tip and increasing average deformation were likely due to adsorption of gas-stream borne molecules, which agrees with SCA measurements. Notably, different tips were used for studies for different samples (Figs. 5–7), and thus adhesion values reported at different RHs may vary due to differences in tip radius. However, for the study reported in Fig. 9b the same tip was used; therefore, nanomechanical mapping values obtained under different conditions can be unambiguously compared. Lower adhesion at dry conditions (≤ 3 %RH) compared to that at high humidity, is consistent with the surface force data reported in Fig. 8.

We note that once domain structures formed, they did not disappear on drying, but rather showed a partially reversible change in height with humidity. This is a strong indication that the water content of the hillocks changed with RH, and that the hillocks consisted of a mixture of water and CaCO₃-comprising species. Here, we explore how a change in water content would affect the tip-surface vdW force. In these calculations we assumed that the dielectric properties of the mixed liquidified (l) CaCO₃ / water (w) layer (nᵢ, εᵢ) are given as linear combinations of those of CaCO₃ and water, i,e.: 

\[ nᵢ = (1 - X_w)n_{CaCO₃} + X wn_w \]  
\[ εᵢ = (1 - X_w)ε_{CaCO₃} + X wε_w \] 

where \( X_w \) is the volume fraction of water. A similar approach has been used previously for calculating vdW forces between hydrated surfactant layers [40]. The results of these calculations are shown in Fig. 10, where the Hamaker constant clearly decreases with rising water content.
Fig. 9. Freshly cleaved calcite surface: (a) wettability measured by SCA; (b) height, adhesion and deformation changes measured by AFM. Scan size 10 × 10 μm². Timeline at the top of the figure represents time of the finished scan. Experiments performed: 7 h of exposure to nitrogen gas at 75 %RH, drying at ≤ 3 %RH for 14 h (<1.5 %RH SCA experiments), and 75 %RH exposure for additional 7 h. The graphs regarding surface wettability and domains height demonstrate average values with standard deviations based on about 40 different droplets measured at each condition (for surface wettability), and about 10 measurements on different surface areas (for domains height). The number of measurements could increase due to potential surface heterogeneity. The graph distinguishes between continuous domains appearing over time (filled triangles) and new ones – appearing only while drying the surface (open triangles). Distribution histograms for adhesion and deformation displayed below the corresponding scan.
development of surface heterogeneities, including domains with higher forces at higher humidity, as seen in Fig. 8. We also observed development at around 50 %RH from a 2-dimensional water layer at the calcite surface into a 3-dimensional layer. At low RH, the growth of the water layer is then limited to one monolayer, while at higher RH it can increase to a few monolayers (around 15 Å). In the second model [6,25], the water layer thickness remains constant at around 15 Å regardless of the humidity, but instead the density of the layer varies. In this model one distinguishes between two layers, a low density region (approximately 0.1 g/cm³) and a capillary region. With increasing humidity, the thickness of the low density region increases from 0.6 to 2 Å, while the water density in the capillary region increases with humidity from 0.6 to 0.9 g/cm³ and this layer becomes more ordered. Such significant differences between the two models can be caused by different experimental conditions, material properties, or, as suggested by Bohr et al. [6], by variation in surface roughness between the samples studied. If so, the surface from the first model was apparently slightly more uneven (above 2 Å), while in the second one, the surface was relatively flat (below 2 Å), as in our study. However, considering the ion diffusion model, our work is more consistent with the presence of a more extended water layer at higher humidity, as seen in the first model. This is supported by a vdW force dominated interaction at low humidity towards the appearance of capillary forces at higher humidity, as seen in Fig. 8. We also observed development of surface heterogeneities, including domains with higher water content at increased humidity (from about 25 %RH). Note that the AFM technique cannot be used to image a fluid water layer on top of the surface since it will be pushed away by the tip. However, the influence of the water layer on surface interactions can, and was, observed.

In this work, we designate the first process occurring in humid environment to be a surface rearrangement process stirred by dissolution of ions in the thin water layer. As a fundamental principle, dissolution occurs more easily at high-energy sites. Such sites are expected at the edges and steps, but at such positions it is difficult to observe small topographical changes. Next, ions diffuse in the water layer to even out concentration gradients. When the ion concentration is sufficiently high and binding to the underlying surface favorable, domains start to form at such positions [8]. In our case, we observed formation of hillocks both on terraces (Figs. 5 and 7) and at steps (Fig. 6). On terraces we also noticed trenches formed from where we expect ions could have been dissolved. High-energy sites can occur on terraces due to mechanical stresses induced by cleavage of the calcite surface. Another matter to consider is the volume of the observable domain, where the hillock volume is much greater than that of the trenches and the difference is too large to be explained by the around 50% water content of the hillocks. This suggests that the major locations for ion dissolution are at step edges or that many trenches may be small and narrow, both of which are difficult to observe by AFM.

At high humidity conditions, more water adsorbs to the surface, and consequently a larger amount of calcium and carbonate ions can dissolve. Thus, we expect the surface rearrangement process to go faster at higher humidity, which we also observed. From molecular dynamics simulation performed by Rahaman et al. [28], it is known that formation or readjustment of the water interface on the calcite surface at different humidity takes just several nanoseconds. It was presented that the distribution of water is not uniform leaving uncovered “dry patches”, appearing both on heterogeneous surfaces with defects, and on the flat areas [28]. The occurrence of such water clusters could be explained by a low density of water molecules and their strong hydrogen bonds with the calcite surface. Rahaman et al. [28] demonstrated, that the mobility of adsorbed water is slightly greater in the horizontal (HD) than the vertical direction (VD). The movements of water molecules vary marginally with humidity (diffusion coefficient at 100 %RH: 5.50 × 10⁻¹⁰ m²/s (HD), 2.05 × 10⁻¹⁰ m²/s (VD), and at 50 %RH: 2.38 × 10⁻¹⁰ m²/s (HD), 5.40 × 10⁻¹¹ m²/s (VD)) [28]. As a comparison, the self-diffusion coefficient of bulk water at 25 °C is 2.57 × 10⁻¹⁰ m²/s [41], i.e. about a factor of 10 larger than observed for the diffusion in the horizontal direction in the work performed by Rahaman et al. [28]. The theoretical 2D diffusion for Ca²⁺ and CO₃²⁻ ions in a continuous thin water layer (with the same viscosity as bulk water) can be calculated from the equation,

\[
\sqrt{x^2 + y^2} = \sqrt{4Dt}
\]

where \( D \) is the diffusion coefficient (m²/s), \( t \) the diffusion time (s), and \( x \) and \( y \) are the diffusion lengths in two perpendicular directions (m). The diffusion constants at 20 °C in bulk water are \( 7 \times 10^{-10} \text{ m}^2/\text{s} \) for calcium ions and \( 8 \times 10^{-10} \text{ m}^2/\text{s} \) for carbonate ions [42]. Using these values the average diffusion length of calcium and carbonate ions are presented in Table 4. Even though surface features may obstruct diffusion, it is clear that ion diffusion is sufficiently rapid to rationalize our observations. This is true even if the diffusion constant is a factor of 10 lower than in bulk water, found for the horizontal diffusion of water in the simulation presented by Rahaman et al. [28]. In this context we note that the recrystallization process can be accelerated in industrial environment by high temperature 100–200 °C [38], and this is consistent with the mechanism discussed above.

From the change in hillock height upon drying (a factor of about 2), we can estimate their water content to be about 50%. Thus, from Fig. 10 we can assess that the Hamaker constant has a value about 20% lower on the hillocks than on the terraces that are expected to consist of pure calcite. If the adhesion force was primarily due to vdW forces, we would then expect the adhesion force on the hillocks to be about 20% lower than on the terraces. In the RH range 25–95 % we found experimentally that the adhesion on the hillocks was 75–85% of that on the terraces, which strongly supports the notion that changes in the vdW interaction was the primary cause for the lower adhesion on the hillocks.

3.4. Model of calcite surface behavior at varied humidity

Our results demonstrate calcite surface rearrangements facilitated by humidity, i.e. water adsorption. Considering previous research, such as Bohr et al., and Kendall et al. [6,8], ion diffusion appears to be typical for calcite surfaces, and at least two models can be distinguished. The first one [8,24] indicates a clear transition at around 50 %RH from a 2-dimensional water layer at the calcite surface into a 3-dimensional layer. At low RH, the growth of the water layer is then limited to one monolayer, while at higher RH it can increase to a few monolayers (around 15 Å). In the second model [6,25], the water layer thickness remains constant at around 15 Å regardless of the humidity, but instead the density of the layer varies. In this model one distinguishes between two layers, a low density region and a capillary region. With increasing humidity, the thickness of the low density region (approximately 0.1 g/cm³) is suggested to increase slightly from 0.6 to 2 Å, while the water density in the capillary region increases with humidity from 0.6 to 0.9 g/cm³ and this layer becomes more ordered. Such significant differences between the two models can be caused by different experimental conditions, material properties, or, as suggested by Bohr et al. [6], by variation in surface roughness between the samples studied. If so, the surface from the first model was apparently slightly more uneven (above 2 Å), while in the second one, the surface was relatively flat (below 2 Å), as in our study. However, considering the ion diffusion model, our work is more consistent with the presence of a more extended water layer at higher humidity, as in the first model. This is supported by a vdW force dominated interaction at low humidity towards the appearance of capillary forces at higher humidity, as seen in Fig. 8. We also observed development of surface heterogeneities, including domains with higher RH it can increase to a few monolayers (around 15 Å). In the second model [6,25], the water layer thickness remains constant at around 15 Å regardless of the humidity, but instead the density of the layer varies. In this model one distinguishes between two layers, a low density region and a capillary region. With increasing humidity, the thickness of the low density region (approximately 0.1 g/cm³) is suggested to increase slightly from 0.6 to 2 Å, while the water density in the capillary region increases with humidity from 0.6 to 0.9 g/cm³ and this layer becomes more ordered. Such significant differences between the two models can be caused by different experimental conditions, material properties, or, as suggested by Bohr et al. [6], by variation in surface roughness between the samples studied. If so, the surface from the first model was apparently slightly more uneven (above 2 Å), while in the second one, the surface was relatively flat (below 2 Å), as in our study. However, considering the ion diffusion model, our work is more consistent with the presence of a more extended water layer at higher humidity, as in the first model. This is supported by a vdW force dominated interaction at low humidity towards the appearance of capillary forces at higher humidity, as seen in Fig. 8. We also observed development of surface heterogeneities, including domains with higher
To summarize, we demonstrate our concept of calcite surface behavior at varied humidity in a model (Fig. 11). The first image illustrates a freshly cleaved flat surface without surface domains. The second demonstrates the effect of humidity encouraging calcite ions dissolution, formation of trenches and further ions diffusion into hillock-like domains consisting of a hydrated CaCO₃ phase. Even though from this study, we do not have any information on the nature of the CaCO₃-comprising species present in the hillocks, one may speculate, that together with excess water, it is present as a relatively stable monohydrate [4,43,44], or soluble amorphous form of CaCO₃ [43–46]. At low humidity conditions, that is below 50 %RH, slower carbonation and lower crystallinity compound is expected [47]. During drying (third image in Fig. 11), the hydrated phase of CaCO₃ undergoes dehydration into a less water-rich structure [45,46,48,49] decreasing to 50% of its height (hillocks). This conveys that domains are most likely composed from a mixture of calcium carbonate and water. Over the longer time of drying, we expect that the hillock structure would subsequently transform back into the most stable polymorph of CaCO₃, calcite [4,45,46,49–51]. Even though dehydration decreases the mobility of the water within the hydrated salt of CaCO₃, making further dehydration more challenging [43], certain water residues may remain on the surface allowing further ion diffusion and formation of some narrow-sized domains at lower rate, as seen on Fig. 9. We assign these to water evaporation inducing deposition of CaCO₃ from previously dissolved ions. A softer surface layer is then clearly formed as water is evaporated, and substances previously dissolved in the aqueous surface layer are likely to be the cause for this. With de novo increasing humidity, as in the last image from Fig. 11, the surface hydrates again and the ions, including small hillocks which occurred upon drying, are resolubilized in the aqueous layer, allowing further ion redeposition at the large hillock-like domains.

To understand further the surface properties under different humidity conditions, the next query concerns the elemental structure of the observed domains, which should be the scope for further studies. For such studies the use of surface sensitive techniques that provide chemical information with high lateral resolution would be necessary.

### 4. Conclusions

We reported a study of time dependent properties of relatively flat calcite surfaces (terraces roughness up to 1.1 Å) in controlled environment of relative humidity (from ≤3 to 95 %RH). We observed a development of trenches with average depth of −3.5 Å and hillock-like domains with low adhesion and high topographical deformation reaching a well-defined height corresponding to around 1–2 monolayers of hydrated CaCO₃, i.e. 7.0 Å. The domain lateral dimension increased with time, and more rapidly at higher humidity. The process could be substantially terminated by surface dehydration at ≤3 %RH, where the height of the hillocks decreased by 50%. Upon drying, new smaller hillocks appeared due to deposition of ions previously present in the aqueous layer, and these redissolved upon rehydration. The domain shape is expected to vary mainly due to diffusion barriers, such as steps.

We applied a new approach for analyzing surface forces on growing surface domains, which demonstrates decreased AFM tip adhesion on the hillock-like domains. Typical van der Waals forces could be observed in dry conditions (≤3 %RH), while with increasing water adsorption capillary forces occurred at high humidity (95 %RH). The water content within the hillock domains was estimated to be about 50%, and calculations show that the expected van der Waals force between the AFM tip and such domains is about 80% of that between a tip and a calcite surface. This is consistent with the lower adhesion (75–85%), and increased deformation of the domains compared to the calcite surface without such domains. As an effect of the aging, the wettability of calcite surfaces decreased presenting less hydrophilic characteristics (contact angle up to 22 ± 8° at 75 %RH) and this effect continued even upon drying at ≤3 %RH (33 ± 18°). This is likely to be an effect of adsorption of gas-stream borne substances. Deposition of such substances upon drying also made the surface notably softer as was observed as an increased surface deformation.

We proposed a surface property model for freshly cleaved calcite exposed to humid environment under nitrogen. The results suggest that the observed surface changes are likely due to calcium and carbonate ion dissolution in the adsorbed water layer, followed by ion diffusion to energetically favored areas for recrystal-
lization into CaCO\textsubscript{3} hydrated form. Ion diffusion on calcite surfaces was studied in previous works, where two models can be identified, with either a clear transition from a 2-dimensional water layer at the calcite surface into a 3-dimensional layer at around 50 %RH [8,24], or constant water layer thickness regardless of the relative humidity, although with a density of the water layers that change with the humidity [6,25]. Our data concur with an increasing thickness of water with increasing humidity and time, but note that surface changes are observed even below 50 %RH.

The overall results emphasized the significance of the aging process of CaCO\textsubscript{3} essential for optimizing industrial applications, and provided a more detailed view of the changing calcite surface properties, which involves both adsorption of gas-stream borne molecules and dissolution and redeposition of CaCO\textsubscript{3}. The adsorption of gas-stream borne molecules is, as judged from contact angle measurements, not reversible with humidity changes, whereas changes in the thickness of the redeposited hillocks are reversible. The presence of adsorbed water, leading to hydrated CaCO\textsubscript{3}-containing species, results in an estimated approximate 20% decrease in refractive index, and this reduction in refractive index at the surface can be expected to impact on the light scattering properties in practice. The growth and redeposition of polymorphic CaCO\textsubscript{3}, furthermore, may be considered an important factor in defining the effectiveness, or otherwise, of subsequent surface-energy dependent applications. To advance our understanding further, we need to gain more insight into the elemental and phase heterogeneities of the calcite surface. We plan to undertake such investigations in the future.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcis.2019.01.047.

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