

Chiral Water Structures on the Dolomite(104)-S Surface Enantiomer

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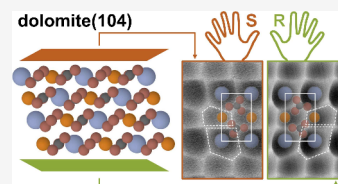
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ABSTRACT: The particular distribution of dolomite over geological time scales and the challenges of growing dolomite under geological conditions in a laboratory setting are still some of the most intriguing scientific puzzles. So-called organogenic models that suggest the role of molecules, especially of extracellular polymeric substances in the liquid phase, in dolomite formation currently challenge the attempts to understand dolomite formation in the context of kinetic constraints. Here, we confirm the presence of chirality on dolomite(104) surfaces by atomic-scale imaging with noncontact atomic force microscopy. Two enantiomers are mapped at the two opposing crystal surfaces. Chiral signatures are further identified in the adsorption of single water molecules, and chirality transfer to a full water monolayer is imaged. Links between chiral specificity of dolomite growth and chiral selectivity of biomolecules on earth, mediated by the liquid phase, appear to be a so far overlooked jigsaw piece in understanding the formation processes of dolomite.

KEYWORDS: dolomite, water, chirality, noncontact atomic force microscopy



Dolomite ($\text{CaMg}(\text{CO}_3)_2$) is among the most intriguing minerals on earth.¹ The particular distribution of dolomite over geological time scales and the failures of growing ordered dolomite in a laboratory setting under geological conditions highlight the lack of understanding of the involved processes in this so-called “dolomite-problem”.² In particular, dolomite is significantly more prevalent in ancient sedimentary rock formations than in Holocene sediments^{3–5} and it hardly precipitates from the modern ocean despite a dolomite supersaturation in seawater.^{3,6} The latter observation goes along with the challenges of laboratory-based synthesis of dolomite under geological conditions: Running reactions even as long as 32 years at room temperature failed to form ordered dolomite;⁶ laboratory-based precipitation has so far only been realized at elevated temperatures (150–300 °C).^{7,8}

The term dolomite describes a rock-forming mineral series within the class of carbonates that encompasses varying chemical composition, order, and lattice structure.² The dolomite problem concerns the fabrication of ordered dolomite where the Mg:Ca ratio is near to 1:1 and the cations are ordered (i.e., alternating along [001]) within the crystal lattice structure. Reports on disordered dolomite or proto-dolomite are steps along the path of researching ordered dolomite crystal growth and even quantifying order in experiments can be a challenge.⁹ While kinetic factors set by constraints of the geological environment have intensively been discussed as factors in controlling and steering dolomite formation,² microbe-facilitated mechanisms i.e. as in organogenic models, might offer alternative explanations.¹⁰ In particular, the decomposition of organic matter into extracellular polymeric substances in the surrounding solution has been suggested to generate favorable environments for dolomitization,¹¹ with mechanisms involving elusive stabiliza-

tion capabilities of cations by negatively charged chemical moieties stemming from larger biomolecules.¹⁰ Yet, a consensus has been reached that mineral formation processes involve hydrated layers;² the formation of dolomite and many other minerals require the presence of fluid phases.¹² Most interestingly, chiral water structures have been mapped around chiral biomolecules.^{13–15} Thus, structural aspects on generating the particular dolomite cation order in the presence of chirality, imprinted on the liquid phase by chiral biomolecules, appear to be an overlooked aspect.

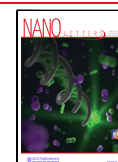
In this paper, we deliver compelling evidence for the presence of chiral (104) faces of dolomite, a property following from the bulk crystal structure, and image chirality transfer to the first water monolayer. Conclusions are drawn based on noncontact atomic force microscopy (NC-AFM) data acquired with CO-functionalized tips, partnered with density functional theory (DFT) calculations and image simulations. Strong molecule–surface interactions are revealed that mediate the chirality transfer. Our results deliver a new angle on the dolomite problem and disclose chirality as a so far hidden variable in the processes that concern ordered dolomite. Based on the mapping of chiral water structures around chiral biomolecules,^{13–15} our findings further suggest the function of water as a transducer from chiral selectivity of biomolecules to dolomite formation.

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The {104} faces resemble the most stable cleavage planes of dolomite, a common property also for the related carbonate minerals calcite (CaCO_3) and magnesite (MgCO_3).¹⁶ The rectangular (1×1) surface unit cell has dimensions of $0.771 \text{ nm} \times 0.481 \text{ nm}$ ^{17,18} and contains one Mg^{2+} ion, one Ca^{2+} ion, and two carbonate CO_3^{2-} groups. The carbonate groups are rotated within the surface plane such that one oxygen atom (O_{top}) of the carbonate group protrudes from the surface, O_{middle} lies mostly within the Mg–Ca plane, and O_{bottom} is located below the Mg–Ca plane, see side view in Figure 1(a). In fact, the dolomite crystal structure (crystallographic space group $R\bar{3}$ ¹⁹) dictates the presence of two enantiomeric (104) and ($\bar{1}0\bar{4}$) faces on two opposite crystal sites,²⁰ see Figure 1(a).

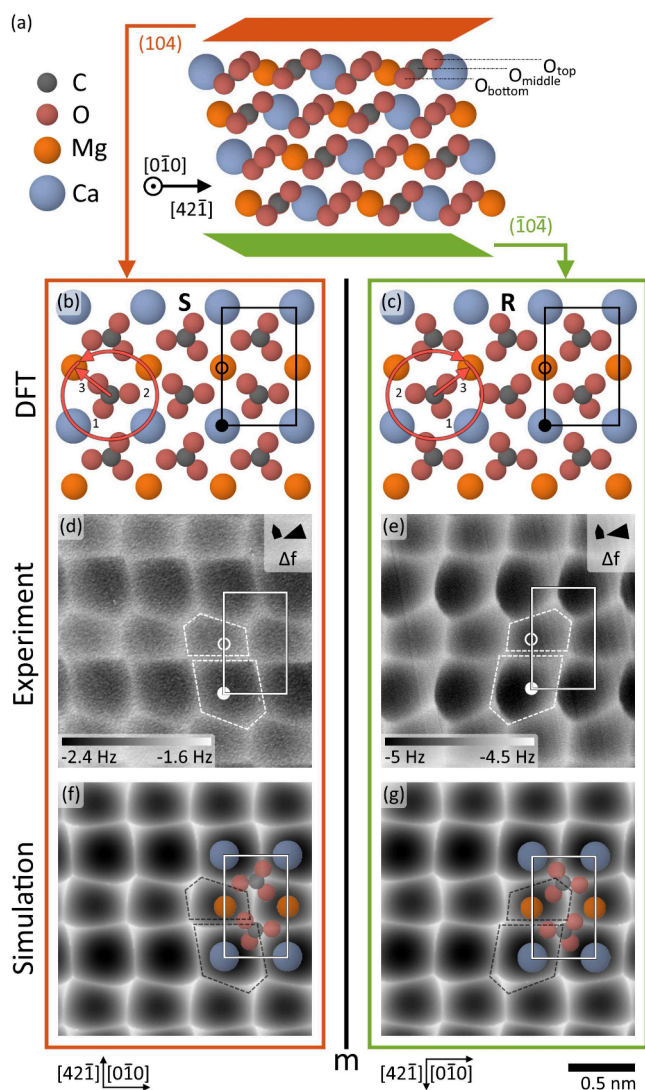


Figure 1. (a) Dolomite bulk crystal structure with two enantiomeric (104)^S and (104)^R surface planes. (b,c) DFT-optimized geometry of the dolomite(104)^S and (104)^R surfaces (unit cell marked by black rectangle; priorities of 1 to 3 around chiral carbon centers assigned to carbonate oxygens; enantiomeric assignment using the CIP rule visualized by red arrows). (d,e) Experimental high-resolution frequency shift data obtained with CO-functionalized tips on two opposing dolomite crystal surfaces and (f,g) corresponding simulated images, extracted at $z = 830 \text{ pm}$ (z is measured relative to the average topmost Ca plane). Unit cells marked by white rectangles.

To confirm this indication, we perform DFT geometry optimizations (see Supporting Information (SI) section A for details on the methods) to find the optimal structures of both the (104) and ($\bar{1}0\bar{4}$) surfaces. In fact, the structures in Figure 1(b,c) represent the optimized geometries of the two enantiomeric surfaces resulting from independent DFT runs, whereby the surface species only undergo minor relaxations from the bulk-truncated positions (Mg/Ca less than 1 pm and surface O maximum relaxations around 50 pm).

In analogy to molecular chirality, we assign the chiral centers on these surfaces to the carbon atoms. By adapting the Cahn-Ingold-Prelog rule (see also SI section B), we allocate priorities to the three carbonate oxygens based on the atomic numbers Z ($Z_{\text{Mg}} = 12$, $Z_{\text{Ca}} = 20$) of the neighboring surface ions, resulting in the highest (lowest) priority for the oxygen O_{bottom} (O_{top}). Therefore, we find a counterclockwise rotation of the arrangement of the species of the (104) plane shown in Figure 1(b), which is reversed in a clockwise manner for the ($\bar{1}0\bar{4}$) surface as indicated in Figure 1(c). Consequently, we refer to the (104) surface as enantiomer (104)^S and to the ($\bar{1}0\bar{4}$) surface as enantiomer (104)^R.

While the mirror symmetry between these two models is already apparent visually, the chiral property of these two structures is confirmed within DFT accuracy by a numerical symmetry analysis, see SI section C. As a rule of thumb, the position of the topmost oxygen atom O_{top} next to the magnesium cation is either left (enantiomer S, Figure 1(b)) or right (enantiomer R, Figure 1(c)) of the central carbon atom (see also red straight arrows in Figure 1(b,c)). This chiral submotif is mirror-symmetric to each other; yet, it cannot be superimposed on each other without reflection. Note that the unit cells are positioned in such a way that the mirror symmetry is directly apparent. With this choice, the $[42\bar{1}]$ direction proceeds in opposite directions between the two cases, highlighting that a careful assignment of the surface directions is required as a direct result of the presence of the two enantiomers.

While the bulk crystal structure and the DFT results already make a strong case for the presence of chiral surfaces, it is important to provide experimental validation and thereby exclude a symmetry-inducing surface reconstruction. The study of insulating mineral surfaces turned out to be a challenge with established charge-based experimental methods. Instead, the measurement of interaction forces by atomic force microscopy enables imaging of insulator surfaces including carbonates,²¹ yet, the complexity of tip–surface interactions for dolomite(104) turned out to complicate data interpretation.²² Data quality on insulator surfaces has only recently been significantly elevated by the use of Cu oxide²³ or carbon monoxide (CO)^{24,25} functionalized tips that enabled unambiguous unraveling of the atomic structures.

We succeeded in imaging the atomic structures of the two opposing (104) and ($\bar{1}0\bar{4}$) sites of the same dolomite crystal. Key for the measurements is the usage of CO-terminated tips that were precharacterized on a Ag(111) surface mounted adjacent to the dolomite crystal²⁶ (see SI section D). The $[42\bar{1}]$ and $[\bar{4}21]$ directions are determined macroscopically from the birefringence property²⁷ and images are aligned such that the respective direction points upward in all image data. The image data in Figure 1(d,e) resemble a pattern consisting of pores enclosed by a bright lattice structure. One pore (marked by a solid circle) is spatially larger than the other

(marked by an open circle). Based on the smaller ionic radius of Mg^{2+} compared to Ca^{2+} and considering the findings on calcite(104) where the bright lattice intersections are roughly located at the position of the O_{top} atoms of the carbonate groups,²⁴ we can tentatively assign the large (small) pore to the Ca (Mg) sites and center the unit cell outline vertices on Ca as indicated. Most intriguingly, the chiral character of the surfaces is directly evident: the pores express an asymmetric, pentagonal shape. The shapes marked in the images of the two crystal sides in Figure 1(d,e) by dashed white lines are clearly two enantiomers as they are nonsuperimposable mirror images of each other. At this point, we exclude a chiral center at the tip causing this difference due to our careful tip preparation protocol and the precharacterization by inverse imaging of $\text{CO}/\text{Ag}(111)$, see SI section D. Running measurements at 5 K while compensating for vertical drift²⁸ also excludes drift and creep artifacts as the source for the observed asymmetry. By imaging many different surface sites on each crystal side, we can further exclude the formation of different enantiomeric domains on a polycrystalline sample. Finally, the extended image series in SI section E highlight the presence of chirality across a large tip–sample distance range.

To precisely assign the different surface sites in the NC-AFM data, we perform image simulations for the DFT models in Figure 1(b,c), reproduced in Figure 1(f,g) with a partial overlay of the atomic geometry. There is clearly an excellent agreement between experimental and simulated data, reproducing all features. Further, the large (small) pore can unambiguously be assigned to the calcium (magnesium) site, while the bright lattice structure evolves from the interaction between the CO tip and the carbonate groups, in particular with the topmost oxygen atoms O_{top} . We note that we did not find any evidence in the experimental data and DFT models for a surface reconstruction, i.e. for a (2×1) reconstruction as has been observed and explained before on the related calcite(104) surface.^{24,29}

Next, the properties of intrinsically achiral water molecules in contact with a dolomite surface enantiomer in light of surface chirality is studied. A particular focus is set on chirality transfer as has been observed before on chiral surfaces.^{30–32} Water is dosed on a $(104)^{\text{S}}$ surface of a cooled (~ 120 K) dolomite crystal with subsequent thermal equilibration at temperatures of up to ~ 175 K (the onset of water desorption is observed above 185 K in ultrahigh vacuum). Samples with coverages in the submonolayer regime up to a single water layer are investigated by CO-tip assisted NC-AFM.

Figure 2(a) presents a topography image of the dolomite(104)^S surface covered with about 0.13 ML of water; corresponding high-resolution images acquired with a CO tip at two vertical tip–sample distances differing by about 80 pm are shown in Figure 2(b,c). Single water molecules are directly identified as features present in addition to two CO molecules as well as the dolomite(104)^S surface structure; two characteristic individual water molecules are marked by white arrows. The general contrast at large tip–sample distance in Figure 2(b) of single water molecules is similar to that of the CO-tip–water interaction already known from the calcite(104)– (2×1) system.²⁵ When additionally resolving the dolomite lattice in Figure 2(c), most water molecules are found to be located on a Ca row (large pores), while a smaller fraction resides on a Mg row (small pores). Water adsorption at these two distinct positions with a preference for the Ca row is a general observation across all experiments; we therefore

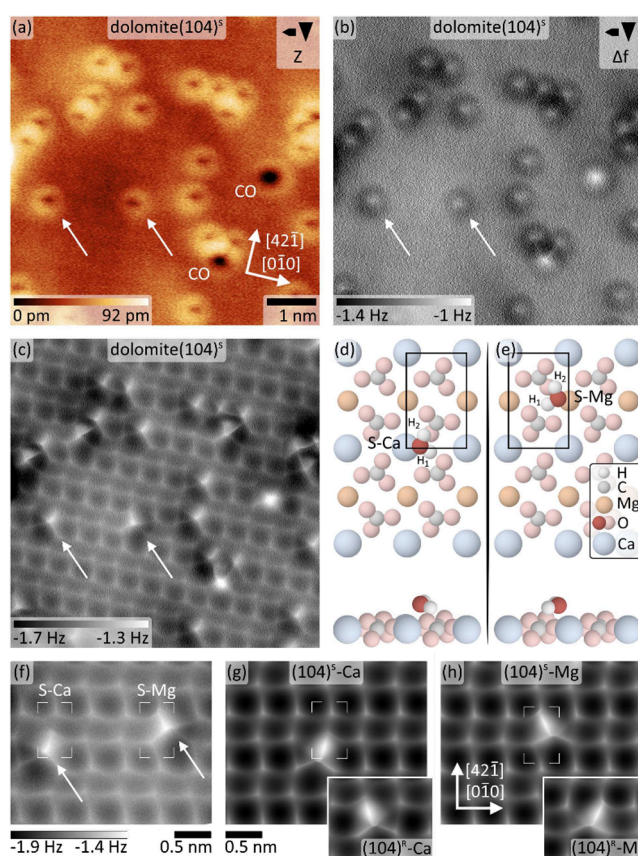


Figure 2. (a) Topography image of a dolomite(104) surface covered by water and a few CO molecules, acquired by NC-AFM at 5 K with a CO-terminated tip ($\Delta f = -1.2$ Hz and $U_{\text{sample}} = 10$ V). Single CO molecules appear as dark depressions (two CO molecules are named in panel (a)) while water molecules are imaged as bright protrusions with a smaller dark spot (two examples marked by white arrows). (b,c) High-resolution frequency shift images of the surface area shown in (a) acquired in constant-height mode with a CO-terminated tip. Images are vertically separated by 80 pm ($U_{\text{sample}} = 10$ V; vertical stability is ensured by active drift compensation²⁸). (d,e) Optimized DFT geometries of the S–Ca and S–Mg water systems. Lengths of indicated bonds are given in Table 1. (f) Close-up high-resolution image of the two S–Ca and S–Mg adsorption cases. (g,h) Simulated NC-AFM images of S–Ca and S–Mg water. Insets: mirrored images represent the R–Ca and R–Mg enantiomers.

contrast the S–Ca water with the S–Mg water in the detailed high-resolution image in Figure 2(f) and further investigate these adsorption positions on the $(104)^{\text{S}}$ surface by DFT.

Lowest energy adsorption geometries for the S–Ca and S–Mg water resulting from calculations are shown in Figure 2(d,e) with simulated NC-AFM images of these models reproduced in Figure 2(g,h). We here only focus on the $(104)^{\text{S}}$ surface enantiomer, results for the $(104)^{\text{R}}$ surface would directly follow from symmetry as shown by the mirrored insets in Figure 2(g,h). We first note an excellent agreement between the experimental and simulated NC-AFM data and thereby confirm the DFT geometries. From inspecting the models more closely, water is found to bind to the dolomite surface both via an ionic bond between the water oxygen and respective surface cation as well as via a hydrogen bond between the water H_1 and one topmost oxygen surface atom. A third bond between the second hydrogen H_2 and another surface oxygen atom is longer than what would be expected for

a hydrogen bond. The different bond lengths (see Table 1) readily justify the difference in the adsorption energy of about

Table 1. Adsorption Energies and Atomic Distances for the S–Ca and S–Mg Water Enantiomers^a

	S–Mg	S–Ca
E_{ads}	−0.98 eV	−1.03 eV
E_{ads} ref 33	−0.94 eV	−0.98 eV
$\text{O}_{\text{water}} \cdots \text{cation}$	2.12 Å	2.37 Å
$\text{H}_1 \cdots \text{O}_{\text{surf}}$	2.06 Å	1.70 Å
$\text{H}_2 \cdots \text{O}_{\text{surf}}$	2.29 Å	2.45 Å
$\text{O}_{\text{water}} \cdots \text{H}_1 \cdots \text{O}_{\text{surf}}$	3.01 Å	2.69 Å
$\text{O}_{\text{water}} \cdots \text{H}_2 \cdots \text{O}_{\text{surf}}$	3.07 Å	3.11 Å
$z_{\text{O}_{\text{water}}}$	2.02 Å	2.14 Å

^aElement identifications are introduced in Figure 2(d,e). $z_{\text{O}_{\text{water}}}$ describes the height of the O_{water} atom above the surface plane defined by the average center position of the surface cations along z .

50 meV between the two sites, in full agreement with independent recent DFT calculations.³³ The lower adsorption energy at S–Ca also confirms the experimental prevalence over S–Mg. In addition, the water oxygen–surface cation distance is by 25 pm smaller at the Mg site when compared to Ca and the H_1 (H_2) hydrogen bond of S–Mg is accordingly longer (shorter) than of S–Ca. Overall, the water oxygen atom moves 12 pm along z closer to the surface at the Mg site. The surface only undergoes minor relaxation upon adsorption of a single water molecule, see SI section F.

The strong molecule–surface interactions, different at the two cation sites, directly explains the presence of two enantiomers for each water adsorption site; the single water molecule geometry differs considerably depending at which cation site the water is adsorbed. This is a significant result as it proves chirality transfer from the dolomite(104) and ($\bar{1}0\bar{4}$) mineral surfaces to the achiral water molecule, leading to chiral signatures in the adsorption of single water molecules. This enantiospecific adsorption is a consequence of the strong interaction between surface and molecule; a templating effect is at work with the surface dictating the adsorption positions of the single water molecules. This is in full agreement with earlier findings of chirality transfer from chiral (mostly metallic) substrates to achiral molecules.^{30,31}

Chirality transfer is also apparent when investigating the fully hydrated surface at 1 ML water coverage. A corresponding constant-height overview image in Figure 3(a) reveals the assembly of water molecules. We start the investigation with the optimized 1 ML DFT model geometry in Figure 3(b). An analysis of the average bond lengths (see Table 2 in SI section H) highlights that the adsorption geometries at the Mg and Ca sites are rather similar to the single water cases. This finding again hints toward strong molecule–surface interactions while the water–water forces are small—supporting the templating effect and, thereby, the persistent presence of the two enantiomers. An analysis of the atomic shifts (see SI section G) between the pristine and water-covered dolomite(104) surface models further reveals that the surface atoms react with shifts of up to 25 pm to the adsorption of a full water monolayer.

While these results already hint toward chirality transfer also into the full monolayer, we give a clear answer to this central question by performing both a structural analysis of the water layer DFT geometry and a symmetry analysis of the

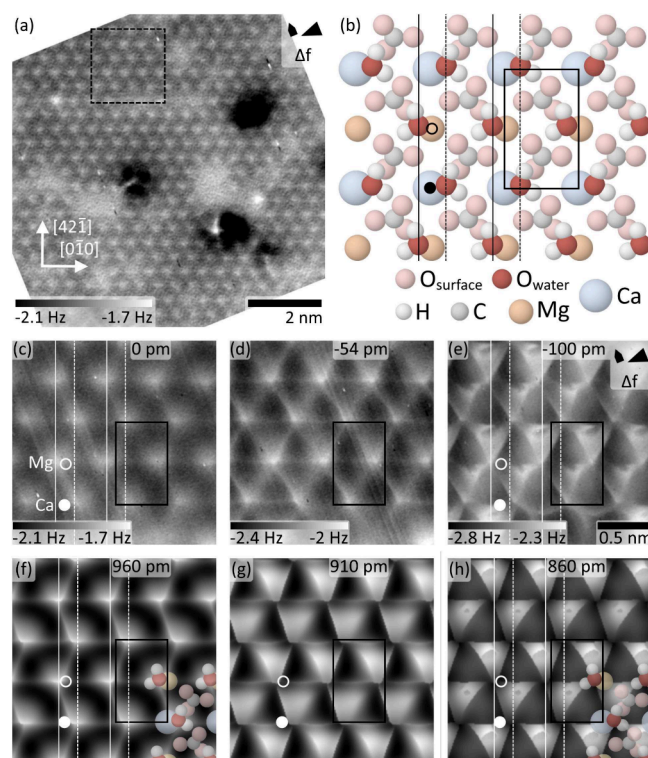


Figure 3. (a) Large-scale constant-height image (acquired at large tip–sample distance) of the dolomite(104)^S surface covered with a single layer of water molecules. (b) DFT-optimized geometry of the dolomite(104)^S surface covered by 1 ML of water. (c–e) Series of experimental constant-height images (decreasing tip–sample distance) resolving the water structure. (f–h) Simulated images of the water structure on the dolomite(104)^S surface (tip–sample distances relative to average top Ca plane included). Cation positions in (c,e) according to comparison with model, see inset in (f,h). Vertical lines in (c–h) mark the position along the horizontal axis of the primary bright features.

experimental NC-AFM data. In case of chirality transfer, there should be a notable difference between the H_2O water layer on a dolomite(104)^S and (104)^R surface. We quantify this difference by performing an adapted continuous chirality measure^{34,35} and Hausdorff distance analysis^{36,37} on the isolated water structure from the water/dolomite(104)^S model and the mirrored variant (see SI section I, also for bare dolomite). As the DFT methodology does not express any chiral bias, confirmed by the independent calculations for the pristine surface, Figure 1(b,c), we now focus only on the (104)^S surface. We calculate the translation vector $T = (\vec{r}, \theta)$ that shifts the atomic positions of the isolated water structure onto its mirrored variant while minimizing the root-mean-square deviation (RMSD) of the atomic positions, resulting in an optimal overlap of the two structures. For the isolated water/dolomite(104)^S surface we find an optimum of RMSD ≈ 16.6 pm and a corresponding Hausdorff distance of $h \approx 26.7$ pm. This means that there is no translation-rotation vector that can superimpose the water layer onto its mirror image – the isolated water layer is chiral. Overall, the DFT results give strong evidence for chirality transfer into the first water layer and allow the unambiguous identification of the two enantiomers within the DFT model as a result of the dolomite surface chirality.

Finally, we extend the analysis to the experimental data for substantiating the theoretical conclusions. We first note that the series of high-resolution NC-AFM data acquired across a tip–sample distance range of 100 pm in Figure 3(c–e) are in excellent agreement with image simulations in Figure 3(f–h), already giving evidence for the validity of the 1 ML water/dolomite(104)^s DFT model and the associated chiral property. By superimposing the atomic structure in Figure 3(f,h), the bright regions at large tip–sample distances are identified to be positioned between the water oxygen atoms and surface cations. Bright linkers appear at intermediate tip–sample distances, Figure 3(d,g), roughly in-between the water oxygen atoms, but offside of the water–carbonate hydrogen bonds. At very close tip–sample distances, these linkers evolve into triangular shapes in Figure 3(e,h). While an analysis of the shape and contrast within these individual patterns, i.e. the different separation along the $[0\bar{1}0]$ as marked by solid and dotted vertical lines, would already highlight the chiral property, we follow a comprehensive numerical approach for analyzing the symmetry, inspired by the *pg* symmetry test developed before for calcite(104) data.²⁴ This test calculates the mean squared error (MSE) from adding the pixelwise deviation between the data within one (1×1) unit cell and inside the mirrored version of one surface unit cell. Resulting MSE values are shown along one coordinate (*y*) in Figure 4(a).

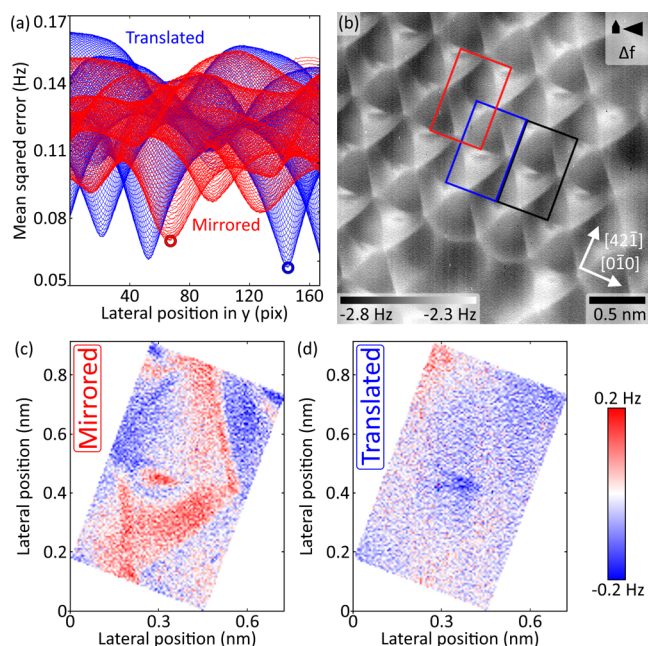


Figure 4. Symmetry analysis of the data acquired for 1 ML water on the dolomite(104)^s surface. (a) Mean squared error (MSE) for the mirrored (red) and translated (blue) variants. Minima are marked by circles. (b) Experimental data with markers for the reference unit cell in black as well as the optimum mirrored (red) and translated (blue) unit cell. (c,d) Pixel-wise deviation for the (c) mirrored and (d) translated unit cell.

Due to the surface structure, mirror axes not parallel to the $[42\bar{1}]$ direction can directly be excluded. In turn, we allow ranges along the *x* and *y* axes larger than one unit cell to find the optimum in positioning the mirrored unit cell. The minimum MSE for the mirrored unit cell marked by a red circle in Figure 4(a) corresponds to the red cell marked in Figure 4(b). To take account of experimental noise that will

fundamentally inhibit an excellent overlap with zero MSE, we compare the numbers from this chirality test with the case of a translated unit cell. Data in Figure 4(a) (blue curves) directly show a smaller MSE (blue circle) at optimum shift for the unit cell placed nearby the original one (blue rectangle in Figure 4(b)). The pixel-wise comparison within the single unit cell for these two cases directly substantiates the difference between these values: There is a strong contrast along the triangular structures in Figure 4(c) for the mirrored version, while the translated cell basically expresses noise.³⁸ Further details on the method are given in the SI section J. To conclude, the numerical analysis did not reveal a mirror symmetry in the experimental data. Instead, the water monolayer follows the enantiomeric surface structure and, thus, expresses chirality.

In summary, we deliver clear proof from experiments and simulations for the presence of two enantiomers on opposite $\{104\}$ faces of ordered dolomite and thereby confirm the expectation from the bulk crystal structure. Both enantiomers are imaged by NC-AFM using CO-terminated tips and their structures are confirmed via DFT simulations. Due to the strong molecule–surface interactions, chirality is transferred into the local structure of single water molecules as well as into the assembly of a full water monolayer, ultimately causing an achiral molecule to exhibit handedness. The energetic difference of 50 meV between water adsorption at the Ca and Mg sites suggests a measurable effect also at room temperature.

The presence of chiral dolomite surfaces has widespread implications and is of particular importance in the context of organogenic models for dolomite growth. As a consequence of chiral selectivity in biomolecules on earth, extracellular polymeric substances will consist of only one enantiomer of amino acids that is expected to favor one enantiomer of the dolomite(104) faces – either directly due to different adsorption properties of enantiomeric molecules on dolomite, or indirectly via transfer by chiral water layers. In fact, strong evidence has been given for chiral water structures in the vicinity of an antiparallel β -sheet protein,¹³ in the minor grooves of a DNA strand,¹⁴ and within assembled sugar complexes.¹⁵ With a homochiral imprint on water structures, chiral selectivity effects are expected when homochiral water is in contact with either face of dolomite. It will be the task of future studies to both quantify the extent of the surface-induced chiral imprint into higher water layers and to determine the presence of a direct or indirect chirality transfer between dolomite surfaces and biomolecules. In particular amino acids^{39,40} could contribute to the the growth of dolomite, hinting towards links between chirality of dolomite{104} and the origin of homochirality of life.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.6c03227>.

Methods, nomenclature, symmetry analysis, tip characterization, constant-height image series, atomic shifts of single water molecules, atomic shifts of water monolayer, comparison of single water and full layer distances, quantification of chirality, and symmetry testing on experimental data (PDF)

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Author Contributions

[†]P.L. and J.H. contributed equally. P.L. and J.Heggemann performed the experiments and analyzed the experimental data. J.Huang and A.S.F. performed the calculations. P.R. conceived the project, supported the experiments, contributed to the data analysis, and wrote the first manuscript draft. All authors discussed the results and contributed to finalising the manuscript.

Notes

The authors declare no competing financial interest.

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