

Electronic Supplementary Information

Positive and negative forms of calcite (CaCO_3) crystal. New open questions from the evaluation of their surface energies.

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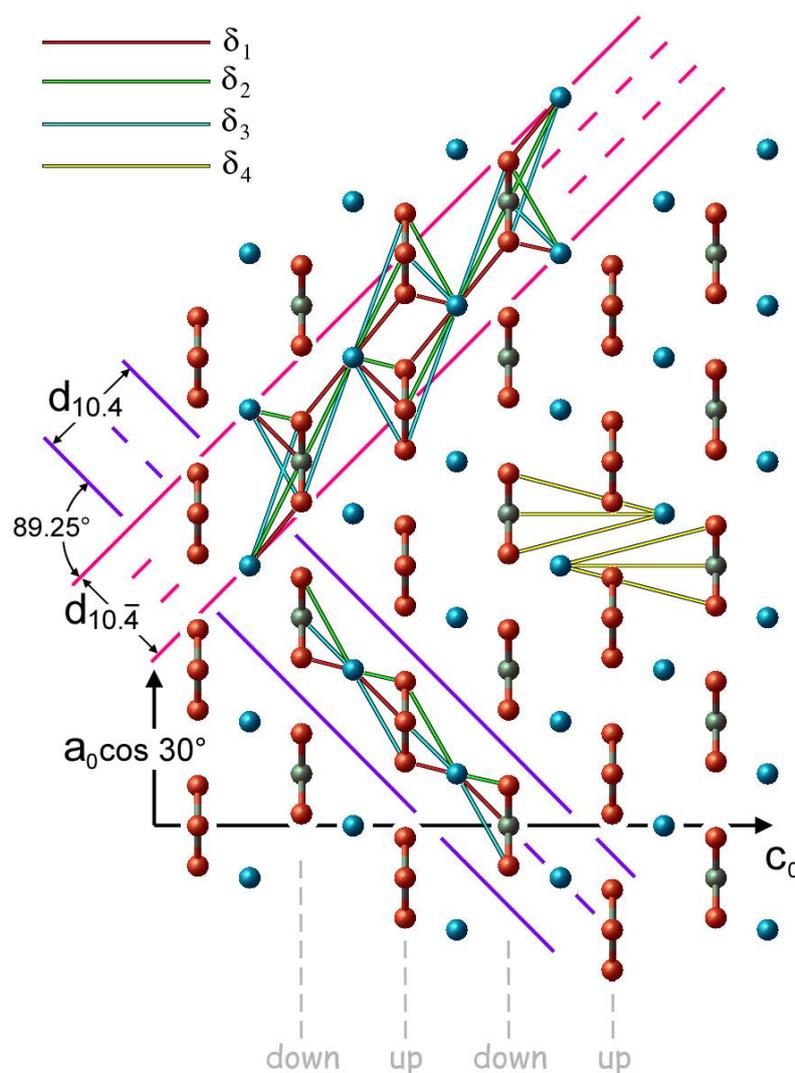


Figure S1. Projection of the calcite structure along the direction $[010]$. Comparison between the slices $d_{10.4}$ and $d_{10.4\bar{}}$. Weaker δ_4 bonds are omitted, within the $d_{10.4\bar{}}$ slice, for the sake of clarity. The spacing $a_0 \cos 30^\circ$ and c_0 are indicated, along with the thickness of the slices $d_{10.4}$ and $d_{10.4\bar{}}$ parallel to

the face (10.4), of the cleavage rhombohedron, and to the negative rhombohedron ($10\bar{4}$), respectively.

The labels “UP” and “DOWN” indicate the orientation of the carbonate ions, i.e. if the apical oxygen atom of the ion points outwards or downwards with respect to the drawing plane.

The lengths of the Ca–O bonds belonging to the short range coordination of calcium are:

$\delta_1 = 2.3597 \text{ \AA}$; $\delta_2 = 3.4588 \text{ \AA}$; $\delta_3 = 4.2826 \text{ \AA}$, while the length of the three weaker Ca–O bonds that are symmetrical along the c_0 axis is $\delta_4 = 4.4536 \text{ \AA}$.

1) Looking at the $d_{10.4}$ slice, it comes out that:

- i) The frontiers separating adjacent equivalent slices do not intersect any ion;
- ii) the centres of mass of the ions entering each slice lie on a unique plane (dashed line) located midway of the slice.

2) Concerning the $d_{10\bar{4}}$ slice, sharply different features follow from the distribution of the ions:

- iii) The frontiers separating adjacent equivalent slices do pass through the centres of mass of both positive and negative ions that, by consequence, are shared by two consecutive slices. In other words, only one half of the ions lying on a frontier belongs to a given slice (while the second half belongs to the adjacent one). It follows that the repeat period, along the [010] direction, of the ions belonging to the outmost layer of a ($10\bar{4}$) face is no longer $b_0 = 4.9896 \text{ \AA}$, but $2 b_0 = 9.9792 \text{ \AA}$. This means that the $\{10\bar{4}\}$ surfaces have to be reconstructed in order to calculate their surface energy.
- iv) The centres of mass of the remaining ions belonging to each slice no longer lie on a unique plane but on two planes (dashed lines) symmetrically equidistant from the centre of the slice.

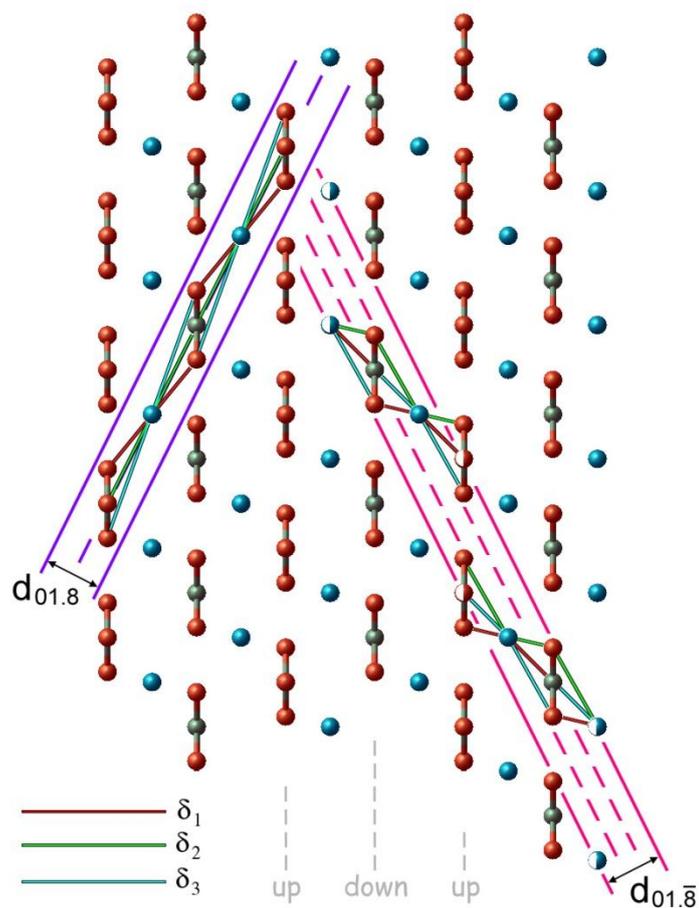


Figure S2. Projection of the calcite structure along the direction $[010]$. Comparison between the slices $d_{01.8}$ and $d_{01.\bar{8}}$. The behaviour of the flat $\{01.8\}$ rhombohedron and of the negative $\{01.\bar{8}\}$ one is strictly analogous to that of the $\{10.\bar{4}\}$ and $\{10.4\}$ forms. The only difference consists in the fact that the stepped character of the $\{01.\bar{8}\}$ form is further enhanced with respect to that of the flat $\{01.8\}$ rhombohedron, because a strong bond discontinuity characterizes the content of the $d_{01.\bar{8}}$ slice.

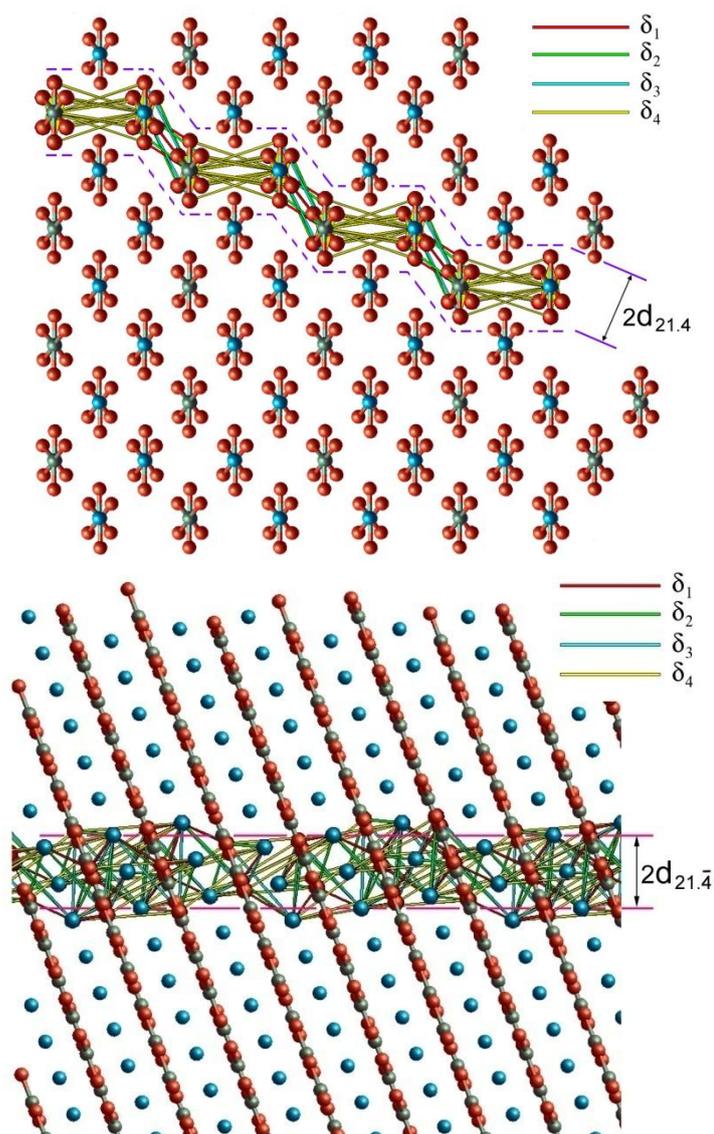


Figure S3. Projection of the calcite structure. Top: along the direction of the PBC $[\bar{4}41]$. Bottom: along the direction $[1\bar{2}0]$. Comparison between the slices $2 \times d_{21.4}$ and $2 \times d_{21.\bar{4}}$.

1) Slice of thickness $2 \times d_{21.4}$.

The $\langle \bar{4}41 \rangle$ chains, perpendicular to the drawing plane, are not bounded within a slice of thickness $d_{21.4}$. To find a correlated growth among them, one has to consider a slice of thickness $2 \times d_{21.4}$. The resulting surface profile is more stable and is composed by alternating segments of $\{10.4\}$ and $\{11.0\}$ nano-facets having the length of 0.315 and 0.382 nm, respectively. The strongest δ_1 , δ_2 and δ_3 bonds link the $\langle \bar{4}41 \rangle$ chains within the $\{10.4\}$ nano-segments, while the $\{11.0\}$ ones are built by the three symmetrical and weaker δ_4 bonds.

2) Slice of thickness $2 \times d_{21.\bar{4}}$.

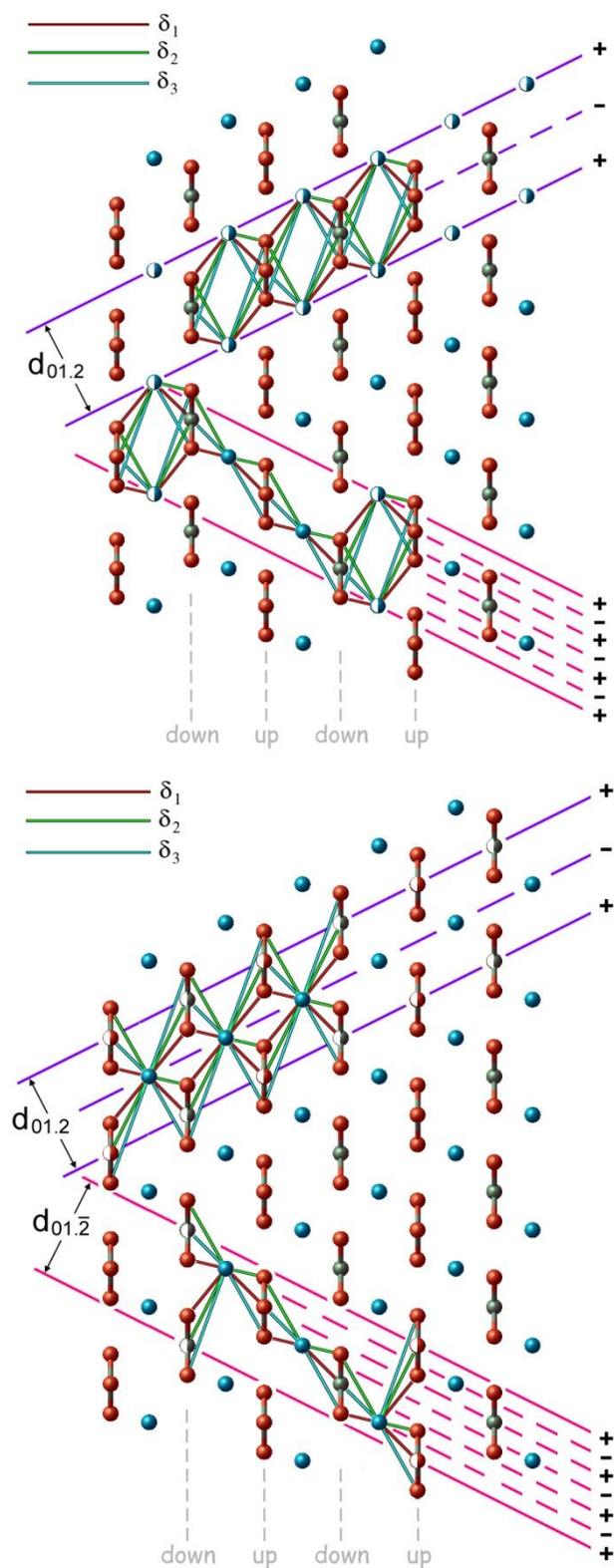


Figure S4. Projection of the calcite structure along the direction [010]. Comparison between the slices d_{012} and $d_{01\bar{2}}$. Weaker δ_4 bonds are omitted, within the $d_{10\bar{4}}$ slice, for the sake of clarity.

1) The slices of thickness d_{012} : (Ca^{2+} ion planes limiting the slices).

Adjacent $d_{01,2}$ slices are separated by planes lying on the centres of the ions and then these “frontier ions” have to be shared between two slices. Their resulting coverage degree is one half. There are two ways to satisfy this constraint: the first one consists in eliminating one [010] Ca^{2+} row over two

while, in the second one, one Ca^{2+} ion over two is eliminated along each [010] row. The first surface reconstruction does not respect the symmetry plane of the surface space group, contrary to the second reconstruction. Consequently, as anticipated in the text of the paper, we adopted the second way because it minimizes the surface energy of the face. When Ca^{2+} planes limit the $d_{01.2}$ slices, the centres of mass of the CO_3^{2-} ions lie on a 01.2 plane midway the frontiers of the slice. This reconstruction of the slice, obtained by applying rigorously the HP method, automatically cancels out the dipole component perpendicular to the slice.

2) The slices of thickness $d_{01.\bar{2}}$: (Ca^{2+} ion planes limiting the slices).

The just mentioned reasoning can be also applied to the reconstruction of the $d_{01.\bar{2}}$ slices. The relevant differences concern:

- the density of the surface charges, which amounts to one third of that of the $d_{01.2}$ slices;
- the number of 01. $\bar{2}$ alternating planes (five) on which are distributed the charges of opposite sign lying in between the frontiers of the slice.