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Surface control vs. diffusion control during calcite dissolution: Dependence of step-edge velocity upon solution pH

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ABSTRACT

The reaction of the $(10\bar{1}4)$ calcite surface during dissolution was studied as a function of pH (HCl) by liquid-cell Atomic Force Microscopy (AFM) under ambient conditions of both temperature (22 °C) and partial pressure of carbon dioxide (P_{CO_2}). A flow through AFM liquid reaction cell was used, and solutions were renewed at a controlled flow rate and sampled for chemical analysis.

In the pH range 7.5–4.3, surface dissolution proceeds via the formation of etch pits delimited by steps of height 3.3 ± 0.3 Å or a multiple of this elementary distance. Rhombohedral pits form and grow at the surface by anisotropic step retreat, at a velocity of 4.2 ± 0.2 nm/s for the steps oriented along the two equivalent directions $[\bar{4}41]_+$ and $[48\bar{1}]_+$, and 1.1 ± 0.2 nm/s for the steps oriented along the other two equivalent directions $[\bar{4}41]_-$ and $[48\bar{1}]_-$. At the pH value of 2.7, the slower rate slightly increases and is equal to 1.6 ± 0.2 nm/s. At the pH value of 1.7, microtopography measurements indicate that micrometric steps have a meandering shape, and move as a *family* at a velocity higher than 10 nm/s. These meandering steps are made of nanometric segments oriented along $[\bar{4}41]_+$, $[48\bar{1}]_+$, $[\bar{4}41]_-$, and $[48\bar{1}]_-$, and they terminate their run against sloped rough etch pits with sides made of narrow terraces delimited by steps oriented along the $[48\bar{1}]_+$.

Finally, the present study indicates that reactive area (i.e., the total amount of reactive atomic sites) of a calcite surface increases in response to higher solution acidity firstly by an increase in the step density, and secondly by production of additional roughness at step edges. The change in step edge-velocity observed below pH = 2.7 was interpreted as the response of the dissolving surface to the loss of buffering capacity at the Stern layer.