



## **Nanoscale observations of growth and dissolution processes on calcite $\{10\bar{1}4\}$ in contact with Mn-bearing aqueous solutions**

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In this study, we present in situ Atomic Force Microscopy (AFM) observations of the phenomena that occur on calcite  $\{10\bar{1}4\}$  surfaces in contact with static aqueous solutions containing different concentrations of Mn. These phenomena consist in the dissolution of the original calcite  $\{10\bar{1}4\}$  surface and the formation of nuclei of a new phase. The presence of  $\text{Mn}^{2+}$  in the solution both modifies the typical rhombus-shape of the etch pits forming on the calcite substrate and affects their expansion velocity, which during the initial stages of the process is dependent on the initial concentration of Mn. Our AFM observations indicate that there also exists a clear relationship between the initial concentration of  $\text{Mn}^{2+}$  and the induction period for the formation of the first nuclei of the new phase. These nuclei preferentially form on step edges of the substrate and readily reach a significant height ( $\sim 3.0$  nm), which remains approximately constant during their lateral spread. A clear epitaxial relationship between the islands of the new phase and the calcite  $\{10\bar{1}4\}$  surface has been observed. Moreover, the islands preferentially grow parallel to  $[42\bar{1}]$  in the calcite substrate, which determines that rapidly develop a very elongated morphology. The measurements carried out on series of AFM images have allowed us to establish the existence of a correlation between the expansion rates of the islands along their elongation axis and the initial concentration of Mn in the solution. The lateral growth of the islands leads to their coalescence and the formation of a quite homogeneous nanometric layer. This layer finally armours the calcite substrate from further interaction with the solution, which determines that the dissolution-crystallization process completely stops after a certain

period. In this work, both the degree of coupling between dissolution and growth as well as the nature of the new phase are discussed.