



Rapid supercritical CO₂ fluid migration in calcite crystals

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The transport of supercritical fluids is a determining factor for several geological processes as well fundamental in predicting natural resource accumulation and distribution. Calcite, ubiquitous in geological environments may contain supercritical CO₂ trapped under fluid inclusions commonly assumed to remain static under ambient conditions. Here, we report nano-meter scale observations on calcite crystal surface indicating the occurrence of fast movement of supercritical CO₂ fluid inclusions hosted in the upper part of calcite crystals.

Real time monitoring of calcite samples without observable presence of fluid inclusions, by in-situ Atomic Force Microscopy (AFM), shows a flat state of the calcite surface (after freshly cleaving) and the surface state condition did not change during several hours of scanning. However, AFM observations on calcite samples with visible fluid inclusions show rapid formation of nanometre-scale hillocks spontaneously formed on the surface structure of the calcite. They have an averaged height of 1 nm, and varied horizontal dimensions and geometries. The fact that hillocks formed spontaneously on flat terraces in only a few minutes, without evidence of surface dissolution, was unexpected and suggests that the source of hillock material should be derived within the crystal itself. This phenomenon was observed even changing the experimental conditions such a scan frequency of the AFM tip, environmental temperature (between 5° and 50°C) and the surface area of scanning.

The observed hillocks can form by the fact that CO₂-rich fluid inclusions located just under the mineral surface are at elevated internal pressure and near the rupture limit. Thus, a frail mechanical strain can case them to decrepitated and lose their fluid. Upon reaching the surface, the supercritical CO₂ leaked from the fluid inclusions, mixes with the thin water layer in equilibrium with ambient CO₂ partial pressure at the calcite surface, causing degassing of CO₂ and facilitating calcite precipitation in the form of hillocks.

We estimated CO₂ supercritical fluid transport assuming a minimum depth of the fluid inclusions involved in the fluid movement and an instantaneous precipitation at the surface. We found that supercritical CO₂ fluid transport in calcite is around the value of 10 nm/s. The estimated fast fluid transport rate is about 10 orders of magnitude higher than the estimated low-temperature extrapolation of solid-state diffusion vacancy in calcite crystals.

Classical description of fluid transport recognises several distinct paths only for polycrystalline materials assuming the presence of inter-grain pathways as micro and nano-pore tubes. Fluid transport is usually observed in poly-phase material grains can also exhibit clear indications of multi-path migration even when visible evidence of such paths is lacking. Our study quantifies this process in the case of natural calcite at external standard conditions and be of potential importance in movement of CO₂ rich fluids under supercritical conditions.