

In situ AFM observations of mineral replacement reactions on sulphate and carbonate surfaces

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Replacement reactions involving sulphates and carbonate minerals are ubiquitous on the Earth's Crust [1,2]. Although it is clear that such mineral replacements take place almost exclusively by the coupling of dissolution and crystallisation reactions, both the mechanisms and the kinetics that govern such a coupling on mineral surfaces remain obscure.

Here we present new in situ AFM observations of celestite and calcite surfaces reacting with static Na_2CO_3 and CdCl_2 aqueous solutions, respectively. In the case of celestite, the reaction with Na_2CO_3 solutions leads to the dissolution of the original surface and the formation of a layer (presumably of SrCO_3). On calcite faces, dissolution in CdCl_2 solutions is coupled with the growth of $\text{Cd}_x\text{Ca}_{1-x}\text{CO}_3$ solid solution. Observations indicate that a rapid dissolution of the original surface always precedes the growth of the new layers. The crystallisation of the replacing phases involves the formation of two-dimensional nuclei, which preferentially occurs on steps of the dissolving substrate. The induction period for two-dimensional nucleation strongly depends on the substrate, the solubility product of the overgrowth and the concentration of the initial solution. While on calcite surfaces the first nucleation of $\text{Cd}_x\text{Ca}_{1-x}\text{CO}_3$ is observed after a few seconds in all the experiments, on celestite surfaces the induction time for nucleation increases as the concentration of the Na_2CO_3 solutions decreases (from 3 to 25 minutes). In both cases, a few seconds after nucleation, two-dimensional nuclei reach a considerable thickness (~3 nm), which remains constant during the whole replacement process. When the subsequent lateral spreading and coalescence of the nuclei leads to the formation of a homogeneous layer further dissolution of the substrate is prevented. For the reaction between celestite and Na_2CO_3 solutions, several dissolution-growth cycles have occasionally been observed before the replacement process stops. This suggests that the coupling between dissolution and crystallisation is, in this case, especially complex. Our measurements on series of AFM images provided quantitative information about coupled dissolution-growth rates.

References

- [1] Baldasari, A. and Speer, J.A. (1979) *AM* **64**, 742-747.
- [2] Sanz-Rubio et al. (2001) *Sediment. Geol* **140**, 123-142.