Geophysical Research Abstracts
Vol. 13, EGU2011-8279, 2011
EGU General Assembly 2011

The role of the boundary fluid-mineral interface in the control of crystal growth

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Crystal growth can only take place from solutions supersaturated with respect to the precipitating phase. However, atomic force microscopy (AFM) experiments have shown that growth on mineral surfaces can occur from solutions when the bulk composition is undersaturated with respect to the precipitating phase. The implication is that the composition of the solution in the fluid boundary layer in contact with the mineral surface must become supersaturated with the new phase growing at the mineral surface. This has been observed in a number of systems, including the growth of new phases on calcite cleavage surfaces, such as Ca phosphonates [1], and on gypsum surfaces, such as Ca phosphates [2], where the partial dissolution of the substrate provides ions included in the new phase. The precipitation of calcite from pure water flowing over a stressed calcite surface is a clear example of a boundary layer becoming supersaturated with the precipitating phase when the bulk fluid contains no ions included in the new phase. This can be explained in terms of the increased solubility of stressed calcite allowing the boundary layer to become supersaturated with an unstressed calcite phase, which then precipitates. The thickness of the boundary layer can be deduced from the solution composition and the reacting surface area.

The concept of a boundary layer becoming supersaturated with respect to another phase, which then precipitates, is essential for the understanding of coupled dissolution-precipitation as a mechanism of mineral replacement [3]. Real-time phase-shift interferometry has been used to show the steep compositional gradient at the surface of a crystal of KBr being pseudomorphically replaced by KCl [4] and this has been used as a model system for more complex Earth systems involving mineral-fluid reactions during such processes as metasomatism, metamorphism and weathering.

[1] Ruiz-Agudo E. et al. (2010) Crystal Growth and Design, [2] Pinto A. et al. (2010) American Mineralogist, [3] Putnis A. and Putnis C.V. (2007) Journal of Solid State Chemistry, [4] Putnis C.V., et al. (2005) American Mineralogist.