

Heterogeneity of mineral surfaces and its role in geochemical surface reactions

ANDREW PUTNIS¹, JOSÉ M. ASTILLEROS¹,
CARLOS M. PINA², AND CHRISTINE PUTNIS¹

¹Institut für Mineralogie, Universität Münster, D-48149, Germany. ²Departamento de Cristalografía y Mineralogía, Universidad Complutense de Madrid, 28040. Spain. (putnis@nwz.uni-muenster.de)

Many of the classical models of crystal growth have been verified by Atomic Force Microscope (AFM) studies over the last decade, particularly the relative importance of screw dislocations, step growth and two-dimensional nucleation. The role of fluid supersaturation and the surface crystal structure in controlling the growth mechanisms and morphology in pure aqueous solutions is relatively well understood but the effect of impurities still presents some fundamental problems. When impurities are known to slow down the rate of step advancement, classical models explain this by either pinning of the step motion or by changes in the supersaturation of the fluid due to the impurity incorporation. *In situ* AFM observations of the inhibition of growth by organic molecules appear to confirm the pinning model, with the molecules preferentially incorporated at steps. When the impurities are 'foreign' cations a different approach is required and it is necessary to consider their incorporation into the growing crystal in terms of solid solution – aqueous solution (SS-AS) systems. The supersaturation of the solution must be defined relative to the whole range of solid solution compositions which can be formed. This is important when considering the mechanism of uptake of heavy elements onto mineral surfaces.

AFM observations of crystal growth in a number of different systems based on calcite and barite as substrates show that step velocities depend very much on the chemical composition of each growth layer, and that the growth behaviour of the first layer can be very different from subsequent layers. The control of the substrate over this growth sequence is reflected by the fact that the step morphology of the starting substrate is exactly reproduced by each subsequent growth layer. In contrast to the step-pinning or impurity incorporation models there is no unique value for step advancement for a given supersaturation and foreign ion concentration. These observations have implications for continuous and oscillatory zoning in solid solution crystals.

Isotopic tracing of a mineral replacement reaction: the KCl-KBr-H₂O system as a model example

C.V. PUTNIS AND K. MEZGER

Institut für Mineralogie, Corrensstr. 24, 48149 Münster, Germany (putnisc@uni-muenster.de)

From observations of mineral compositions and textures (such as porosity), it is known that one mineral can be replaced by another. Such replacements are common when the surrounding fluids are not in equilibrium with the primary minerals. The actual processes involved in these reactions are not clearly understood, mainly because the start and end conditions are not known.

A replacement process was investigated where the aqueous fluid and solid compositions were known precisely before and after the replacement. In the system KCl-KBr-H₂O, a single crystal of KBr was reacted with a KCl solution and replaced by a single crystal of K(Br,Cl). A previous study analysed the Br/Cl exchange (Pina et al, Pollok et al, in prep.) and a mechanism of replacement was postulated in terms of relative solubilities of the end members. However, the exact exchange mechanism of K was not known. In this study, we have traced the movement of K in the replaced crystal from a solution enriched with ⁴⁰K. The ⁴⁰K/³⁹K ratio was determined by thermal ionisation mass spectrometry, as a function of the distance the replacement front moved across the KBr crystal. As expected from mass balance, due to dissolution equilibrium exchange with the fluid, the new solid solution crystal contained K derived proportionally from the original isotopically enriched KCl solution and the dissolved KBr. This observation provides strong evidence for a total replacement mechanism, where the bonding in the original KBr structure was completely broken and the new K(Br,Cl) solid solution had a new composition and texture. During the reaction, the crystallographic orientation was maintained, but the newly formed KBr was porous - a result of the difference in solubility of the end members (KBr being more soluble than KCl results in a volume deficit). In a naturally occurring mineral, a porous texture can be an indication that a replacement reaction has taken place.