Solvation effects on mineral reactivity

ENCARNACIÓN RUIZ-AGUDO¹, CHRISTINE V. PUTNIS²³, Alejandro Burgos-Cara¹, Carlos Rodriguez-Navarro¹ and Andrew Putnis²⁴

¹Departamento de Mineralogía y Petrología, Universidad de Granada, 18071 Granada, Spain, encaruiz@ugr.es

- ²Institut für Mineralogie, Universität Münster, 48149 Münster, Germany
- ³Nanochemistry Research Institute, Department of Chemistry, Curtin University, Perth 6845, Australia
- ⁴The Institute for Geoscience Research (TIGeR), Curtin

University, Perth 6102, Australia

Commonly, water in contact with rock-forming minerals contains significant and variable amounts of ions in solution. The effect of such ions on dissolution and growth rates has been traditionally ascribed to changes in solubility. However, experimental studies performed on different minerals have shown that the dependence of growth or dissolution rates on ionic strength is complex, and that the effect of ionic strength is not independent of the ionic species producing it. Here, we report Atomic Force Microscopy investigations on the kinetics of growth and/or dissolution of a series of carbonate and sulfate minerals (calcite, dolomite and gypsum) aimed at addressing the basic hypothesis that mineral growth and is ultimately governed by the that dissolution effect background electrolytes have on the solvation environment of ions building the crystal, in a similar way to the systematic effects of inorganic ions on precipitation, structure and function of organic macromolecules (i.e., the Hofmeister effect). We find that the dependence of growth or dissolution rates on ionic strength is not independent of the ionic species producing it, and the systematic trends found for the different ions are interpreted in terms of characteristic parameters of background ions. Entropic effects associated with the ordering of solvent molecules induced by constituting cations from the crystal ultimately dictate how electrolytes affect dissolution rates. These results open the possibility of a new understanding of very diverse phenomena in geochemistry and demonstrate the need for the inclusion of this "hydration effect" in the development of predictive models that describe crystal growth and dissolution in complex systems, such as those found in nature. Furthermore, we can hypothesise that ion-assisted dehydration of trace and minor element ions could occur in biological systems, thus affecting their incorporation and providing interesting insights into the origin of anomalies found in systems used as environmental proxies and the socalled "vital effects".