Determination of Reaction Rates at Crystal Surfaces using 4D X-ray Microtomography

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Investigations of mineral surface reactivity have recently challenged the classical approach of determining dissolution rates from mineral powders as crystals often exhibit heterogeneous and/or anisotropic reactivity. However, face-specific measurements are restricted to small areas at the surface, limited depth, and ignore the contribution of the crystal edges to the whole process. Here, we provide a detailed characterization of the dissolution kinetics of single calcite crystals in 3D using X-ray micro-tomography with a resolution below 1 µm [1]. The imaging method allows 3D mapping of the crystal surface topography at different time intervals, providing a description of the time-dependent local dissolution fluxes all over the crystal surface, and the calculation of the crystal dissolution rates. The global rate determined at the crystal scale integrates the contribution of all the crystal features, including the faces, edges and corners, which can be detailed in the local rate distributions. Under acidic conditions, etch pits developped at the $[10\bar{1}4]$ surface dominate initially the surface topography, whereas the long-term evolution of the crystal morphology is dominated by the reactivity of edges and corners, whose contribution to dissolution is on average 1.7 to 3.6 times higher than the crystal faces. These results suggest that dissolution reaction preferentially occurs at the crystal edges and corners, something not considered in most studies of mineral dissolution.

[1] Noiriel C., Oursin M., Saldi G., and Haberthür D. (2019) **Direct determination of dissolution rates at crystal surfaces using 3D X-ray micro-tomography**. ACS Earth and Space Chemistry, vol 3, n°1, 101-108, DOI: 10.1021/acsearthspacechem.8b00143