APPLICATIONS OF TIME-RESOLVED SYNCHROTRON X-RAY DIFFRACTION TO MINERAL-FLUID REACTIONS

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Within the last decade, advances in XRD detector technology have combined with developments in environmental cells to open a new frontier in dynamical crystallography. Image plates, particularly in concert with the highly intense and monochromatic radiation at synchrotron sources, allow for the collection of full-circle diffraction patterns from small quantities of powdered samples in minutes. Flow-through environmental cells, such as the SECReTS (Small Environmental Cell for Real-Time Studies) design of Parise et al. (2000), have made it possible to perform time-resolved X-ray diffraction (TR-XRD) studies of mineral-fluid reactions that emulate those occurring within soils.

We have extended TR-XRD techniques to several areas of importance to the cycling of metals in soils, including cation exchange, stable isotope fractionation, and the nucleation and growth of nanoscale oxyhydroxides. These latter studies have offered new insights into long-held conundrums regarding aqueous precipitation. For example, low-temperature soil systems commonly contain nanophases, such as anatase and akaganéite, that are metastable when particle sizes are macroscopic. By inducing the crystallization of metal chlorides from solutions at moderately high temperatures (100 to 200 ^{o}C), we used TR-XRD to monitor the evolution in crystal structure as a function of crystal size. Additionally, we developed an in-house rate minimization algorithm to calculate kinetic equations from TR-XRD data for the appearance and dissolution of intermediate phases. Combined with molecular dynamical calculations with J. Kubicki (Penn State), these studies have suggested mechanistic pathways for the crystal growth of Fe and Ti oxides, and they indicate that surface defects (particularly at corners and edges) stabilize "metastable" phases at the nanoscale.

Microbes are among the most important participants in the creation and alteration of soils. Because X-rays are lethal to bacteria, capturing bacterial alteration of a soil mineral *in flagrante delicto* seemed beyond the realm of possibility. However, in collaboration with M. Tien and S. Brantley (Penn State), we designed a reaction cell that exploited membrane fractions of the soil bacterium *Shewanella oneidensis*. These fractions contained the enzymatic machinery to reduce and dissolve the Mn oxide birnessite. Freezing the membranes stops their activity without destroying them, and intense X-radiation does not inhibit their function. Consequently, for the first time we succeeded in monitoring mineral bioreduction and biomineralization using TR-XRD techniques. These studies suggest that *in situ* crystallographic analyses of dissolving solids can distinguish among different mechanistic pathways of structural collapse.