Real-time*, in situ* hyperspectral Raman imaging of mineral-fluid reactions

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Information on the mechanism of fluid-driven phase transformations is usually obtained by *ex situ* analyses of the reaction products after quenching the experiments. *Ex situ* experiments, however, deliver mineralogical and textural information only after the sample has been cooled down to RT and dried so that it is often difficult to gain information about the dynamics of the alteration process. To overcome such drawbacks, we have applied *in situ* and real-time hyperspectral Raman spectroscopic imaging to investigate the aqueous fluorination of tooth at 21°C, the corrosion of borosilicate glass at 70°C, and the replacement of celestin by strontianite at 21°C. Using Raman spectroscopy, structural and chemical information can be obtained such as, e.g., interfacial strain, phase composition of binary solid solutions, concentrations of aqueous oxo-anions and their speciation (often pH sensitive) at the solid-fluid boundary. For the *in situ* investigations, we designed and built special fluid cells that allow measuring the formation of the reaction product(s) and the solution with the direction of the laser beam parallel to the direction of the reaction front plane with a lateral resolution in the order of 5 to 10 μm. With this setup, the dynamics of the respective process could be studied. For example, during aqueous corrosion of borosilicate glass at 70°C in 0.1*M* HCl we observed the fast formation of amorphous silica that replaced the glass and initially acted as a protective barrier, slowing down the corrosion process. With increasing reaction time, however, the sudden formation of a crack/gap at the glass-silica interface could be observed that caused an increase of the glass-silica replacement rate. Future experiments will be carried out with solutions that are labeled with ^{18}O and/or D. Since the incorporation of ^{18}O and D in solid and aqueous species will cause a large frequency shift or even new isotopologue bands [1], their concentration in the various phases can be quantified. This will allow, for instance, studying *in situ* the transport of chemical species such as H_2O, OH, and aqueous oxoanions through the growing product phase(s) and possibly the fraction of isotopes between solid and fluid during the process.

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