Short pulse length laser spectroscopy highlights mineral-fluid reactions

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To understand chemical effects like mineral dissolution or recrystallization that occur under the harsh conditions within the earth, the point of zero charge (PZC) can provide insight into atomic-level interactions of fluids with crystal phases and help group minerals into classes. This PZC is the pH value where all the surface oxide sites are just neutralized with protons. A surface nonlinear optical method known as second harmonic generation (SHG) gives a unique way to determine the PZC, which differs even for different crystal faces of the same material. Understanding the PZC and its relationships to chemical reactions help describe the changes in oxide minerals like quartz within the earth's crust, which have been exposed over geologic times to hot liquids at high pressure.

In the SHG experiment, an ultrashort laser pulse is focused on the oxide surface, and a new beam of light at a new wavelength is created by the sample. The intensity of the new beam can be related to the extent of surface charge. Thus the intensity varies as the solution pH above the surface is changed, somewhat akin to an acid/base titration experiment. Our experiments on single crystal rutile (a form of titanium dioxide) show that the SHG signal depends strongly on solution acidity and the resulting electric charge at the oxide surface. Further work contrasting these results with signals from other solid oxides will enable us to probe the differences between materials, and for different crystalline facets of the same material. This ability to probe the surface characteristics of the different individual facets will enable us to understand the differences in surface reactivity (dissolution, precipitation, and binding reactions) that control the chemistry of oxide solids in complex environments.