

## Structure and reactivity at mineral surfaces: Kinetic, microscopic and spectroscopic investigations

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Sorption of dissolved species to mineral surfaces leads to increased concentrations of reactants in a thin layer near the surface with properties which are different from those of the bulk solution. More importantly, strong and specific interactions with surface sites can lead to large changes in the structure and reactivity of adsorbed species.

Surface mediated transformations on solid phases are of crucial importance for metal and nutrient cycling in the environment, and surface catalyzed reactions on synthetic solids with specially designed properties find wide application in industrial processes.

This presentation will focus on the investigation of reactions on the surfaces of aqueous metal(hydr)oxides with kinetic, spectroscopic and microscopic methods. The combination of different methods is crucial, as metal(hydr)oxides can undergo photoinduced and thermal dissolution, with cycling between dissolved species and newly precipitated phases and generation of reactive species in solution and on the surface. Examples of mechanisms deduced from batch experiments and kinetic modeling of thermal and photo-induced reactions will be shown.

A special focus will be on the investigation of surface complexes and reactions with spectroscopic methods and the distinction between inner- and outer-sphere surface complexes. *in situ* Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) is a powerful method to obtain structural information on surface complexes of small organic compounds. However, the interpretation of spectral data is often challenging and the distinction between different coordination modes is not straightforward, for example when strong hydrogen bonding is involved. *in situ* ATR-FTIR studies under UV-irradiation can potentially help to distinguish between surface structures. Inner-sphere complexation of organic ligands on the surface of iron(hydr)oxides appears to be an important factor for the efficient photo-transformation of adsorbed compounds. In contrast, most organic ligands are indiscriminately and completely oxidized and degraded on the surface of rutile and anatase particles under UV-A irradiation.

Progress in various research groups is rapidly advancing our understanding of reactions on aqueous surfaces.

## The CO<sub>2</sub> sink potential of the Indo-Tibetan collision zone

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The fluvial geochemical data of major rivers draining the Himalayas and the Tibetan Plateau are compiled from literature and supplemented with data from the author's group to explore the spatial variability in the major element and strontium isotopic compositions and in the silicate weathering rates and concomitant drawdown of atmospheric CO<sub>2</sub>. The results indicate that carbonate weathering dominates the major element compositions of these rivers, and when the silicate contributions are carefully separated, these are highest in the rivers draining the Himalayan front. The eastern Tibetan Plateau rivers are not very radiogenic in their <sup>87</sup>Sr/<sup>86</sup>Sr ratios, their silicate contributions are low, and the CO<sub>2</sub> consumption rates are on the order of  $\sim 100 \times 10^3 \text{ mol} \cdot \text{km}^{-2} \cdot \text{y}^{-1}$ . The two syntaxes of the Himalayas, the Indus and the Brahmaputra, have variable <sup>87</sup>Sr/<sup>86</sup>Sr, the silicate contributions are higher than the eastern Tibetan Plateau rivers, but the total CO<sub>2</sub> uptake rates are low because of lower runoff in the headwaters. The Ganges tributaries draining the Himalayan front can be extremely radiogenic, have higher median silicate contributions than the eastern Tibetan Plateau rivers, and the CO<sub>2</sub> consumption rates are about twice as high. Exposure of silicate lithologies with radiogenic Sr and high runoff seems to be responsible. However, even the high CO<sub>2</sub> consumption rates of the Himalayan front are not anomalous globally, considering the uncertainties with spot sampling and calculation of silicate fractions. The rate of CO<sub>2</sub> draw-down by silicate weathering in the Himalayan front rivers are on the same order of magnitude as other orogenic rivers of the world, although fluxes of <sup>87</sup>Sr are higher. The <sup>87</sup>Sr/<sup>86</sup>Sr ratios do not necessarily correlate with the relative input from silicate weathering, indicating that <sup>87</sup>Sr/<sup>86</sup>Sr cannot be used as a general proxy for silicate weathering. Sources of uncertainty in the analyses presented here and areas of future development will be suggested.