

## Tracking interfacial acidities, charge density, potential, and energy density at carboxylic acid-functionalized silica/water interfaces using second harmonic and sum frequency generation

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The protonation state of surface-bound carboxylic acid functional groups at mineral-water interfaces is critical for understanding and predicting how biopolymers control heterogeneous processes in the environment. Using the nonlinear optical laser spectroscopy broad-band vibrational sum frequency generation (SFG), we have characterized custom-designed carboxylic acid-functionalized siloxanes on glass. Subsequent second harmonic generation (SHG)  $\chi(3)[1]$  measurements yielded the full thermodynamic state information for silica-water interfaces functionalized with the same carboxylic acid-functionalized silanes between pH 2 and 12. Surprisingly, the monoprotic, terminal carboxylic acid results in two acid-base equilibria with  $pK_a$  values of  $5.6 \pm 0.2$  and  $9 \pm 1$ , the latter being consistent with lateral hydrogen-bonding among adjacent surface-bound carboxylic acid groups as proposed in a recent ATR-FTIR study. [2] At pH 7, we find that the carboxylic acid-functionalized silica-water interface is  $>95\%$  neutral. Tracking the surface charge density directly at the liquid-solid interface as a function of pH results in a highly sensitive determination of the interfacial potential change, namely between 0.01 and 50 mV, and the interfacial energy density change, namely between  $10^{-10}$  and  $10^{-3}$  J  $m^{-2}$ , as the pH increases from 2 to 12. Our experimental approach is highly flexible through structural and chemical control of the surface-bound silanes and is applicable for studying more complex organic adlayers.

### References

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## NMR spectroscopic techniques for the study of organic ligand interaction with calcite surfaces

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Calcite is an important reactive component of many soil and aquatic environments. Dissolved organic ligands are well-known to interact strongly with the calcite surface, altering precipitation/dissolution rates, crystal morphology, and possibly the ability of calcite to sequester metal contaminants. We have recently shown that under constant-addition conditions, calcite grown in the presence of organic ligands can incorporate significant concentrations as a coprecipitate, including citrate ( $>1$  wt. percent) and lesser amounts of simple amino acids (glutamate and aspartate). On the other hand, phthalate was not detectably incorporated, although previous work has shown that it sorbs strongly to the calcite surface[1]. Using double-resonance NMR methods, such as cross-polarization and heteronuclear correlation, with selective isotopic labels enabled us to firmly establish unit-cell scale spatial proximity between included citrate and carbonate in the calcite host. We are extending these methods to study interactions of dissolved organics with the calcite surface, which is likely an important factor in coprecipitation.

Experiments with oxalate sorption on calcite illustrate these approaches. We reacted pre-equilibrated (pH 8.3) calcite suspensions ( $10 \text{ m}^2 \text{ g}^{-1}$  specific surface area;  $0.5 \text{ g L}^{-1}$ ) with  $^{13}\text{C}$ -labeled oxalate. Suspensions containing less than one-half monolayer of oxalate were slightly supersaturated and gave  $^{13}\text{C}\{^1\text{H}\}$  CP-MAS NMR peaks for a crystalline surface precipitate when reacted for 24 h, but not for short reaction times (20 min.). Comparison of the NMR results with crystallographic data indicate that the surface precipitate is Ca(II)-oxalate tri-hydrate, rather than whewellite, which is less soluble. Very slow injection of oxalate (55  $\mu\text{moles per L}$  of suspension, over 16 h) to yield ca. 6.5 oxalate  $\text{nm}^{-2}$  does not give a precipitate. However, no  $^{13}\text{C}\{^1\text{H}\}$  CP-MAS signal was detected from the sorbed oxalate, suggesting that it remains in a surface layer in which the proton bearing species are mobile. We also observe that calcite typically contains enough rigid H-bearing defects to yield a carbonate  $^{13}\text{C}\{^1\text{H}\}$  CP-MAS signal.

### Reference

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