Protolytic equilibria at 'inert' — electrolyte interfaces

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In major physical chemistry journals, the question whether hydroxide ions interact with inert surfaces is currently a hot issue. Macroscopic measurements suggest that such interfaces have isoelectric points of about 2 to 4. This is explained by a strong affinity of hydroxide ions for the interfacial water present at these surfaces. Consequently it is suggested that hydroxide ions can be found at these interfaces and are strongly preferred say at pH 5 compared to protons although the hydroxide ion concentration in bulk solution is 4 orders of magnitude lower than the proton concentration. Molecular Dynamic simulations would predict that protons have a stronger affinity to such surfaces. Also experimental data with proton and hydroxide, at concentrations above millimolar, clearly confirms the prediction of the Molecular Dynamics simulations.

The contradiction of the Molecular Dynamics simulations to the experimental work at lower proton and hydroxide concentrations remains and is probably difficult to resolve and thus the origin of the unexpected pH-dependent behaviour of a wide variety of surfaces that bear no surface functional groups is not clear. Whatever the origin of the pH dependent charging of these inert interfaces might be, it should be important to consider it in mineral surface – electrolyte studies of geochemical interest. Thus for example the isoelectric points of many alumina single crystal samples have been reported to be rather low (actually around pH 4) and they presently remain largely unexplained. More interestingly, available isoelectric points are within or close to the range reported for the inert interfaces. This would indicate that the work on the alumina single crystals might involve reactions that have so far not been considered in the geochemical literature.

We report some experimental results on a range of inert surfaces to show how they all agree with each other and relate them to data on alumina samples. Our data confirm the previously reported experimental data at the millimolar scale. One possible explanation for the continuing discrepancy might be that the extrapolation of results for the above millimolar to the below millimolar concentration range is not appropriate. In particular we show that in some of the systems, we see clear changes in patterns like the salt dependency of zeta-potential at about millimolar concentrations.

Microbial mediated carbon-sulphur-metal cycling in fluidized mud ecosystem off French Guiana

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The fluidized mud ecosystem off the French Guiana coast is a unique and globally important sedimentary environment. Due to rigorous physical reworking and reoxidation, anoxic and iron-rich sedimentary deposits remain nonsulphidic, even though C_{org} degradation rates and pore water sulphate (~ 20-28 mM) are relatively high. Benthic microbial communities respire nitrate and manganese oxides in a matter of minutes, but the bulk of organic matter is remineralized through ferric and sulphate respiration. High rates of sulphate and sulphur reduction (~10 – 20 nmol cm^{-3} day^{-1} and 5- 60 nmol cm^{-3} day^{-1}) and high phylogenetic diversity of *dsr* gene libraries, as well as the *dsr* mRNA/DNA ratio further confirms the role of a sulphate-and sulphur-reducing microbial guild in biogeochemical cycling. The presence of transient CRS and S^0 hints on alternative pathways of the oxidative sulphur transformation. High rates of dark CO_2 fixation and fast regeneration of sulphate (up to 80 nmol cm^{-3} day^{-1}) together with an abundance of ferric hydroxide implies complete reoxidation of solid phase reduced sulphur by yet an unknown microbial chemolithoautotrophic metabolism, which couples metal, sulphur and carbon cycles. Stable isotope probing with ^{13}C bicarbonate revealed a complex chemolithoautotrophic community dominated by sulphur bacteria.