Specific ion effects on the wettability of sandstone particle

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Specific ion effects control most reactions in nature. Adhesion, between organic molecules and mineral surfaces in aqueous solution, depends not only on the behaviour of the molecule and substrate but also on the specific set of dissolved ions. The complex behaviour between ions, water and organic molecules is reflected in various versions of what is known as the Hofmeister series where ion activity depends on size, charge and electron configuration. There is a wealth of experimental data on how organic molecules interact with sandstone, from oil industry work and from environmental studies of soil, sediments and aquifers but the picture of molecular scale interactions is not clear.

By using force spectroscopy and chemical mapping with AFM (atomic force microscopy) we can observe contact behaviour with a variety of molecules on real sand grains, while solution composition is changed. By using tips functionalised to behave as pure alkane (CH3), we have probed sand grains, and examined adhesion in NaCl solutions, with ionic strength close to that of seawater. Changing composition of the solution by adding small amounts (12 mM) of specific divalent ions (Ca2+, Mg2+), corresponding to about 2% relative to the number of Na+ ions, caused a dramatic adhesion increase between the alkane tips and the surface - by as much as 50%. Increased adhesion is a clear response to higher divalent ion density at the surface. However, in 0.5 M NaCl, the electrical double layer collapses to much less than the thickness of a single water molecule so the understanding of the data can only be founded in mechanisms involving ions and their behaviour specifically, at the molecular scale.

The biogeochemical ice core record: A new perspective on nitrate

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A major motivation in studying ice core nitrate is to reconstruct the atmospheric loading of its precursor, nitrogen oxides (NO_x). NO_x concentrations in the atmosphere play a significant role in determining tropospheric chemical composition and oxidizing capacity. Today, NO_x emissions are primarily the result of fossil fuel burning, with important contributions from biomass burning, lightning and biogenic processes in soils. The result of these emissions is deposition of nitric acid (i.e., nitrate), a component of acidic precipitation and a bioavailable nutrient. Recent studies utilizing the isotopic composition of nitrate in ice cores offer the possibility to trace the sources and chemical processes that contribute to nitrate deposition over time.

Studies of the isotopic composition of nitrate in surface snow and snowpits at Summit, Greenland reveal an atmospheric nitrate signal that is well preserved in recent snow. A seasonally resolved ice core record of the isotopic composition of nitrate, together with highly resolved (> 22 samples yr^{-1}) elemental and chemical tracers are used to investigate changes in NO_x sources and chemistry since 1760 C.E. A marked negative trend in $\delta^{15}N$ since industrialization (pre-industrial-era average of 12.0‰ vs. air N_2 to a modern-era average of 3.6‰) parallels a nearly three-fold increase in nitrate concentration, as well as pronounced increases in tracers such as excesss lead and non-sea-salt sulfur. This, along with independent estimates of oil burning and transport studies, indicate that North American oil combustion is the primary driver of the negative trend in $\delta^{15}N$ of nitrate. The pre-industrial record of nitrate and tracers such as amonium and black carbon ties the high, positive $\delta^{15}N$ values to biomass burning. Overall, this record provides constraints for $\delta^{15}N$-NO_x source signatures, which are poorly characterized. A quantitative tracer of the pre-industrial sources and chemistry of NO_x would allow for detailing connections between the atmosphere (lightning, chemistry, transport), the biosphere (biomass burning, soils), and climate.

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