

Hydrogen bonding and molecular ordering of water at mineral-solution interfaces

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Aqueous interfaces play crucial roles in many geochemical systems, and the atomic scale details of the mineral substrate structure and composition are essential to understanding and predicting their chemical and physical properties. Here we compare the results of molecular dynamics (MD) simulations for the atomic density profiles, atomic surface density distributions, hydrogen bonding configurations, and orientational ordering of H₂O molecules at interfaces with several minerals, which may be considered typical for many hydrophobic and hydrophilic inorganic oxide and hydroxide surfaces [1, 2]. The atomic density profiles of water show substantial layering at all surfaces, with the details significantly different and strongly dependent on the composition and crystal structure of the mineral substrate. Relative to bulk water, the average density of water at the hydrophobic talc (001) surface is reduced by about 9-15% within 6-10 Å from the interface, which is equivalent to a 0.8Å-thick depletion layer compared to the similar but hydrophilic (001) surface of muscovite.

At the hydroxide surfaces, both cations and anions are effectively stabilized in their adsorbed state via the development of an integrated hydrogen-bonding network among the ions, H₂O molecules, and surface OH-groups, even if the substrate does not charged. For organic anions, such as amino acids, the deprotonated carboxylate groups are the primary strong H-bond acceptors, whereas the deprotonated amine groups serve as only weak additional H-bond acceptors from the surface. The organic species preferably accept H-bonds from H₂O molecules rather than from surface OH-groups due to structural restrictions on the development of tetrahedrally coordinated H-bonding environments for the carboxylate groups at the surface.

[1] Wang, J. *et al.* (2009) *J. Phys. Chem. C*, **113**, 11077.

[2] Kalinichev, A.G. *et al.* (2010) *Phil. Mag.* **90**, 2475.

Paleoproductivity controls on microbial abundance in marine subsurface sediments

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IODP Expeditions 320 and 321 (Paleocene-Eocene Age Transect, PEAT) recovered a continuous Cenozoic record of the equatorial Pacific by drilling at the paleopositions of the Equator at successive crustal ages on the Pacific plate. The drilled sites passed the high productivity area of the equatorial upwelling at different times.

Microbial cell abundance in several PEAT cores strongly deviates from the expected steady decrease with depth. We compared cell count profiles with several sedimentological, physical and geochemical parameters. Several of the observed excursions in cell abundance correlate with distinct sedimentological and geochemical horizons, which are ultimately caused by changes in paleoproductivity.

Colour changes in the sediment indicate changes in redox conditions from more oxidized to reducing, they also mark the time intervals during which the site was in the high productivity zone of the equatorial upwelling. Also, distinct turning points in the cell count profiles correlate well with redox fronts, being indicated by peaks in dissolved porewater constituents like Fe²⁺ and Mn²⁺.

The new PEAT data allow an insight into how past changes in productivity are influencing current patterns of microbial abundance and activity.