

***In situ* FTIR study of protonation reactions at the bacteria-water interface**

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Bacterial surfaces are highly reactive and display a strong affinity for metal cations, including heavy metal contaminants and radionuclides. The reactivity of bacterial surfaces arises directly from the presence of proton active organic functional groups on the bacterial cell wall. However, recent experimental studies based on bulk potentiometric titration experiments have reported contradictory results on the types of reactive functional groups on the bacterial surface for identical bacterial species. In order to resolve this disagreement, we have applied a synchrotron-based Fourier Transform Infrared (FTIR) technique to identify and characterize bacterial surface functional groups *in situ* and *in vivo*.

FTIR experiments were performed with the filamentous cyanobacteria *Calothrix sp.*, which form trichomes up to several 100 μm long and are surrounded by a thick sheath (up to 5 μm in thickness). In order to identify the proton active surface sites, IR spectra of individual intact cells and isolated sheath material were collected *in situ* at solution pH values from 3.3 to 9.6. The experiments were carried with a Nic-Plan IR microscope in transmission mode using a Spectra Tech flow through fluid cell with two IR transparent windows (BaF₂ and ZnSe) separated by a Mylar spacer with a path-length of 6 μm . A 0.01 M NaCl electrolyte solution was flowed through the fluid cell at a constant flow rate, and the pH of the input solution was adjusted to the desired pH using 0.1 M HCl and 0.1 M NaOH.

The IR bands of intact *Calothrix* cells display a combination of protein, lipid and carbohydrate functional group peaks. IR spectra from isolated sheaths lack the distinct protein peaks and are dominantly composed of polysaccharide bands in the region between 1200-900 cm^{-1} . IR measurements of intact cells show a change in peak intensity at $\sim 1400 \text{ cm}^{-1}$ corresponding to the symmetric vibrational stretching of deprotonated carboxylate functional groups. Identical IR spectra taken with isolated sheaths did not show a change in peak intensity at 1400 cm^{-1} suggesting that the reactive carboxyl functional groups are concentrated on the cell wall and not the extracellular polysaccharides. However, a distinct change in peak intensity was detected for the isolated sheaths at 1238 cm^{-1} corresponding to P=O asymmetric stretching of $>\text{PO}_2^-$ phosphodiester functional groups, indicating the presence of proton active phosphoryl sites. This study demonstrates that *in situ* FTIR spectroscopy can be used to identify the reactive functional groups on bacterial surfaces and to investigate the protonation reactions at the bacteria-water interface.

Fluid geochemistry of mud volcanoes at the accretionary prism in southern Taiwan

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Worldwide, most diapiric mud volcanoes are situated at convergence plate-boundaries and are closely related to accretionary wedges. Taiwan, located at the collision belt between the Eurasia plate and the Philippine Sea plate, possesses a typical accretionary wedge and has developed numerous mud volcanoes both on-land and offshore. The gases from most mud volcanoes in Taiwan are mainly CH₄ (>90%) with minor N₂ and CO₂ content. Available helium isotopic data demonstrate the gases are dominated by crustal components, although some samples showed mantle-derived gas signatures. To better understand the evolution of mud volcanoes at the developing accretionary prism, fluid compositions from various mud volcanoes in different tectonic environments of southern Taiwan were compared.

Fluid samples of representative mud volcanoes from three tectonic settings in southern Taiwan were collected for geochemical analysis. The principal component method was utilized to evaluate potential factors affecting chemical variations. Preliminary results show that two factors explain 78% and 16%, respectively, of the observed chemical variation of the fluid samples. Factor F1 controls most of Cl⁻, Na⁺, K⁺, Mg²⁺, Ca²⁺ variations in the fluids and is considered to be mainly the contribution of marine sedimentary pore water. The F2 factor affects mainly SO₄²⁻ concentrations, which may be a result of meteoric water addition, although the amount is generally small.

Mud volcanoes in southern Taiwan can be divided into two categories based on their fluid geochemistry. The mud-volcano fluids from the foreland basin show more F1 contribution than those from the hinterlands. This suggests that fluids from the hinterlands may have undergone a higher grade of diagenesis and hence exhibit more signature resulting from water-rock reaction and dehydration of clay minerals. Another alternative is that deeper thrusts may exist in the hinterland, which consequently could provide a pathway for deep dehydration water addition.