

Speciation of trivalent metal ions at the silica/water interface studied by second harmonic generation

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The nonlinear optical technique of second harmonic generation (SHG) is used to study the interactions of Al (III), Y (III), La (III), and Gd (III) with the fused silica/water interface. Specifically, the Eisenthal $\chi^{(3)}$ technique [1] is employed in order to quantify several thermodynamic binding parameters of these ions as a function of background electrolyte concentration. Using this highly surface specific technique, we are able to quantify binding constants, adsorption free energies, absolute number densities, and interfacial charge densities in real-time and without the use of labels. We also examine the relationship between the measured adsorption free energies and the electric double layer interfacial potential at each electrolyte concentration to elucidate the charge state and possible binding pathways for each ion at the fused silica surface.

Our results show that the binding of each trivalent ion is fully reversible under the experimental conditions employed in this study. Adsorption isotherms are measured under dynamic flow conditions and fit using the Triple Layer model. We employ an analysis that takes advantage of the additive adsorption free energy expression in which the observed free energy is modeled as a sum of the electrostatic free energy and the intrinsic chemical free energy [2]. From this analysis, we find that the Al (III) ion binds to the fused silica surface as a fully hydrated trivalent species in a bidentate geometry. In contrast, the Y (III), La (III), and Gd (III) ions are each shown to adsorb to the silica surface in a reduced valence state. Despite identical oxidation state, the extent and mode of binding varies between each ion. These SHG studies provide valuable data that can be used to predict the transport these metal ions are throughout the environment.

[1] Salafsky & Eisenthal (2000) *J. Phys. Chem. B* **104**, 7752–7755. [2] Langmuir, D. *Aqueous Environmental Geochemistry*, Prentice Hall, Upper Saddle River, NJ, 1997.

Hydrate destabilization and methane release events during last glacial episode in Bay of Bengal

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We report here for first time episodic methane expulsion events in the Krishna-Godavari basin, Bay of Bengal during the marine isotope stage 4 (MIS-4) and at the transition of MIS-4 and MIS-5. We have observed sharp negative carbon isotope excursions in the isotope profiles of planktonic (*G. ruber*) and benthic (*Uvigerina sp.*) foraminifera in a core MD161-8, recovered on board *Marion Dufresne* as part of our gas hydrate exploration program in 2007. Depleted carbon isotope excursions in both benthic (B₁, B₂ and B₃) and planktonic (P₄, P₅ and P₆) foraminifera suggest that the methane expulsion events not only altered the carbon stable isotopic composition of the bicarbonate pool near the sediment waters interface, but also that of the shallow water column. A significant fraction of methane gets oxidized to HCO₃⁻ via anaerobic methane oxidation (AMO) at or below the sediment water interface. Depletion in carbon stable isotope ratios of the dissolved inorganic carbonate (DIC) pool depends on the carbon stable isotope ratios of methane advecting from deeper layers. Reported¹ $\delta^{13}\text{C}_{\text{CH}_4}$ values (-75 to -85 ‰ VPDB) and C1/C2+C3 ratios (1110 to 3354) suggest presence of biogenic hydrocarbon gases within the methanogenic zone at the site MD161-8. Carbon stable isotope ratios of infaunal benthic foraminifera like *Uvigerina sp.* may get significantly influenced by incorporation of isotopically depleted carbon as HCO₃⁻ in the calcitic shell during growth and considered as a potential proxy for paleo-methane seepage. On the other hand, the depleted carbon isotope excursions recorded for the corresponding planktonic foraminifera, *G. ruber*, suggests that a part of the expelled methane reached the upper mixed layer (0-25m) where aerobic methanotrophy resulted in the depletion of carbon stable isotope ratios of the DIC reservoir.

We attribute the methane emission events to destabilization of the base of gas hydrate stability zone (BGHSZ) due to shale tectonics induced focused fluid flow. Fluid released from the over-pressured mud, possibly played important role in creating fractures as well as advection of the gases in K-G basin.

[1] Mazumdar *et al.* (2009) *G-cubed* **10**, 1–15.