

## Correlating Bioavailability with Metal Toxicity using a Suite of Analytical Techniques

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To better understand metal cycling in contaminated anaerobic sediments, our research focuses on the complex cause and effect relationships between metals and microbes. We are interested in how microbes respond to metal stress on a molecular level and consequently how microbes control metal speciation. Recently published XAFS results show that various microbial species coordinate zinc differently (Webb et al., 2001), indicating unique coping mechanisms. The research presented here specifically addresses how metal speciation affects bioavailability and ultimately, toxicity.

### Experiments

Organisms X and D (isolated under metal pressure from zinc-rich Lake DePue sediments), their nearest relatives, *C. xylanolyticum* and *C. magnum*, and *E. coli* were exposed to increasing amounts of zinc in a minimally complexing media (containing small amount of yeast extract). Metabolism and growth were monitored by following changes in absorbance, protein production and glucose consumption. Total, dissolved, and electrochemically labile zinc levels were measured at time zero and time final to confirm that the organisms were being exposed to significant amounts of zinc.

Additional metal tolerance experiments will use a lower complexing media (no yeast extract) with other metal-tolerant organisms and with different metals such as Cd, Pb and Hg. We are also correlating the response of a whole-cell metal biosensor with the electrochemically labile fraction to establish voltammetry as a surrogate for bioavailability.

### Results

Metabolism and growth drop off at elevated levels of zinc ranging from 75-100  $\mu$ M, lower than the mM ranges previously reported for zinc-tolerant microorganisms. (Nies, 1999) The oligotrophic nature of the media may decrease the organisms' ability to tolerate higher levels of zinc but more accurately reflects what they would see in their natural environment.

### References

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## Mineral dehydration at Eastern Mediterranean mud volcanoes: Evidence from stable isotope analyses

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The Eastern Mediterranean Ridge is a pronounced morphological feature representing the accretionary wedge related to the subduction of the African plate underneath the Eurasian plate. Numerous active mud volcanoes are situated along this ridge as seafloor manifestations of fluid seepage.

Like other seep structures in the forearc regions of subduction zones, these mud volcanoes can be considered as windows to the fluid source and therefore provide valuable insight to processes occurring within the basal sediments of subduction zones. Particularly the stable isotopic signature of the fluid holds information on the fluid source and fluid-rock interactions.

During ODP Leg 160, two mud volcanoes of the Olimpi Mud Volcano field south of Crete were sampled by drilling transects of four bore holes each. Pore waters were retrieved from the sediments and analysed for major solutes as well as for their stable isotopic composition. A striking peculiarity of the pore water chemistry are largely varying Cl concentrations throughout the mud domes. Whereas several cores show an imprint of Messinian evaporites underlying the upper sediment column (up to 5.4 M Cl), there is evidence for a strongly Cl-depleted fluid at two crest sites (down to 60 mM Cl).

Potential processes causing such Cl-depletions in accretionary prism fluids are mainly gas hydrate dissolution, meteoric water input, and dehydration of clay minerals. With  $\delta^{18}\text{O}$  values of up to +9 ‰ and  $\delta\text{D}$  as low as -22 ‰, gas hydrate dissolution and meteoric water input is ruled out and clay mineral dehydration is shown to be the most likely reaction causing a dilution of the pore fluids.

Therefore, it can be concluded that compaction related dewatering is succeeded by continuously ongoing smectite-illite transition, being the dominant low temperature alteration reaction. The application of geothermometers using alkaline (earth) concentrations of the fluids results in temperatures of 50-150°C, which is in perfect agreement with the temperature range of this transition (60-160°C).

However, to achieve the observed dilution of chloride, a rather large amount of water has to be released from the surrounding sediments. This can be explained by a large catchment area along the décollement that fuels the seepage at mud volcanoes. Deep-rooted faults within the compacted sediment are serving as fluid conduits distinctively separating fluids with different origin.