

## Microbial Activity in Deeply Buried Marine Sediments

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Ocean Drilling Program Leg 201 was the first ocean drilling expedition dedicated to the study of life deep beneath the seafloor. Its sites were selected to represent the general range of subsurface environments that exists in marine sediments throughout most of the world's oceans. In water depths as great as 5300 meters and as shallow as 150 meters, the expedition drilled up to 420 meters into oceanic sediments and the underlying rocky crust. The sediments ranged in temperature from 1°C to 25°C and in age from 0 to almost 40 million years.

Leg 201 scientists found evidence of active microbial respiration throughout the sediment column at every site. Subseafloor respiration is supported at all sites by the diffusion of sulfate down from the overlying ocean, as well as by the dissolution of iron- and manganese-bearing minerals. At the open Pacific sites, respiration deep beneath the seafloor is also supported by the transport of sulfate, nitrate and oxygen from water circulating through the underlying basaltic crust. At both the open Pacific sites and the Peru margin sites, electron-accepting pathways often described as competitive consistently co-occur beneath the seafloor. Iron reduction and manganese reduction often co-occur with sulfate reduction and methanogenesis. Sulfate reduction and methanogenesis co-occur everywhere.

The recovered sediments and fluids will be studied further to document the controls on rates of subsurface activity, the influence of past oceanographic conditions on current activity in deeply buried sediments, and the effects of subseafloor biogeochemical processes on Earth's surface world.

## Surface reactivity of clay nanoparticles as studied by polarized EXAFS

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Sorption of heavy metal ions on mineral surfaces strongly affects the fate and mobility of heavy metals and radionuclides in the geosphere. Therefore an atomic/molecular level understanding on the surface reactivity of clay nanoparticles with respect to metal uptake is of fundamental importance for maintaining environmental quality and for assessing the long-term stability of waste repositories. On clay particles several uptake modes of metal ions have been proposed: Sorption on edge sites, sorption on interlayer sites and the formation of lamellar nucleation phases such as neoformed layer silicates and mixed layered double hydroxides.

In this study powder EXAFS and polarized EXAFS (P-EXAFS) were used to investigate the uptake mechanisms of Ni(II) onto montmorillonite. Montmorillonite is an abundant dioctahedral smectitic clay mineral responsible for the retention of metals in the geosphere. At elevated pH and Ni concentrations the uptake of Ni onto montmorillonite resulted in the formation of a Ni-phylosilicate-like phase. These neoformed phylosilicates were oriented with respect to montmorillonite layers. The resulting sequestration of sorbed metals in sparingly soluble phylosilicate structure may durably decrease their migration in the geosphere.

At near neutral pH and low Ni concentrations P-EXAFS measurements revealed the formation of Ni inner-sphere mononuclear surface complexes located at the edges of montmorillonite platelets. Heavy metals binding to edge sites is therefore a possible uptake mechanism for dioctahedral smectites. Over a time period of one year no change in the uptake mechanism under the employed reaction conditions could be observed. Specifically the diffusion of Ni atoms into the montmorillonite structure could be excluded. It was observed that the structural order of the surface complexes was increasing with time. This finding could explain why even at trace element concentrations the observed release rate of Ni sorbed onto montmorillonite decreased with prolonged reaction time. The observed attachment of metal ions specifically bond to clay mineral surfaces can therefore severely reduce their bioavailability and mobility in soil and water environments.