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Environmentally important nanoparticles from a massive acid mine drainage site

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Nanoparticles of ferrihydrite and a vernadite-like mineral (Fe and Mn oxide hydrates, respectively), in samples collected from the riverbed and floodplains of the river draining the largest mining contaminated site in the United States (the Clark Fork River Superfund Complex), have been discovered and studied with transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) analysis. These poorly crystalline nanophases are environmentally critical in this system because they readily and consistently take up contaminant heavy metals (As, Cu, Pb, and/or Zn) in the system. In several field specimens, the ferrihydrite and vernadite-like minerals are intimately mixed on the nanoscale, but they can also occur separately. It is suggested that the vernadite-like mineral, found separately, is produced biogenically by Mn oxidizing bacteria, while the same phase associated with ferrihydrite is produced abiotically via the heterogeneous oxidation of $Mn^{2+}_{(aq)}$ starting on ferrihydrite surfaces. Laboratory experiments show that the rate of this important abiotic heterogeneous Mn oxidation reaction is greatly increased in the presence of smaller and smaller nanoparticles of iron oxides. This is probably due to a change in the geometric and electronic structure of surface atoms as the particle size changes through the nanoregime.

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Gas hydrate formation and dissociation in the environmental scanning electron microscope

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Both natural and laboratory-synthesized gas hydrate were studied under methane and nitrogen gas atmospheres in an environmental scanning electron microscope (ESEM) equipped with a cryostage, video recorder, and mass spectrometer. Hydrate and water ice formation and dissociation were imaged while simultaneously collecting gas samples for analysis. Massive gas hydrate crystals were grown epitaxially under a methane atmosphere in the ESEM as shown in Figure 1, whereas only loosely agglomerated water ice crystallites were observed under a N_2 gas atmosphere. The peak rate of gas hydrate dissociation in natural sediment samples occurred at 217 ± 2K; however, the peak rate was at 236 K for artificial methane hydrate synthesized from crushed ice. The differences might be attributable to differences in hydrate crystal size and sample compaction that constrain the ability of free gas to escape from the interior of a highly compacted pure ice/hydrate core; however, we cannot rule out as yet unidentified differences in the physicochemical properties of natural versus synthetic gas hydrates as another potential cause.

The gas hydrate condensation reactions observed in the ESEM occur under P-T conditions that are apparently well above equilibrium P-T conditions determined with bulk gas hydrate samples. The availability of mobile orientational defects is known to strongly impact clathrate hydrate formation at T > 140 K. Formation of these defects from interaction of the electron beam with the clathrate/ice surface might enhance clathrate hydrate formation. The observed growth of various clathrate hydrates under cryogenic conditions at low pressure has important implications for predicting the presence of clathrates in extraterrestrial environments.

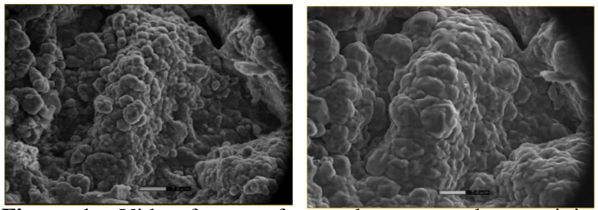

Figure 1. Video frames of natural core sample containing methane hydrate captured during ESEM analysis under a methane gas atmosphere. Image on the left is at 203 K and image on the right was taken at 213 K.