

Contrasting mineral authigenesis and methane activities in deep-sea sediments offshore SW Taiwan

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Deep-sea sediment cores, MD052911 and MD052914 collected from the gas-hydrate potential area offshore SW Taiwan were studied by SEM, XRD, and elemental analysis. A model was proposed to elucidate the occurrence of contrasting mineral authigenesis at the two sites with implications for two distinct styles of methane activities.

It is proposed that two past periods of methane venting in the vicinity of the MD052911 core site gave rise to the formation of ferric smectite pellets in the upper and lower sections of the sediment core that showed evidence of rapid sulfate reduction in porewaters [1], with Fe^{2+} - and methane-rich fluids brought to positions slightly above the seawater-sediment interface where ionic exchange and oxidation occurred. Authigenesis of pyrite framboids was probably contemporaneous with or immediately followed the sedimentation of ferric smectite pellets and detrital materials. The same sections were also characterized by prominent pyrite overgrowths, limited carbonate-nodule formation, and neof ormation of filamentous pyrite within ferric smectite pellets, involving a later methane seepage event, as evidenced by a shallow sulfate-methane interface and high AVS concentrations in the upper section [1][2]. The MD052911 middle section probably represents a period of rapid sedimentation and is presently under the influence of a reducing fluid. It has restricted neof ormation of vivianite crystal clusters, relatively high reactive iron [3] and low pyrite contents, and high Fe^{2+} concentrations in porewaters [4], with no features similar to those described above.

The MD052914 core represents a fossil site of methane seepage and is believed to be affected by methane seepage to the least extent in the region at present day. It is characterized by intense framboidal pyrite formation and overgrowth associated with low detrital magnetite concentrations [5] in the depth interval of 19-22 m, with no other authigenic minerals in other depth intervals. In contrast, the MD052911 location can be portrayed as a site that has been actively and repeatedly affected by methane activities, with an unusual occurrence of complex mineral authigenesis.

[1] Yang (2005) *Cent. Geol. Surv. Rept.* **94-26-F**. [2] Lin (2005) **94-26-E**. [3] Horng (2005) **94-26-G**. [4] You (2005) **94-26-D**. [5] Horng (2006) **95-26-G**.

Stabilization of nanoparticulate HgS and ZnS by thiols and humic substances during metal-sulfide precipitation

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Hg-sulfide, Zn-sulfide, and other metal-sulfide nanoparticles (or colloids) are known to persist both in oxic and anoxic aquatic environments. These nanoparticles potentially increase the mobility of the pollutant metals and control their bioavailability. Despite the importance of nanoparticulate metal-sulfides, the processes that govern their stability, morphology and surface chemistry in natural waters remain poorly understood. The objective of this study was to evaluate the role of dissolved natural organic matter (NOM) for stabilizing nanoparticulate metal-sulfides by coating nucleated particles and preventing aggregation. We monitored the growth of HgS and ZnS particles that were precipitating in solutions containing dissolved humic acid. Growth of metal-sulfide particles was also tested in the presence of low-molecular weight organic acids that are prevalent in soil and sediment porewater. Particle formation and size was monitored over time by dynamic light scattering. Observed growth rates of HgS and ZnS aggregates varied by orders of magnitude, depending on the type and concentration of organic ligand in solution. Humic acid decreased observed growth rates by at least one to two orders of magnitude. Furthermore, in the precipitation studies with low-molecular weight ligands, stabilization of nanoparticles was observed with the thiol-containing ligands (cysteine, glutathione, and mercaptoacetate). In contrast, HgS and ZnS particle growth rates were generally not affected by the oxygen- and amine-containing ligands: oxalate, serine and glycolate. The particles were further characterized for elemental composition by X-ray photoelectron spectroscopy. The results indicated that the molar ratio of metal to sulfur in the particles was approximately 1:1, suggesting that HgS and ZnS were precipitating in the mixtures. These studies highlight the importance of NOM for stabilizing naturally-occurring and anthropogenic metal-sulfide nanoparticles in the aquatic environment.