

The reduction of Hg(II) and complexation of Hg(0) with natural dissolved organic matter in aquatic environments

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The mercuric ion, Hg²⁺, has been generally considered as the species that form complexes with natural dissolved organic matter (DOM) such as humic acid (HA), a key component that affects mercury chemical and biological transformation and cycling in aquatic environments. Although the dissolved elemental mercury, Hg (0), is also widely observed in sediments and water, complexation reactions between Hg (0) and DOM have been largely overlooked and their effect on the biotic or abiotic transformation of mercury has never been examined. We report that DOM, especially the reduced HA, can strongly complex with dissolved Hg (0). The estimated binding capacity is about 3.5 $\mu\text{mol Hg (0)/g HA}$ and a partitioning coefficient is greater than 10⁶ mL/g. However, the complexation capability is found to vary with different DOM isolates and diminishes when DOM becomes oxidized. Humic acids are also capable of reducing the ionic Hg²⁺ to Hg (0) under anaerobic conditions: the purgeable Hg (0) is found to increase with increasing HA initially, maximize at the addition of $\sim 50 \mu\text{mol Hg (II)/g HA}$, but decrease at higher levels of HA due to the formation of Hg (0)-HA complexes. These findings suggest that Hg (0)-DOM complexes likely constitute an important yet unexplored pool of Hg in anoxic sediments and water columns, and this pool of Hg could potentially impact on biological production of toxic methylmercury under such a reducing environment.

Redox variations indicated from rare earth elements of the authigenic carbonates from cold seeps of the Gulf of Mexico

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The anaerobic oxidation of methane (AOM), which is mediated by consortia of methane-oxidizing archaea and sulfate-reducing bacteria, is the key biogeochemical process at cold seeps. This process leads to an increase of carbonate alkalinity and consequently the precipitation of carbonate minerals. The AOM leads to sulfate depletion in sediment pore water, which induces a change in redox conditions. Rare earth elements (REE) of seep carbonates that as a reliable indicator of this redox variations.

The total REE of the matrix of the carbonate samples from Bush Hill (GC 185), Alaminos Canyon lease area 645 (AC 645), and Green Canyon lease area 238 (GC 238) is from 7.1 to 20.8 ppm, which is higher than that of cements and bivalve shells ranging from 0.4 to 3.1 ppm.

The shale-normalized REE patterns of two Bush Hill seep carbonate samples show pronounced negative Ce anomalies, suggesting precipitated under oxic conditions. However, the patterns of the other five seep carbonate samples show no or slightly positive Ce anomalies, indicating formed under anoxic conditions. Thus, it seems that the redox conditions at Bush Hill seep site is variable spatially. The shale-normalized REE patterns of the seep carbonate from GC 238 shows no Ce anomaly, indicating formed under reduced condition. In contrast, all samples including the matrix, cement, and bivalve shell from AC 645 all show pronounced negative Ce anomalies, indicating that the formation condition for Alaminos Canyon seep carbonates is distinct oxic.

Overall, our results show that apart from anoxic, oxic conditions are common at seep environments. It is suggested from our data that formation conditions of authigenic carbonates at cold seeps are variable and complex.

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