Ligand and surface effects on the reduction of Hg^{II} by Fe^{II}

Bhoopesh Mishra[1, 2], Timothy Pasakarnis[3], Maxim I. Boyanov[2], Edward J. O'Loughlin[2], Michelle M. Scherer[3], Kenneth M. Kemner[2]*

[1]Physics Department, Illinois Institute of Technology, Chicago, IL 60616
[2]Biosciences Division, Argonne National Laboratory, Argonne, IL 60439
[3]Department of Civil and Environmental Engineering, University of Iowa, Iowa City, IA 52242

Abiotic redox transformations of Hg are an integral part of Hg dynamics in reducing environments. The presence of complexing ligands can significantly modify the reduction potential of Hg^{II} and provide an important control on its redox state. We tested the ability of magnetite, a biogenic mineral commonly found in subsurface environments, to reduce Hg^{II} complexed with carboxyl, chloride, and sulfhydryl ligands. These ligands are important constituents of subsurface geomedia and span a wide range of complex formation constants with Hg^{II}. We also investigated the reduction of the Hg-chloride complex by magnetite of varying Fe^{2+} content x ($x = Fe^{2+}/Fe^{3+}$, for stoichiometric magnetite x=0.50).

Hg^{II} adsorbed to *Bacillus subtilis* at high and low Hg:biomass ratios (corresponding to Hg complexation predominantly with carboxyl and sulfhydryl groups, respectively) was reacted with magnetite under anoxic conditions, and the solid phase was examined by Hg L_{III} edge XAS. When Hg^{II} was bound predominantly to carboxyl groups, reduction of Hg^{II} to Hg^0 occured within 2 h and 2 d at pH 6.5 and 5.0, respectively. When Hg^{II} was bound to sulfhydryl groups, it was not reduced by magnetite after 2 months of reaction at pH 6.5 or 5.0. In the presence of chloride, Hg^{II} was rapidly reduced to Hg^0 by near stoichiometric (x=0.48) magnetite. The reduction of the Hg^{II}-chloride complex by more oxidized forms of magnetite (x=0.38 and 0.28) was kinetically hindered due to the formation of calomel ($Hg^{I}_2Cl_2$) as a stable intermediate reaction product. However, reaction kinetics slowly progressed towards reduced Hg^0 after 4 months of reaction. These results suggest that the complexation of Hg^{II} with carboxyl, chloride, and sulfhydryl exhibits a progressively increased inhibition of the reduction of Hg^{II} to Hg^0 by magnetite. Since Hg is typically present in aquatic and terrestrial systems at low concentrations, binding of Hg^{II} to high affinity sulfhydryl sites on bacteria could have important implications for the potential reduction of Hg^{II} to Hg^0 and the overall mobility of Hg under Fe-reducing conditions.

While the interaction between Hg^{II} and $Fe^{II/III}$ minerals is an important reduction pathway in the Hg cycle, Fe^{II} associated with the surfaces of minerals or biomass is ubiquitously present in reducing environments and may also have a significant influence on Hg^{II} redox transformations. We have tested the ability of Fe^{II} adsorbed to carboxyl-functionalized microbeads to reduce Hg^{II}. Samples were prepared with 0.1 mM Hg^{II}, 1.0 mM Fe^{II}, and 4.2 g/L beads (approx. 0.5 mM surface carboxyl ligands) at pH 7.5 and 8.4. X-ray absorption spectroscopy measurements at the Hg L_{III} edge showed that Hg^{II} in the solid phase was rapidly reduced to Hg^0, regardless of the presence or absence of dissolved chloride. The results suggest that carboxyl-adsorbed Fe^{II} could also act as a reductant for Hg^{II} in the Fe-reducing subsurface environments.

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*Presenting Author: Bhoopesh Mishra (bmishra3@iit.edu; bmishra@anl.gov)