

## Structural and mechanistic characterization of Hg transformations

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**Project Abstract:** Bacteria and archaea possessing the *hgcAB* gene pair methylate inorganic mercury (Hg) to form monomethylmercury (MMHg). HgcA consists of a corrinoid binding domain and a transmembrane domain, and HgcB is a ferredoxin. However, their detailed structure and function have not been thoroughly characterized. We modeled the HgcAB complex by combining metagenome sequence data, coevolution analysis, and ab initio structure calculations. In addition, we overexpressed HgcA and HgcB in *Escherichia coli* and confirmed spectroscopically that they bind cobalamin and [4Fe-4S] clusters, respectively, and incorporated these cofactors into the structural model. Surprisingly, the two domains of HgcA do not interact with each other, but HgcB forms extensive contacts with both domains. Conserved cysteine residues are likely involved in transferring Hg<sup>II</sup> into position for methylation, removing methylmercury, or both.

Although anaerobic microorganisms are the primary producers of MMHg, the abiotic formation of dimethylmercury (DMHg) from MMHg has been suggested to account for a large portion of DMHg formation. Previous experimental work has shown that abiotic formation of DMHg from MMHg can be facilitated by reduced sulfur groups on mineral particles. Although a mechanism was proposed for this transformation, a more detailed investigation of this reaction is warranted. Thus, we performed density functional theory (DFT) calculations to explore mechanisms of DMHg formation on the surface of a nanoparticle model. We found that coordination of MMHg substituents to adjacent reduced sulfur groups protruding from the surface facilitates DMHg formation and that the reaction proceeds through direct transmethylation from one MMHg substituent to another. Coordination of Hg by multiple S atoms provides transition state stabilization and activates a C-Hg bond for methyl transfer. These findings provide insight into abiotic DMHg formation and fill gaps in our understanding of Hg transformation and cycling in the environment.