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BIOGEOCHEMISTRY

Mercury methylation on ice

Metagenomic analysis of Antarctic sea-ice and brine reveals the presence of *hgcAB*-like genes in the microaerophilic marine bacterium *Nitrospina*. These are similar to ones responsible for mercury methylation in anaerobic microorganisms and provide a plausible mechanism for mercury methylation in oxic marine environments.

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In 2013, nations of the world agreed on the first global treaty to curb anthropogenic mercury (Hg) release into the environment. One of the main goals of this agreement was to mitigate the many deleterious health outcomes associated with methylmercury (CH_3Hg^I) exposure[1]. Divalent inorganic mercury (Hg^{II}) is converted by microorganisms into CH_3Hg^I, which is biomagnified in apex marine predators such as tunas and cetaceans to a millionfold higher concentration than seawater, levels that can be toxic for both humans and wildlife[1]. 2013 also marked a scientific breakthrough when researchers began to "crack the mercury methylation code" by identifying a two-gene cluster (*hgcA* and *hgcB*) in microorganisms involved in Hg methylation[2,3]. The *hgcA* gene encodes for a putative corrinoid protein capable of transferring a methyl group to Hg^{II}. The HgcB protein returns HgcA to a redox state that enables it to receive a new methyl group[2]. The presence of these genes has so far been restricted to anaerobic sulfate and iron-reducing bacteria and methanogens[4], leaving researchers wondering how to explain high CH_3Hg^I concentrations and active methylation of Hg^{II} observed in oxic marine waters[5,6].

In this issue of *Nature Microbiology*, Gionfriddo *et al.*[7] compare the gene sequences of microbial communities in Antarctic sea-ice and brine to those known to be capable of CH_3Hg^I production. The authors propose a microaerophilic nitrite-oxidizing bacterium, *Nitrospina*, as a novel and key contributor to marine Hg methylation in Antarctic sea-ice, and the mesopelagic waters of the North Pacific and North Atlantic. *Nitrospina* possess genes with some slight rearrangements compared to the *hgcAB* genes identified in prior work[2], which the authors suggest may also be capable of methylation. This work continues recent scientific advances in identifying microbial Hg methylators in much more diverse environments than previously realized.

Most of the Hg in the environment, including polar ecosystems, is present as Hg^{II} and elemental Hg (Hg^0). Reduction of Hg^{II} to Hg^0 and subsequent evasion to the atmosphere reduces the amount of Hg^{II} available for methylation. Thus, the simultaneous occurrence of Hg^{II} reduction and methylation are critical for understanding factors driving the pool of Hg^{II} available in the oceans for methylation and subsequent accumulation by higher-level organisms. In addition to identifying the *hgcAB*-like genes in sea-ice microorganisms, Gionfriddo *et al.*[7] also identified *mer* operons from Proteobacteria, which enable microorganisms to reduce Hg^{II}. This work confirms the simultaneous presence of microbial communities responsible for both Hg^{II} methylation and reduction in polar sea-ice.

Paradoxically, in recent years some of the highest Hg^{II} and total methylated Hg species (ΣMeHg) measured in seawater and biota have been reported in the remote Southern Ocean[8]. In addition to the potential for *in situ* methylation reported by Gionfriddo *et al.*[7], ice-cover suppresses Hg^0 evasion from marine surface waters, thereby increasing the pool of Hg^{II} available to methylating bacteria. Additionally, Gionfriddo *et al.*[7] find that ice melt contributes over 48 kmol of total Hg to seawater each year, which is more than an order of magnitude higher than some Arctic Ocean estimates[9]. Retention of atmospherically deposited Hg by snow and ice in polar environments is

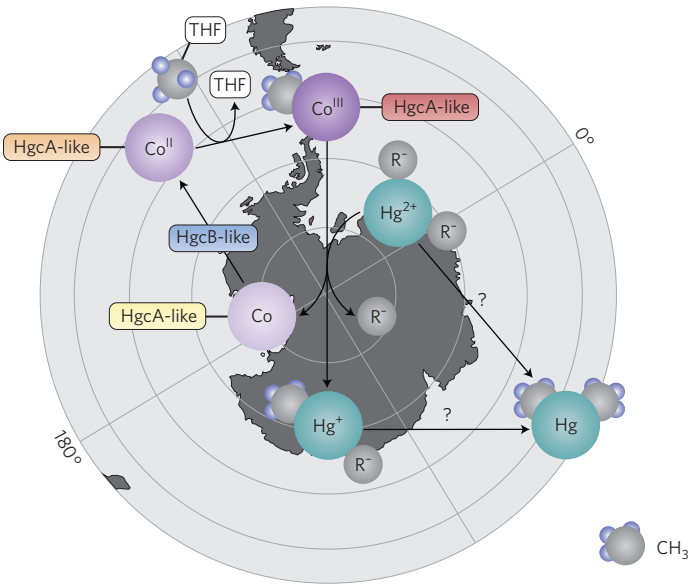

Figure 1 | Proposed mechanism by Parks *et al.*[2] for the role of the HgcAB proteins in methylation of inorganic Hg (Hg^{II}). Gionfriddo *et al.* propose a similar mechanism for methylmercury formation mediated by a microaerophilic nitrite-oxidizing bacterium, *Nitrospina*, in Southern Ocean sea-ice containing an HgcA-like protein. Inorganic mercury (Hg^{II} bound to negatively charged ligands R^-) is converted to CH_3Hg^I by *Nitrospina* containing HgcA-like protein. The change in colour of the HgcA-like protein in the figure denotes a shift in the redox state of cobalt (Co). The role of HgcB is to return HgcA to a redox state that allows it to receive a methyl group. The mechanisms of biotic $(CH_3)_2Hg$ formation in sea-ice and marine waters are unknown. Map generated with Ocean Data View.

uncertain since it can be reduced back to the volatile Hg^0 species. Fluxes measured by Gionfriddo *et al.*[7] suggest accumulation in the ice and snow of the Southern Ocean is substantial. Prior work indicates the presence of halides next to ice leads in polar springtime stabilizes atmospherically deposited mercury[10], perhaps explaining the observed high concentrations and large inputs to seawater from polar ice[7].

In summary, Gionfriddo *et al.*[7] propose the novel hypothesis that Hg methylation may be carried out by bacteria such as *Nitrospina* in microenvironments such as brine pockets and biofilms associated with trapped and decaying organic matter. The capacity for methylation by microorganisms has not been linked to Hg detoxification, thus some have suggested that CH_3Hg^I production is unintentional. The sporadic occurrence of *hgcAB* genes within a genus suggests that they may provide an evolutionary advantage but the native function of the two-gene cluster remains unknown. In addition, possession of *hgcAB*-like genes does not necessarily confer capability for methylation. Presently, we know little of the ecology and physiology of the genus *Nitrospina*. Pure strains of *Nitrospina* do not contain *hgcAB*-like genes identified in this work, suggesting it may be strain-specific. This is also observed in other methylating genera — only half of *Desulfovibrio* species tested have demonstrated the ability to methylate[11]. Laboratory experiments that isolate the strains of *Nitrospina* containing *hgcAB*-like genes and tests for Hg methylation capability are needed to confirm the compelling hypothesis for methylation in oxic marine environments. As such, this research represents a first step towards understanding the mechanism of Hg methylation in the marine environment. While additional work is needed to fully 'crack' the mercury methylation code, we are now moving towards being able to relate anthropogenic Hg pollution to MeHg concentrations in marine fish. ❐

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