

Focus on Hg methylation and demethylation by sulfate-reducers at the cellular scale: The use of isotopic tracers to determine transformation rates, uptake and subcellular localization

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Microbial Hg methylation is a key process in the Hg cycle controlling the MeHg concentrations in the aquatic environments (1). Despite our improved understanding of the microbiological mediated Hg methylation in the environment and the identification of the involved bacteria, we have only a vague idea of the underlying mechanisms and of the parameters that control the efficiency of that transformation. Because methylation extent can be controlled by both cellular uptake and reversible demethylation pathways, the use of multiple isotopically labelled Hg species may provide additional mechanistic insights of such processes (2).

In this work, pure sulfate reducing strains were incubated in the presence of isotopically labelled mercury species (¹⁹⁹Hg (II) and ²⁰¹MeHg) under controlled anaerobic conditions. The quantification of the remaining and formed Hg species in the different subcellular fractions (periplasm, cytoplasm, membranes) has allowed:

- to quantify simultaneously methylation and demethylation rates of the different isolated strains,
- to determine the differential reactivity and assimilation of the added and formed Hg species,
- to assess the localization of the added and formed species at the subcellular level.

The results confirm that sulfate reducers have both methylating and demethylating capacities and highlight the fact that Hg methylation/demethylation processes are specific metabolic reactions whose extent varies among the different bacterial strains. The differential reactivity of the two isotopic tracer species has also allowed to investigate the relative rate of the cell uptake and further metabolic transformation.

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Aluminate speciation in H₂O at high pressures and temperatures

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The solubility of corundum in H₂O is low even at high *P* and *T* [1], and it is often assumed that Al is immobile during fluid-rock interaction. However, field and experimental studies suggest that Al solubility is enhanced in the presence of Si-rich or alkaline or acid solutions [2, 3]. We carried out a Raman-spectroscopic study of Al speciation in aqueous fluids at high *P* and *T*, in an externally heated diamond-cell. Spectra were collected with a Horiba Jobin-Yvon Labram HR spectrometer using the 514 nm line of an Ar laser for excitation. A first set of experiments investigated speciation of Al in 1 M KOH with corundum, up to 1 GPa and 700 °C. The Raman spectra show a prominent band at 618 cm⁻¹, which is due to Al-O stretching of monomeric [Al(OH)₄]¹⁻. At higher *P* and *T*, additional vibrational modes appear at 200 cm⁻¹ and 374 cm⁻¹, most likely due to bending modes of [(HO)₃-Al-O-Al-(OH)₃]²⁻ or similar polymeric species. Upon cooling from high *P-T*, some oversaturation appears to occur: peaks at 930 and 1066 cm⁻¹ appear upon cooling, probably due to colloidal Al hydroxide. We also studied Al speciation in pure H₂O with corundum, to 2 GPa and 1000 °C. Spectra are devoid monomeric alumina; however, bands at 374 cm⁻¹ become apparent starting at 718 °C, suggesting that all detectible aqueous Al is polymerized. This differs from dissolved silica, which forms a mixture of monomers and dimers under similar conditions [4, 5]. Finally, Al speciation was studied in H₂O with corundum and quartz, up to 1 GPa and 900 °C. The 375 °C spectrum shows a prominent band at 766 cm⁻¹ due to Si-O stretching in the [Si(OH)₄] monomer. At higher *P* and *T*, additional bands appear at 944, 608, 360 and 200 cm⁻¹, attributable to Al-Si polymers, including [(HO)₃-Al-O-Si-(OH)₃]¹⁻. Comparison to the SiO₂-H₂O system suggests that in the presence of Al, polymerization is enhanced.

- [1] Tropper & Manning (2007) *Chem. Geol.* **240** 54–60.
[2] Manning (2007) *Geofluids* **7** 258–269. [3] Wohlers & Manning (2009) *Chem. Geol.* **262** 326–333. [4] Zotov & Keppler (2000) *Am. Mineral.* **85** 600–604. [5] Newton & Manning (2003) *Contrib. Mineral. Petrol.* **146** 135–143.