

## Influence of the L-methionine on the mackinawite oxidation stability

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Effective remediation of sediment contaminated with mercury is essential to minimize the contamination of fish and shellfish and, consequently, the human exposure to methyl mercury. Elevated mercury concentrations in fish are the leading cause of fish advisories. In 2008, 43% of the total lake acres in the United States were under advisory for mercury [1]. In situ capping (ISC) is one of the remediation methods that have been related as effective to reduce the mercury contamination, and mercury methylation in sediments, using mackinawite as an isolating material [2].

Mackinawite has low oxidation stability that can restrict its use. To obtain mackinawite more resistant to oxidation, we modified its surface using L-methionine as organic ligand.

The results showed that L-methionine improved the oxidation resistance of mackinawite in pH range 4 to 8, in 67%, considering the time to start the bulk oxidation, as resulting of the attachment orientation, and its chemical composition, as well.

The oxidation resistance improvement by L-methionine it seems to occurs through the control of polysulfide chains formation that works as a passive film, preventing the fast bulk oxidation.

[1] U.S. Protection Environmental Agency–USEPA (2009) The National Study of Chemical Residues in Lake Fish Tissue. EPA-823-R-09-006. U.S. Environmental Protection Agency, Office of Water, Washington, DC. [2] Liu, J. *et al.* (2009) *Environ. Eng. Sci.* **26**, 833–840.

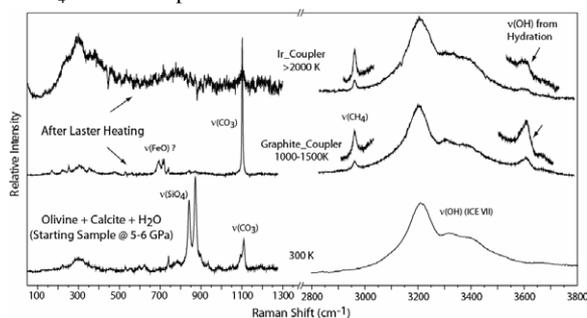
## Methanogenesis via carbonate reduction in mantle minerals

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Earlier studies [1, 2] have shown evidence of methanogenesis via carbonate reduction in the 5-6 GPa and 500-1500 °C range using FeO, CaCO<sub>3</sub> (calcite), and excess H<sub>2</sub>O. The role of carbon, CO, and Fe in various oxidation states for a carbonate reduction pathways have also been established [2]. In this study, we have explored the FeO-CaCO<sub>3</sub>-H<sub>2</sub>O reaction by replacing FeO with San Carlos (SC) Olivine (representative mantle mineral), and Synthetic Fayalite to model a silicate enriched system. *In situ* experiments were performed in the 5-6 GPa and temperatures up to 2000 °C with diamond anvil cells.

Methanogenesis was observed in the (SC)Olivine-Calcite-Water, Fayalite (syn)-Calcite-Water system at temperatures greater than 2000 °C and less than 650 °C respectively. Fayalite-Magnesite-Water system experiments show rapid CH<sub>4</sub> formation with decarboxylation of magnesite (from 3.8 GPa at 325 °C to 6.5 GPa at 650 °C). Methane in this case is present with CO<sub>2</sub> with no indication of any carbonyl phase in the system. A series of control experiments were also performed to constrain the source of carbon and clearly establish the role of carbonate reduction as the major source of CH<sub>4</sub> in those experiments.



**Figure 1.** Methanogenesis in Olivine-Calcite-H<sub>2</sub>O system accompanied by formation of hydrous phases.

[1] Scott *et al.* (2004) *Proc. Nat. Acad. Sci.* **39**, 14023–14026.  
[2] Sharma *et al.* (2009) *Energy Fuels*, DOI 10.1021/ef9006017.