

# INFLUENCE OF TEMPERATURE ON THE STRUCTURAL EVOLUTION OF POLLUTED AGENTS TRAPPED BY SMECTITES: A TOOL TO UNDERSTAND THE EVOLUTION OF POLLUTED SEDIMENTS

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## INTRODUCTION

Mercury is a trace element characterized by a very low natural background level (about 50 ppb) in sediments. However its high toxicity makes it an environmental contaminant of continuing concern in industrial, mining, and domestic wastes, even in limited amount (some ppm can be harmful for living organisms, including human beings). Hg toxicity strongly depends on its chemical form and on its interactions with other molecules. Hg shows three valences states (I, II, and 0), a great reactivity towards organic and inorganic matter and a complex environmental behavior, also including the possibility of disproportionate reactions. When addressing environmental science, the most common reactive functional groups (ligand sites) in soil are humic, carboxylic and phenolic acids. Although N- and S-bearing ligands are less abundant respect to S-bearing ligands, they may establish high-affinity bonds with heavy metal cations. Hg(II) forms covalent bonds with reduced sulphur and thus shows a very high affinity for reduced forms of organic sulphur (and inorganic sulphides) as also confirmed by the Lewis acid-base theory: Hg(II) is a soft Lewis acid and should in fact strongly bind with thiol, which is a soft Lewis base.

## MATERIALS AND METHODS

Synchrotron based extended X-ray absorption fine structure spectroscopy (EXAFS), X-ray diffraction at room and high temperature, thermal analyses combined with mass spectrometry of evolved gas, and chemical analyses remarkably contributed to the characterization of heavy metal binding to the mineral structure, which becomes of fundamental importance to predict the mobility and long term behaviour of heavy metals in natural systems. In this study, we characterized the thermal behaviour of two silicates layer: montmorillonite (International Standard of Clays and Clay Mineral Society, STx-1 sample from Gonzales County, Texas) and vermiculite (from Bikiti, Zimbabwe). The form of the chemical bonds between Hg and the amino acid, in pre-treated samples, was also investigated in order to evaluate its effect on the release of Hg, previously entrapped into the mineral-amino acid complex, after temperature increase.

**Solutions:**  $1 \times 10^{-2}$  M Hg(II);  $1 \times 10^{-2}$  M of amino acid cysteine.

**Treated Samples:** MHg and VHg, natural montmorillonite and vermiculite exchanged with Hg(II) aqueous solution, respectively; MHgCys and VHgCys, natural montmorillonite and vermiculite respectively, exchanged with cysteine and successively with Hg(II) aqueous solutions.

## EXPERIMENT

Hg L<sub>III</sub>-edge XANES spectra of HgO, Hg(OH)<sub>2</sub> and HgS compound show that the adsorption edge for all the samples is at the same energy, characterizing a divalent oxidation state. Two well defined features located at about 12.281 and 12.296 KeV has to be assigned to the 2p core state transition to 5d<sub>5/2</sub> and 5d<sub>3/2</sub>-y<sub>2</sub> states, respectively. However, the position of peaks B in the XANES spectrum of

XANES spectra collected at room temperature are located at about 12.280 and 12.294 KeV respectively, the same as in the HgO and Hg(OH)<sub>2</sub> model compounds, thus suggesting that the nearest neighbour setting of mercury atoms in both samples is similar to mercury oxide and hydroxide; nevertheless distances refined in previous works suggest that in the first coordination shell there are also Hg(II) cations bound to water molecules, which well fit with the model of mercury hydroxide. When temperature increase this frameset changes remarkably; in fact whereas in vermiculite the features observed at room temperature persist up to 700°C, in montmorillonite they disappear in the thermal range 150=T(°C)=400. The XANES spectra of both samples do not clearly show A and B features, but just present broad peaks, hinting to large distortion effects of the first shell around the Hg(II), increasing with increasing temperature.

At room temperature the spectra of the amino acid treated samples are comparable to the one of HgS; in addition there is no evidence for a variation of the oxidation state. Typical features of Hg compound are well maintained up to 400°C indicating that the local environment of Hg(II) does not change with temperature. Furthermore up to 400°C, except for a different absorption coefficient related to the different amount of adsorbed metal, the two Hg and cysteine treated samples do not show any significant difference, further stressing that the bonding in the adsorbed molecules does not significantly depend on the features of silicate layer. The main difference between the two samples is that in the vermiculite like layer the Hg-S bond is maintained up to greater temperature with respect to the montmorillonite layer.

## DISCUSSION AND CONCLUSION

The reactions at different temperature in both the clay minerals treated with Hg(II) and cysteine evidences the formation of various complexes, not easily removable from the silicate layer. At room temperature the presence of Hg<sup>2+</sup>S bonds of 2.33 and 2.30Å and of Hg<sup>2+</sup>Hg distances of 4.22 and 4.20Å from the central Hg atom (for Hg-cysteine-vermiculite and Hg-cysteine montmorillonite respectively) supports the hypothesis that adsorbed Hg-cysteine complexes form a linear chain in which Hg bonds only to sulphur. Thermal analyses curves, and especially the high temperature EXAFS data, suggest that not only the thiol (R<sup>2</sup>SH), but also the disulphur functional group (R<sup>2</sup>SS-R) play an important role in the complexation reactions. This features is quite helpful also to explain how Hg-cysteine complexes can be formed, starting from Hg<sup>2+</sup>H<sub>2</sub>O complex and Hg(OH)<sub>2</sub> molecules. In fact, in both aqueous suspension used for the preparation of VHgCys and MHgCys samples, at least at the beginning of the experiment, the number of ligand containing free oxygen is greater than free sulphur atoms. As also predicted by Lewis theory, the survival and/or the formation of bonds like (Hg<sup>2+</sup>O), (O-Hg<sup>++</sup>-S) cannot be excluded.

Binding between mercury hydroxide and sulphur atom follows from the loss, during batch treatments, of an [(OH)-] group from the mercury hydroxide and from the subsequent saturation of the excess of charge via binding with a sulphur atom of the amino acid.

These results suggest that treatments with amino acids may enhance the stability of Hg sorbed by montmorillonite minerals and efficiently retard the release of mercury ions into the geosphere.