EXAFS and XPS study of arsenate adsorption on manganite (γ-MnOOH) surfaces

DIPANJAN BANERJEE, HANNA NELSON AND PER PERSSON

Department of Chemistry, Umeå University, S-90187 Umeå, Sweden (dipanjan.banerjee@chem.umu.se; hanna.nelson@chem.umu.se; per.persson@chem.umu.se)

Introduction

The introduction of toxic metalloid arsenic in the environment is of worldwide concern. Arsenic occurs in several oxidation states but in oxic environments the speciation is dominated by arsenate (As[V]), which is extremely reactive towards transition metal oxyhydroxide particles. The aim of this study is to characterize the structure and composition of arsenate species adsorbed on Mn oxyhydroxide surfaces as a function of pH and surface coverage.

Experiment

Batch experiments were conducted where arsenate was adsorbed onto manganite (γ-MnOOH) surfaces as a function of pH and surface coverage. A minimum of 72 hours equilibration time was allowed before the samples were centrifuged and the wet pastes were analyzed using EXAFS spectroscopy and cryogenic XPS techniques.

Results and Discussion

Arsenic K-edge EXAFS spectra were collected for manganite-arsenate samples over a wide range of pH and arsenate concentrations. The data reveal that there are no major differences in the spectra as a function of pH whereas minor differences are observed in the weak second shell features of the Fourier transforms. Data fitting indicates a first coordination shell of 4 oxygen atoms at the expected arsenate distances (ca. 1.7 Å) and a second shell caused by Mn back-scattering together with multiple scattering within the first shell of As-O bonds. A complete quantitative evaluation of the EXAFS data is in progress.

Cryogenic XPS study on the same samples revealed that close proximity of the As 3d and Mn 3p lines makes it difficult to interpret the commonly used As 3d spectra, especially at low arsenic concentrations. In such cases, we found that the As 2p line is significantly more useful in order to understand the oxidation state, surface abundance and speciation of arsenic, as well as improving the detection limit for arsenic by a factor of 4 due to its high ionization cross-section. Consequently, we systematically analyzed the As $2p_{3/2}$ binding energies and corresponding auger parameters of several arsenic oxide reference compounds (As_2O_3, As_2O_5, $NaAsO_2$ and Na_2HAsO_4) and calculated the atomic sensitivity factor. These data were subsequently used in the analysis of As $2p_{3/2}$ spectra of the manganite-arsenate samples.

References

Chiu V.Q. and Hering J.G. (2000) *Environ. Sci. Technol.* **34**, 2029-2034.

Direct dating of archean microbial ichnofossils

N.R. BANERJEE[1], A. SIMONETTI[2], H. FURNES[3], K. MUEHLENBACHS[2], H. STAUDIGEL[4], N. MCLOUGHLIN[3], M. DE WIT[5] AND M. VAN KRANENDONK[6]

[1]Earth Sciences, Uni. of Western Ontario, Canada
[2]Earth and Atmos. Sciences, Uni. of Alberta, Canada
[3]Centre for Geobiology, Uni. of Bergen, Norway
[4]Scripps Institute of Oceanography Uni. of California, San Diego, USA
[5]AEON Uni. of Cape Town, S. Africa
[6]Geological Survey of W. Australia, Perth, Australia

A novel *in situ* laser ablation multi-collector-ICP-MS technique has enabled the first direct radiometric age determination of an Archean microbial ichnofossil. Direct *in-situ* U-Pb dating of titanite ($CaTiSiO_4$) that infills tubular bioalteration textures in pillow basalt rims and hyaloclastites from the ~3.35 billion-year-old Euro basalt of the Pilbara craton, W. Australia (PWA) confirms their Archean Age [1]. A laser ablation spot size of ~40 μm was used to analyze titanite in the "root zones" at the centre of microtubule clusters. Thirteen analyzes in three thin sections gave a weighted average $^{206}Pb/^{238}U$ age of 2921±110 Ma [1]. This late Archean age for titanite formation represents a minimum age estimate for the bioerosion. A pre-metamorphic age for the ichnofossils is consistent with chlorite overgrowths that cause their segmentation.

Multiple lines of evidence suggest that these tubular structures formed by microbial bioerosion of formerly glassy Archean lavas that were subsequently mineralized by titanite [2]. There are striking morphological similarities between Archean tubular structures from both the Pilbara and Barberton (BGB) cratons and microbial ichnofossils found in modern glasses. X-ray mapping shows carbon enriched along the margins of the tubular structures from both the BGB and PWA. Also, disseminated carbonates in the BGB pillow rims have C-isotopes depleted by as much as –16‰, which is consistent with microbial oxidation of organic matter.

References

[1] Banerjee *et al*. (in press). Direct dating of Archean microbial ichnofossils. *Geology*
[2] Furnes *et al*. (2004). Early life recorded in Archean pillow lavas. *Science* **304**, 578-581.