4.2.32

EXAFS signatures of structural Zn at trace level in di- and trioctahedral phyllosilicates

F. JUILLOT[1], G. MORIN[1], G.E. BROWN JR.[2]
AND G. CALAS[1]

[1] Laboratoire de Minéralogie-Cristallographie de Paris, UMR CNRS 7590, Universités Paris 6/7-IPGP,France (juillot@lmcp.jussieu.fr)
[2] Department of Geological & Environmental Sciences, Stanford University, Stanford,U.S.A.

Several recent studies have emphasized the importance of Zn^{2+} ions incorporation in di- and trioctahedral phyllosilicates in the control of Zn behavior in contaminated soils [1-3]. Trioctahedral phyllosilicates precipitate much more rapidly than dioctahedral ones, at room temperature. This difference might suggest that, in Zn-contaminated soils, trioctahedral phyllosilicate incorporate anthopogenic Zn, which can be considered as “new” Zn, whereas Zn in dioctahedral phyllosilicates mainly originate from the geochemical background, which can be considered as “old” Zn.

The aim of the present study was to collect structural information about the local environment of Zn^{2+} ions at trace levels within the octahedral layers of di- and trioctahedral phyllosilicates in order to improve *in situ* distinction of these Zn-bearing minerals in soils. Analysis of EXAFS spectra of Zn-dilute di- or trioctahedral natural and synthetic phyllosilicates with *ab initio* FEFF 8 calculations allowed us to derive spectroscopic features characteristic of Zn incorporated within di- or trioctahedral layers in natural and synthetic samples.

Our results thus indicate that, thanks to its structural sensitivity, EXAFS can help to distinguish anthropogenic Zn from naturally occurring Zn, in the phyllosilicate fraction of contaminated soils. Although other Zn species are known to occur (LDHs, adsorbed species), deciphering between these two phyllosilicate pools of Zn is a key parameter to better assess the long term behavior of Zn in contaminated soils.

References

[1] Manceau et al., (2000) *Am. J. Sci.* **300**, 289-343.
[2] Scheinost et al., (2002) *Env. Sci. & Techn.* **36**, 5021-5028.
[3] Juillot et al., (2003) *Am. Miner.* **88**, 509-526.

4.2.33

Iodine speciation in iodine-rich humic substances by X-ray absorption spectroscopy

M.L. SCHLEGEL[1], F. MERCIER[2], N. BARRÉ[2]
AND P. REILLER[3]

[1] DPC/SCP/LRSI, CEA of Saclay, Bat 391; F-91 191 Gif-sur Yvette Cedex, France (Michel.Schlegel@cea.fr)
[2] UMR 8587, CEA, CNRS and Université of Évry, France (Florence.Mercier@cea.fr; Nicole.Barre@cea.fr)
[3] SECR/LRSM, CEA Saclay, France (Pascal.Reiller@cea.fr)

Introduction

Disposal of spent nuclear fuel in radioactive waste repositories can result in the release of radioactive ^{129}I in the environment [1]. Understanding the migration of ^{129}I in subsurface environments is essential to estimate the long-term exposure of populations to radioactive iodine. Several field studies have demonstrated the quantitative retention of iodine by natural organic matter, such as humic substances (HS) [2]. The present study aimed at disclosing by X-ray absorption spectroscopy the nature and possible diversity of the binding mechanism(s) between organic matter and iodine.

Materials and methodsAnother heading if you want it

Iodine LIII-edge X-ray absorption spectra were collected in fluorescence mode at the ID26 beamline (ESRF, France) on powders of inorganic and organic references, and of lyophylized naturally iodinated HS (NIHS) from a variety of locations. References were diluted with BN powder if required to avoid self-absorption effects. References and samples were recorded as powder samples X-ray data were normalized and reduced using standard procedures [3].

Results and interpretations

The X-ray absorption edge (at half-height of the main edge jump) for all NIHS was located near 4562-4563 eV, at values identical to the positions of organic references, higher that the edge energy of iodide (~ 4561 eV), and lower than the edge energy of iodate (4568 eV). Spectra for NIHF and organic references further displayed a characteristic shoulder at 4560 eV on the the main absorption edge, which was not observed for inorganic references. Significant spectral differences in the number and energy position of post-edge absorption bands further indicate that iodine in the various samples has distinct molecular environements, suggesting different retention mechanisms. Analysis of extended X-ray absorption fine structure data confirmed that covalent binding between iodine and C atoms, possibly from phenol groups, prevailed in all NIHS, in agreement with previous studies [2].

References

[1] M.J. Clark and F.B. Smith. *Nature* **332**, 245-249 (1988).
[2] F. MERCIER F., V.Moulin, et al. *Radiochim. Acta* **88,** 779-785 (2000).
[3] D. Aberdam. *J. Synchrotron Rad.* **5**, 1287-1297 (1998).