

En 2006 nous avons poursuivi notre programme de recherche à long terme sur l'inventaire cristallochimique des éléments traces (ETs) dans les formations superficielles en l'élargissant aux oxydes de fer et de manganèse formés en milieu continental au contact avec des eaux de surface (précipités Fe-Mn à la surface de grains de quartz) et lacustres (encroûtements Fe-Mn du lac Baïkal), et en milieu marin (nodules océaniques).

Nous avons montré que le nickel était soit substitué aux atomes de manganèse dans le feuillet de birnessite, soit adsorbé dans l'espace interfoliaire à l'aplomb des lacunes Mn. Le pourcentage de Ni dans chacun des sites dépend du pH, et donc ce fractionnement cristallochimique est un marqueur du milieu de formation. Le zinc est systématiquement adsorbé à l'aplomb des lacunes de manganèse, mais sa coordinence est tétraédrique à basse concentration (complexe de haute énergie) et octaédrique à haute concentration (complexe de basse énergie). Le plomb, dont la taille est très supérieure à celles du nickel et du zinc, est adsorbé en partie en bordure des feuillets de manganèse et pour une autre partie à l'aplomb des lacunes. Son fractionnement entre les deux sites dépend du taux de recouvrement (rapport Pb/Mn): à basse concentration les atomes de plomb sont fixés préférentiellement sur les sites de bordure puis à concentration croissante sur les sites interfoliaires. Enfin, l'arsenic, qui est sélectivement associé aux oxydes de fer dans le milieu naturel, forme un complexe bidentate avec les octaèdres de fer. Nous avons, pour la première fois, simulé le spectre EXAFS de cette entité chimique en considérant l'ensemble des chemins de diffusion multiples du complexe  $\text{AsO}_4\text{-Fe}(\text{O},\text{OH})_6$ , et ainsi déterminé les parcours les plus probables.

La cristallochimie du cérium et du barium a été également étudiée dans les mêmes échantillons, mais uniquement à l'ALS car les seuils d'excitation ( $L_3$ ) sont situés à basse énergie, et donc moins facilement accessibles sur FAME.

Ces résultats ont été consignés dans trois articles et présentés dans plusieurs congrès.

### **Production scientifique 2006-2007 sur ce thème de recherche**

- Manceau A., Lanson M., Geoffroy N.: Natural speciation of Ni, Zn, Ba and As in ferromanganese coatings on quartz using X-ray fluorescence, absorption, and diffraction. *Geochimica et Cosmochimica Acta*, sous presse.
- Manceau A., Kersten M., Marcus M.A., Geoffroy N., Granina L.: Ba and Ni speciation in a nodule of binary Mn oxide phase composition from Lake Baikal. *Environmental Science and Technology*, soumis.
- Takahashi Y., Manceau A., Marcus M.A., Usui, A.: Chemical and structural control of the partitioning of Co, Ce, and Pb in marine ferromanganese oxides. *Geochimica et Cosmochimica Acta*, soumis.

### **Communications sur ce thème de recherche**

#### Conférence plénière:

- 2006** Manceau A.: Probing the structural chemistry of environmental nanoparticles with micrometer-sized X-ray beams. *Winter Meeting of the Mineralogical Society of Great Britain*. January 5-6, Bath, UK.

#### Conférences invitées:

- 2006** Manceau A., Lanson B.: Natural nanocrystalline birnessites. *Physical Chemistry of Soil & Aquifer Systems: A Symposium in Honor of Garrison Sposito*. American Chemical Society. Sept. 10-14, San Francisco.

Manceau A., Lanson B., Marcus M.A.: Probing the defect structure of natural nanoparticles using micrometer-scale X-ray fluorescence, diffraction and absorption techniques. *13th International Conference on X-ray Absorption Fine Structure (XAFS13)*. July 9-14, Stanford, USA.

Manceau A., Lanson B., Marcus M.A.: Probing the defect structure and chemistry of environmental nanoparticles with micrometer-sized X-ray beams. *Fifth International Conference on Synchrotron Radiation in Materials Science, Advanced Photon Source (APS)*. July 30 - August 2, Argonne National Laboratory, Chicago, USA.

Communication orale:

**2006** Manceau A., Lanson B.: Defect structure and trace element partitioning and incorporation in natural Fe and Mn oxide nanoparticles from quartz coatings. *Joint Meeting of the Clay Minerals Society and French Clay Group*. June 3-7, Oléron Island, France.

**Natural speciation of Ni, Zn, Ba and As in ferromanganese coatings on quartz using X-ray fluorescence, absorption, and diffraction**

Alain Manceau, Martine Lanson, Nicolas Geoffroy

**ABSTRACT**

The mineralogy of natural ferromanganese coatings on quartz grains and the crystal chemistry of associated trace elements Ni, Zn, Ba and As were characterized by X-ray microfluorescence, X-ray diffraction, and EXAFS spectroscopy. Fe is speciated as ferrihydrite and Mn as vernadite. The two oxides form alternating Fe-rich and Mn-rich layers that are irregularly distributed and not always continuous. Unlike naturally abundant Fe-vernadite, in which Fe and Mn are mixed at the nanoscale, the ferrihydrite and vernadite are physically segregated and the trace elements clearly partitioned at the microscopic scale. Vernadite consists of two populations of interstratified one-water layer (7 Å phyllomanganate) and two-water layer (10 Å phyllomanganate) crystallites. In one population, 7 Å layers dominate, and in the other 10 Å layers dominate. The three trace metals Ni, Zn, Ba are associated with vernadite and the metalloid As with ferrihydrite. In vernadite, nickel is both substituted isomorphically for Mn in the manganese layer and sorbed at vacant Mn layer sites in the interlayer. The partitioning of Ni is pH-dependent, with a strong preference for the first site at circumneutral pH and for the second at acidic pH. Thus, the site occupancy of Ni in vernadite may be an indicator of marine vs. continental origin, and in the latter, of the acidity of streams, lakes, or soil pore waters in which the vernadite formed. Zinc is sorbed only in the interlayer at vacant Mn layer sites. It is fully tetrahedral at a Zn/Mn molar ratio of 0.0138, and partly octahedral at a Zn/Mn ratio of 0.1036 consistent with experimental studies showing that the  $^{VI}\text{Zn}/^{IV}\text{Zn}$  ratio increases with Zn loading. Barium is sorbed in a slightly offset position above empty tetrahedral cavities in the interlayer. Arsenic tetrahedra are retained at the ferrihydrite surface by a bidentate-binuclear attachment to two adjacent iron octahedra, as commonly observed. Trace elements in ferromanganese precipitates are partitioned at a few, well-defined, crystallographic sites that have some elemental specificity, and thus selectivity. The relative diversity of sorption sites contrasts with the simplicity of the layer structure of vernadite, in which charge deficit arises only from  $\text{Mn}^{4+}$  vacancies (i.e., no  $\text{Mn}^{3+}$  for  $\text{Mn}^{4+}$  substitution). Therefore, sorption mechanisms primarily depend on physical and chemical properties of the sorbate and competition with other ions in solution, such as protons at low pH for Ni sorption.

**Chemical and structural control of the partitioning of Co, Ce, and Pb in marine ferromanganese oxides**

Takahashi Y., Manceau A., Marcus M.A., Usui, A

## ABSTRACT

The oxidation state and mineral phase association of Co, Ce and Pb in hydrogenetic, diagenetic, and hydrothermal marine ferromanganese oxides were characterized by X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy and chemical extraction. Cobalt is trivalent and associated exclusively with the Mn oxide component (vernadite). Cerium is tetravalent in all genetic-type oxides (detection limit for Ce(III) ~ 5 at. %), including Fe-rich areas (ferrihydrite) of hydrogenetic oxides, and is associated primarily with vernadite. Thus, the extent of a Ce anomaly does not result from variations in redox conditions, but appears to be kinetically controlled, decreasing when the growth rate increases from hydrogenetic to diagenetic to hydrothermal oxides. Lead is divalent and associated with Mn and Fe oxides in variable proportions. According to EXAFS data, Pb is mostly sorbed on edge sites at chain terminations in Fe oxide and at layer edges in Mn oxide (ES complex), and also on interlayer vacancy sites in Mn oxide (TCS complex). Selective dissolution, spectroscopic data, and electrochemical considerations suggest that the geochemical partitioning in the Mn oxide component decreases from Co to Ce to Pb, and depends on their oxidative scavenging by Mn and Fe oxides.

### **Ba and Ni speciation in a nodule of binary Mn oxide phase composition from Lake Baikal**

Manceau A., Kersten M., Marcus M.A., Geoffroy N., Granina L.

## ABSTRACT

The partitioning and incorporation mechanism of Ni and Ba in a ferromanganese nodule from Lake Baikal were characterized by X-ray microfluorescence, microdiffraction, and absorption spectroscopy. Fe is speciated as goethite, and Mn as romanechite (psilomelane) and non-collapsible 10 Å vernadite (buserite) with minor 7 Å vernadite (turbostratic birnessite). Barium is in association with romanechite and Ni with vernadite in distinct and irregularly distributed layers, which are separated by a goethitic matrix. The binary Mn oxide banding pattern is interpreted by a two-mode accretionary model, in which the variation in Ba flux induced by hydrothermal water pulses determines whether a tectomanganate (romanechite) or phyllomanganate (vernadite) is formed during the ferromanganese nodule accretion. Nickel is predominantly substituted isomorphically for Mn in the manganese layer, and is not sorbed at vacant Mn layer sites in the interlayer, in agreement with the circumneutral pH of the lake water.