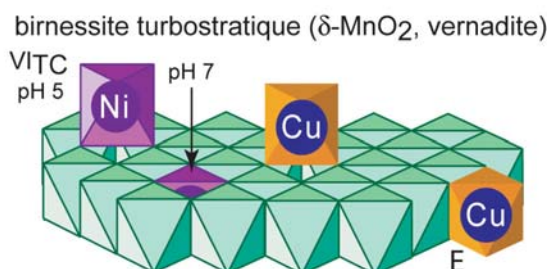
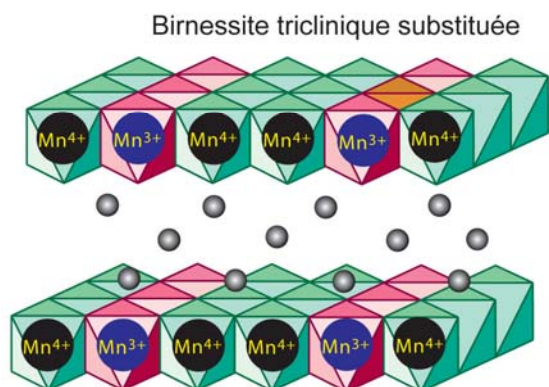
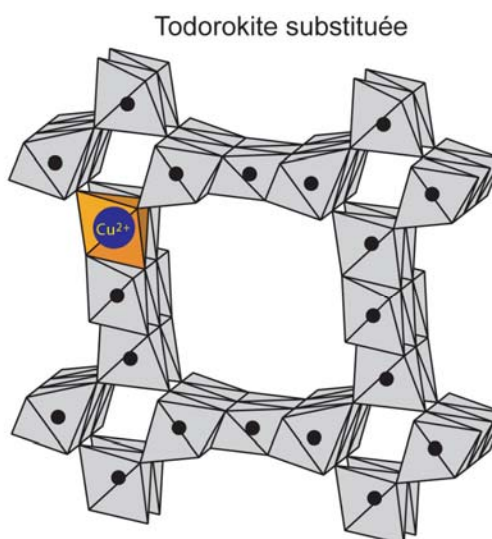
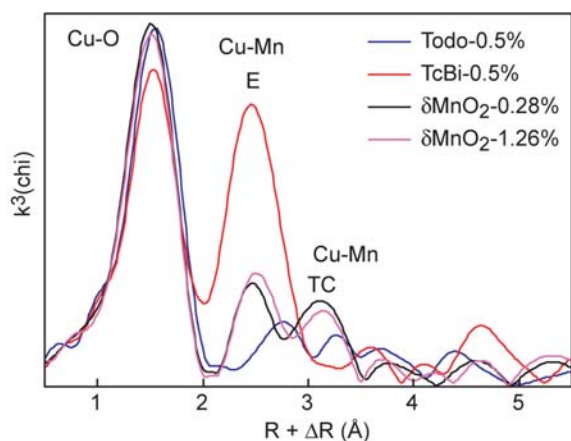


En 2007 j'ai poursuivi mon programme de recherche à long terme sur l'inventaire cristallographique des éléments traces (ETs) dans les formations superficielles. A la suite du nickel, dont les résultats ont été publiés cette année dans trois articles à *Geochimica et Cosmochimica Acta*, j'envisage de travailler dans les deux prochaines années sur le cuivre, à la fois pour des raisons scientifiques et pratiques (optimisation du temps de faisceau) puisque cet élément est également étudié par Anthony Matynia et Thomas Lenoir. Des premières mesures ont été réalisées au printemps sur des oxydes de manganèse modèles synthétisés au laboratoire. Le but est de caractériser dans un premier temps l'ensemble des sites cristallographiques sur lesquels le cuivre est susceptible de se fixer. Puis nous étudierons des échantillons naturels représentatifs des principales formes de piégeage du cuivre en milieu marin. Le milieu continental est de ce point de vue moins intéressant car le cuivre y est fixé principalement à la matière organique, dans une moindre mesure aux argiles, et marginalement aux oxydes de Mn (cf. projets d'Anthony Matynia et de Thomas Lenoir).

Quatre composés modèles ont été étudiés (Figure):

- + une todorokite substituée
- + une birnessite triclinique substituée
- + deux birnessites turbostratiques (également dénommées δMnO_2 et vernadite) sur lesquelles du cuivre a été adsorbé à pH 5 et rapports Cu/Mn = 0.26% et 1.26%.

L'analyse des résultats confirme que l'environnement structural du cuivre est différent dans le tectomanganate et les deux birnessites, et donc qu'il sera possible de distinguer ces trois porteurs dans les échantillons naturels. Cependant, les spectres des deux $\delta\text{-MnO}_2$ sont identiques, ce qui était inattendu. A pH 5, le nickel est fixé à l'aplomb des sites lacunaires ($^{\text{VI}}\text{TC}$) à basse concentration (faible taux de recouvrement surfacique), puis sur les sites de bordure de feuillet (E) à concentration plus élevée. Par contre le cuivre semble s'adsorber indifféremment sur les deux sites à basse (Cu/Mn=0.26%) et moyenne (Cu/Mn=1.26%) concentration, à en juger par la similitude des TF de δMnO_2 -0.28% et δMnO_2 -1.26%. Il existe cependant une ambiguïté sur la localisation du complexe E (distance Cu-Mn courte): a priori il serait situé en bordure de feuillet, mais une diffusion des atomes de cuivre à l'intérieur des sites vacants du feuillet MnO_2 n'est pas exclue. Dans le cas du nickel ce mécanisme se produit à pH 7 lorsque la densité de protons interfoliaires est moindre. Comme le cuivre est plus hydrolysable que le nickel, il n'est pas impossible qu'il se produise ici à plus bas pH. Pour répondre à cette question, il faudrait, (i), varier la densité relative des sites de bordure et des lacunes (cristallinité de la birnessite) et, (ii), adsorber du cuivre à pH 7.



Production scientifique 2007 sur ce thème de recherche

- Bodeï S., Manceau A., Geoffroy N., Baronnet A., Buatier M. (2007) Formation of todorokite from vernadite in Ni-rich hemipelagic sediments. *Geochimica et Cosmochimica Acta*, sous presse
- Manceau A., Lanson M., Geoffroy N. (2007) Natural speciation of Ni, Zn, Ba and As in ferromanganese coatings on quartz using X-ray fluorescence, absorption, and diffraction. *Geochimica et Cosmochimica Acta*, 71, 95-128.
- Manceau A., Kersten M., Marcus M.A., Geoffroy N., Granina L. (2007) Ba and Ni speciation in a nodule of binary Mn oxide phase composition from Lake Baikal. *Geochimica et Cosmochimica Acta*, 71, 1967-1981.
- Takahashi Y., Manceau A., Geoffroy N., Marcus M.A., Usui, A. (2007) Chemical and structural control of the partitioning of Co, Ce, and Pb in marine ferromanganese oxides. *Geochimica et Cosmochimica Acta*, 71, 984-1008

Autres publications sur des expériences FAME-ESRF

- Diesing W.E., Sinaj S., Sarret G., Manceau A., Flura T., Demaria P., Siegenthaler A., Sappin-Didier V., Frossard E. (2007) Zinc speciation and isotopic exchangeability in soils polluted with heavy metals. *European Journal of Soil Science*, sous presse.
- Manceau A., Nagy K.L., Marcus M.A., Lanson M., Geoffroy N., Jacquet T., Kirpichtchikova T. (2007) Formation of metallic copper nanoparticles at the soil-root interface. *Environmental Science & Technology*, Soumis.
- Schlegel M.L., Manceau A. (2007) Zn incorporation in hydroxy-Al- and Keggin Al₁₃-intercalated montmorillonite: a powder and polarized EXAFS study. *Environmental Science and Technology*, 41, 1942-1948.
- Straczek A., Sarret G., Manceau A., Hinsinger P., Jaillard B. (2007) Zinc distribution and speciation in roots of various genotypes of tobacco exposed to Zn. *Environmental and Experimental Botany*. Soumis.

Communications sur ce thème de recherche

Conférences invitées (Keynote Lectures):

- 2008** Manceau A.: *Geochemistry of the Earth's Surface 8*. August 12-22, London.
Manceau A.: Illuminating the complex world of environmental materials with bright synchrotron light. *School on Synchrotron X-ray and IR Methods Focusing on Environmental Sciences*. January 21-23, ANKA, Karlsruhe.
- 2007** Manceau A., Lanson B., Marcus M.A., Nagy K.L.: Multiscale view of trace metal speciation in the rhizosphere. *Annual meeting of the Soil Science Society of America (SSSA)*, Nov. 4-8, New Orleans, Louisiana.

Communications orales:

- 2007** Lenoir T., Lanson M., Geoffroy N., Singh H., Manceau A.: Speciation of Cu in the rhizosphere of paddy soils impacted by the exploitation of a porphyry copper deposit. *Rhizosphere 2*, Montpellier, August 26-31.
- Vespa M., Lanson M., Geoffroy N., Marcus M.A., Manceau A.: Speciation of Pb and Zn in contaminated soils by micro XRF, XRD and XAS. *Frontiers in Mineral Sciences*, Cambridge, June 26-28.

Formation of todorokite from vernadite in Ni-rich hemipelagic sediments

Sabine Bodeï, Alain Manceau, Nicolas Geoffroy, Alain Baronnet, and Martine Buatier

ABSTRACT

Todorokite is considered to form from vernadite in nature and commonly concentrates nickel. However, this mineralogical transformation has never been imaged nor explained mechanistically, and its effect on the

uptake of nickel has never been quantified at the molecular-level. We have characterized these reactions at the macroscopic, microscopic and nanoscopic scales in a marine manganese concretion by combining transmission electron microscopy, electron and X-ray microprobe analysis, powder and micro X-ray diffraction, and Mn and Ni K-edge EXAFS spectroscopy. The concretion was collected during the Ticoflux II expedition near the Nicoya Peninsula, Costa Rica, and is representative of Mn deposits in hemipelagic sediments. It consists of 5 to 25 μm aggregates, shaped like sea-urchins, with a core of 7 \AA -vernadite (1.0 wt. % Ni), a rim of 10 \AA -vernadite (3.8 wt. % Ni), and an outermost region of todorokite fibers (1.9 wt. % Ni) that extend outwards. The crystallites of 7 \AA -vernadite are single- to bi-layered, with hexagonal layer symmetry ($a = b = 2.83 \text{ \AA}$), and an average structural formula of

$\text{Mg}_{0.08}^{2+} \text{Ca}_{0.01}^{2+} \text{K}_{0.01}^{+} \left[\text{Mn}_{0.943}^{4+} \text{Vac}_{0.037} \text{Ni}_{0.02}^{2+} \right] \text{O}_2 \cdot n\text{H}_2\text{O}$. The crystallites of 10 \AA -vernadite contain 10 to 20

layers semi-coherently stacked in the ab plane and uniformly separated in the [001] direction by $\sim 9 \text{ \AA}$ due to the intercalation of hydrated Mg^{2+} cations. The average structural formula of 10 \AA -vernadite is

$\text{Mg}_{0.09}^{2+} \text{Ca}_{0.015}^{2+} \text{K}_{0.01}^{+} \left[\text{Mn}_{0.91}^{4+} \text{Vac}_{0.02} \text{Ni}_{0.07}^{2+} \right] \text{O}_2 \cdot n\text{H}_2\text{O}$ if the layers contain vacancy sites, or

alternately $\text{Mg}_{0.09}^{2+} \text{Ca}_{0.015}^{2+} \text{K}_{0.01}^{+} \left[\text{Mn}_{0.85}^{4+} \text{Mn}_{0.08}^{3+} \text{Ni}_{0.07}^{2+} \right] \text{O}_2 \cdot n\text{H}_2\text{O}$, if they contain Mn^{3+} . The average formula

of todorokite is $\text{Mg}_{0.08}^{2+} \text{Ca}_{0.01}^{2+} \text{K}_{0.01}^{+} \left[\text{Mn}_{0.84}^{4+} \text{Mn}_{0.13}^{3+} \text{Ni}_{0.03}^{2+} \right] \text{O}_2 \cdot n\text{H}_2\text{O}$.

A genetic model is proposed based on combining these new data with previously published results. The thermodynamically unstable 7 \AA -vernadite transforms via dissolution-recrystallization to semi-ordered Mg-rich 10 \AA -vernadite. Nickel is released from dissolved biogenic silica or reduced organic matter, and taken up mainly in the Mn layer of 10 \AA -vernadite. Interlayer magnesium serves as a template to the further topotactic transformation of 10 \AA -vernadite to todorokite. The dimension of the todorokite tunnels in the [001] direction is uniform and determined by the size of the hydrated Mg^{2+} ion (8.6 \AA). The tunnel dimension in the [100] direction depends on the density of Mg^{2+} in the interlayer and the superstructure of the phylломanganate layer. If the parent phylломanganate contains high amounts of Mg^{2+} (i.e., high layer charge), or Mn^{3+} and Mn^{4+} cations ordered following the Mn^{3+} - Mn^{4+} - Mn^{4+} sequence as in synthetic triclinic birnessite, then the tunnel dimension is ideally 3 x 3 octahedral chain widths in both crystallographic directions. Otherwise, the tunnel dimension is incoherent in the [100] direction (i.e., T(3, n) tunnel structure), as has been observed in all natural todorokites. Natural todorokite is defective because the precursor natural phylломanganates either have a layer charge deficit below 0.33e per octahedral site, or rarely are triclinic birnessite. The abundance of Mg in seawater and its key role in converting phylломanganate to tectomanganate with T(3, n) tunnel structure explain why todorokite is common in marine ferromanganese oxides, and seldom present in terrestrial environments. The topotactic phase transformation described here is the only known route to todorokite crystallization. This implies that all natural todorokites may be authigenic because they are formed *in situ* from a phylломanganate precursor.

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 \AA phylломanganate) and two-water layer (10 \AA phylломanganate) crystallites. In one population, 7 \AA layers dominate, and in the other 10 \AA 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 $^{VI}Zn/^{IV}Zn$ 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 Mn^{4+} vacancies (i.e., no Mn^{3+} for 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.

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 phylломanganate (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.

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.

Formation of metallic copper nanoparticles at the soil-root interface

ABSTRACT

Copper is an essential element in the cellular electron-transport chain, but as a free ion can catalyze production of damaging radicals. Thus, all life forms attempt to prevent copper toxicity. Plants diminish excess copper in two structural regions: rare hyperaccumulators bind cationic copper to organic ligands in subaerial tissues, whereas widespread metal-tolerant plants segregate copper dominantly in roots by mechanisms thought to be analogous. Here we show using synchrotron microanalyses that common wetlands plants *Phragmites australis* and *Iris pseudoacorus* transform copper into metallic nanoparticles in and near roots with evidence of assistance by endomycorrhizal fungi when grown in contaminated soil in the natural environment. Biomolecular responses to oxidative stress, similar to reactions used to abiotically synthesize Cu^0 nanostructures of controlled size and shape, likely cause the transformation. This newly-identified mode of copper biomineralization by plant roots under copper stress may be common in oxygenated environments.