Geophysical Research Abstracts,
Vol. 11, EGU2009-12261, 2009
EGU General Assembly 2009

Synchrotron-based redox behavior of chromium during weathering of ultramafic rocks in New-Caledonia

Dr. JUILLOT (1), Dr. FANDEUR (1), Dr. FRITSCH (1), Dr. MORIN (1), Dr. OLIVI (2), Dr. WEBB (3), Dr. HAZEMANN (4), Dr. AMBROSI (5), Dr. BROWN Jr (3,6)

(1) IMPMC - UMR CNRS 759, Universite Pierre et Marie Curie - Universite Paris-Diderot - IPGP, 140 Rue de Lourmel, 75015 Paris, France , (2) Sincrotrone Trieste (ELETTRA), Area Science Park, Strada Statale, 34012 Basovizza,Trieste, Italy, (3) Stanford Synchrotron Radiation Laboratory (SSRL), 2575 Sand Hill Road, Menlo Park, California, 94025, USA, (4) European Synchrotron Radiation Facility (ESRF), BP 220, F-38043 Grenoble, France, (5) CEREGE-CNRS UMR 6635, Universite Aix-Marseille III, BP 80 13545 Aix-En-Provence Cedex 4, France, (6) Department of Geological & Environmental Sciences, Stanford University, Stanford CA 94305-2115, USA

In New-Caledonia, deep weathering of ultramafic rocks (peridotites) has lead to the development of thick lateritic regoliths where Ni, Cr, Co and Mn can exhibit concentration up to several wt%. Such a large occurrence of these potentially toxic elements can represent serious risks for the environmental quality of this '' biodiversity hotspot" and actual risk assessment relies on our capacity at characterizing the natural cycling of these elements. The present study reports the results of a detailed XANES analysis on the redox chemistry of Cr along a 64 meters depth lateritic regolith developed in the ultramafic rocks of the Koniambo outcrops located on the western coast of New Caledonia.

In a first step, bulk XAS data at both the Cr and Mn K-edges have been used to evidence a remarkable correlation between the occurrence of Mn(III,IV)-oxides (mainly asbolane) and that of Cr(VI), at the scale of the studied regolith (Fandeur et al., 2009a). Since Cr mainly occurs as Cr(III)-bearing silicates in the ultramafic bedrock, such a correlation strongly suggests an oxidation of the fraction of Cr(III) released upon the weathering of these silicates to Cr(VI) by the Mn(III,IV)-oxides, as already demonstrated in laboratory studies (Oze et al., 2008). In a second step, μ-XANES mapping of the Cr redox at the boundary between Mn(III,IV)-oxides and Fe(III)-oxyhydroxides (mainly goethite) allowed to depict the actual behavior of Cr(VI) after oxidation. Results indicate an association of Cr(VI) with both Mn-oxides and Fe-oxyhydroxides which suggests that, after oxidation of Cr(III) to Cr(VI) by the Mn(III,IV)-oxides, part of oxidized chromium is desorbed from these Mn-oxides and transported to the surrounding Fe-oxyhydroxides where it accumulates through sorption reactions (Fandeur et al., 2009b). Such a redox-sorption pathway has been confirmed by reacting aqueous Cr(III) with birnessite alone or with a mixture of birnessite and goethite during time-resolved laboratory experiments.

This complex sorption/oxidation/desorption/re-sorption pathway suggests that, in lateritic regoliths, the enhancement of the mobility of Cr possibly induced by its oxidation after sorption on Mn(III,IV)-oxides could be significantly limited by sorption of Cr(VI) onto surrounding Fe(III)-oxyhydroxides.

This work has been supported by the French ANR-ECCO program.

References

Fandeur D., Juillot F., Morin G., Olivi L., Cognigni A., Webb S., Ambrosi J.P., Fritsch E. and Brown Jr. G.E. (2009a). XANES evidence for oxidation of Cr(III) to Cr(VI) by Mn-oxides in a lateritic regolith developed on serpentinized ultramafic rocks in New Caledonia. Environmental Science and Technology, submitted.

Fandeur D., Juillot F., Morin G., Webb S., Hazemann J.L., Proux O., Olivi L., Cognigni A., Ambrosi J.P., Fritsch E., Guyot F. and Brown Jr G.E. (2009b). Crystal-chemistry of Cr and Mn and specific behavior of Cr(VI)

after oxidation by Mn-oxides along a lateritic regolith from New Caledonia. Geochimica Cosmochimica Acta, submitted.

Oze, C.; Bird, D. K.; Fendorf, S. Genesis of hexavalent chromium from natural sources in soil and groundwater. Proc. Nat. Acad. Sci. 2007, 104, 6544-6549.