

## EXAFS analysis of crystal chemistry of Ni in a lateritic weathering profile from New Caledonia

G. DUBLET<sup>\*1</sup>, F. JUILLOT<sup>1</sup>, G. MORIN<sup>1</sup>, E. FRITSCH<sup>1</sup>,  
D. FANDEUR<sup>1</sup>, G. ONA-NGUEMA<sup>1</sup> AND G. BROWN  
JR.<sup>2,3</sup>

<sup>1</sup>Institut de Minéralogie et de Physique des Milieux Condensés (IMPMC), UMR CNRS 7590, UMR IRD 206, Université Pierre et Marie Curie, Université Paris Diderot, IPGP, 2 Place Jussieu, 75005 Paris, France, (\* presenting author)

[gabrielle.dublet@impmc.upmc.fr](mailto:gabrielle.dublet@impmc.upmc.fr)

<sup>2</sup>Stanford Synchrotron Radiation Laboratory, 2575 Sand Hill Road, Menlo Park, California, 94025, USA

<sup>3</sup>Department of Geological & Environmental Sciences, Stanford University, Stanford CA 94305-2115, USA

Weathering of ultramafic rocks under tropical conditions in New Caledonia yield lateritic profiles where metals, mainly Ni, are concentrated to economically valuable contents. The vertical distribution of Ni in these lateritic ores was investigated by analysing Ni K-edge EXAFS data along a 64 m depth lateritic weathering profile, to determine the quantitative role of the various minerals on the crystal-chemical behaviour of Ni upon weathering of ultramafic rocks. Three main units were identified from the bottom to the top of the weathering profile, i.e. the bedrock, the saprolite and the laterite. Our results show that Ni is mainly hosted by primary silicate minerals (olivine and serpentine) in the bedrock, while it is mainly incorporated in secondary phyllosilicates and Fe-oxides (goethite) in the saprolite unit, and in goethite within the upper laterite unit. A small part of Ni is also hosted by Mn-oxides at the bottom part of the laterite unit (transition laterite) which is rich in Mn-oxides. Actual modes of association of Ni with all these mineral species yield interesting information about the behaviour of this element during the lateritic differentiation. Ni content and distribution change within the phyllosilicates from the bedrock to the overlying saprolite, suggesting that several generations of these minerals have formed under different weathering conditions. Moreover, the ubiquitous occurrence of Ni-bearing goethite along the studied lateritic regolith emphasizes the major role of this mineral species on Ni speciation at the different weathering stages. This result suggests that Fe-oxides represent the ultimate host for Ni upon tropical weathering of ultramafic rocks in New Caledonia.

## Trace metal complexation and dissolution by the triscatecholate siderophore protochelin

OWEN W. DUCKWORTH<sup>1,\*</sup>, JAMES M. HARRINGTON<sup>1,2</sup>,  
MARTIN M. AKAFIA<sup>1</sup>, JOHN R. BARGAR<sup>3</sup>, ANDRZEJ A.  
JARZECKI<sup>4</sup>, JAMES G. ROBERTS<sup>5</sup>, LESLIE A. SOMBERS<sup>5</sup>

<sup>1</sup>Soil Science Department, North Carolina State University, Raleigh, NC 27695-7619, USA, [owen\\_duckworth@ncsu.edu](mailto:owen_duckworth@ncsu.edu) (\* presenting author)

<sup>2</sup>U.S. Environmental Protection Agency, National Exposure Research Laboratory, Research Triangle Park, NC 27711

<sup>3</sup>Stanford Synchrotron Radiation Lightsource, 2575 Sand Hill Rd, Bldg 137, MS 69, Menlo Park, CA, 94025 USA

<sup>4</sup>Chemistry Department, the Brooklyn College and the Graduate School of the City University of New York, Brooklyn, NY 11210, USA

<sup>5</sup>Chemistry Department, North Carolina State University, Raleigh, NC 27695-8204, USA

Recent evidence has shown that siderophores, biogenic agents generally viewed as iron uptake agents, may play significant roles in the biogeochemical cycling and biological uptake of metals other than iron. For example, the triscatecholate siderophore protochelin, which is produced by the diazotrophic bacteria *Azotobacter vinelandii*, has been implicated in the uptake of non-ferrous metals [1]. To better understand the effect of catechol siderophores on metal cycling and uptake, we examined the solution chemistry of protochelin, its ability to promote the dissolution of metal oxides, and structure and stability of complexes with environmentally relevant trace metals.

Free protochelin was found to be unstable, decomposing in solution on the timescale of hours to days. Additionally, it is sparingly soluble at pH < 7.5. Electrochemical measurements of protochelin and metal-protochelin complexes revealed a ligand half-wave potential of 200 mV, but no electrochemical activity was observed for the metal centers. These results help to explain patterns in the rates and products of protochelin-promoted dissolution of metal hydroxides.

The structure and reactivity of metal-protochelin complexes was probed by spectroscopic, computational, and chemical methods. The Fe(III)Proto<sup>3-</sup> complex exhibits a shift in coordination mode at circumneutral to acidic pH, as has been observed for structurally related siderophores [2]. The Mn(III)Proto<sup>3-</sup> complex was found to have a stability constant approximately three orders of magnitude lower than for Fe(III)Proto<sup>3-</sup>. Cobalt-protochelin complexes undergo redox cycling of Co with concomitant siderophore degradation. Structural parameters derived from computational and spectroscopic methods provide insights into the stability of the metal-protochelin complexes. These results suggest that common metals may affect the biological uptake of metals by protochelin, and that unique properties of the siderophore may affect its dissolution reactivity and the mechanisms of intracellular metal release.

[1] Kraepiel (2009) *Biometals* **22**, 573-581. [2] Abergel (2006) *J. Am. Chem. Soc.* **128**, 8920-8931.