



Experiment title: Speciation of manganese in plants from New Caledonian lateritic soils

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30-02-938

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BM30b/fa
me

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Local contact(s):
Olivier PROUX

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REPORT

Aims of the experiment and scientific background

In New Caledonia, as a result of the long-term lateritic weathering of ultramafic rocks Ni but also Cr, Co and Mn have been concentrated in the thick regolith and in soils. With such high metal content, New Caledonian soils are deficient in nutrients (N, P, K) and unbalanced for the Ca/Mg ratio. Moreover, about 75 % of its flora is endemic [1]. Under these particular ecological conditions, New Caledonia is recognized as a hot-spot of biodiversity [2] and conservation is a priority. Even if opening new mine is restricted, one of the opportunities for the companies is to retreat mine tailing with phytoextraction technique. In the case of old mine, when the concentration of metals is far too low to continue the extraction, then mining companies are conducted to revegetate mine dump with endemic plant to restore the natural biodiversity. Both purposes are very challenging since, except for nickel, very little is known concerning the strategies developed by plants to grow on such high metal content soils. For example, for Mn (one of the most abundant metal after Ni) even basic information are unknown (Mn concentration, localization and speciation [3]).

Our research group has recently found that two of the major shrubs of the New Caledonian so-called 'maquis minier', *Tristaniopsis guillainii* and *Tristaniopsis calobuxus*, can tolerate manganese. They accumulate up to 1500 mg Mn/kg dry matter (DM) in their leaves, although only 600 mg Mn/kg DM are stored in their roots. Our aim is to determine the Mn speciation during its transfer and transformation from soil, root, twig and leaves in order to better understand its mobility through the plant.

Experiments

Field experiments were conducted in February 2007 in the Koniambo Massif, an isolated ultramafic massif of the West Coast of New Caledonia (20°59'S, 164°49'E). The study site was located on the Pandanus watershed. *Tristaniopsis guillainii* (TG) and *T. calobuxus* (TC), two major phylogenetically-close trees of the New Caledonian so-called 'maquis minier' were sampled as Mn-accumulators from the Myrtaceae family. *Phyllanthus cornutus* (PC) and *P. serpentinus* (PS), two endemic and frequent shrubs, were sampled as Mn-accumulator and Mn and Ni-hyperaccumulator respectively from the Euphorbiaceae family. The plants were chosen along an altitudinal sequence of soils, at site B (750 m) and site D (450 m), in order to test the effect of soil variability on bioaccumulated Mn speciation. On both sites, *Tristaniopsis* and *Phyllanthus* species lived together. The soils were coming from a typical lateritic alteration mantle truncated in the laterite at site B and in the transition laterite at site D.

At each site and for each species, five plants were sampled. For each plant, leaves (L), stems, and roots were collected, as well as their associated rhizosphere (RS) and bulk soils (BS). Rhizosphere soil was the soil surrounding the roots up to 5 cm of distance because of their nodular nature whereas bulk soil was at approximately 40 cm from the roots, in order to not be influenced by the sampled plant. Each plant part was rinsed with deionized water and separated in two halves. One half was oven-dried at 318 K during 48 h whereas the other half was cryogenized: it was frozen at 193 K for one week, transported in dry ice (193 K), and then stored at 248 K until analysis. A great care was taken to maintain samples cryogenized from field to experiments. This cryo-procedure was developed in order to avoid any possible dehydration of those fragile samples and to minimize sample preparation which could lead to a modification of metal speciation in plants.

Mn K-edge EXAFS and XANES measurements on plant and soil samples and Mn K-edge XANES measurements on reference compounds were performed between 5 and 10 K (helium cryostat), to avoid any possible dehydration or oxidation of samples, and improve the signal/noise ratio by decreasing the thermal motion of atoms. They were carried out on beamline BM30B/FAME with a Si(220) crystal monochromator. The ring was operating at 6 GeV and 200 mA. The XAS spectra were all recorded in fluorescence mode, using a thirty-element solid-state germanium detector (Canberra, CT, USA).

During the session no specific problem on the beamline or the ring occurred.

Results

A diversified series of potential Mn-bearing phases was chosen with local environments representative of a soil (Mn(II)-, Mn(III)-, Mn(IV)-oxides) or a leaf (mainly Mn(II)-carboxylates), as referred in the literature. The reference library was completed with some organic compounds of diverse oxidation states. XAS spectra corresponding to these references were classified according to their Mn-oxidation state and kind of ligands into 6 categories from bottom to top (Figure 1c for XANES and Figure 2.2b for EXAFS): (i) Mn(VII) as potassium permanganate, (ii) Mn(IV)-oxide, (iii) Mn(III) references, (iv) Mn(II)-carbonate, -phthalocyanine, and -oxide, (v) Mn(II) bound to bidentate organic ligands, and (vi) Mn(II) bound to monodentate organic ligands.

XANES and EXAFS data were first treated with a principal components analysis (PCA) carried out using SIXPack suite (Webb, 2005). The number of components needed (i.e. of references) was evaluated using the empirical indicator function (IND value), which is minimal for the statistically right number of references to use. Then, statistically suitable references for the analysis of XANES and EXAFS spectra of leaves and soils were identified using the target transformation analysis via the goodness of target transform estimated by the χ^2 (normalized sum of the squared residuals) and R (measure of the percent misfit) parameters. Subsequently, the proportions of Mn-species in experimental spectra were determined by the least-squares linear combination fitting (LCF) method. All possible single component to two component fits were calculated. The fit quality was measured by the normalized sum of the squared residuals (NSSR) parameter (e.g. Isaure et al., 2002; Jacquat et al., 2009):

From the single-component fit with the lowest NSSR, the second component was added as long as the NSSR of the best two-component fit was at least 10 % below the NSSR of the one-component fit, because the accepted sensitivity of metal speciation by this multicomponent spectral-fitting approach is about 10 % (e.g. Isaure et al., 2002; Manceau et al., 2003; Jacquat et al., 2009).

Results presented in table 1 clearly indicate that Mn in soil is mainly under the 3+ and 4+ redox state while in leaves only Mn²⁺ is found. This results shown the active role of plants on the transfer of Mn from soil to leaves.

In the case of leaves whatever the plant, the site, no great differences were found. In all case the speciation of Mn is composed by Mn carboxylic complexes. The main difference concerned the proportion of monodentate v.s bidentate complexing ligand. This surprising result tends to indicate that the mechanisms of plant adaptation are not so different and that the soil type does not influence strongly the transfer.

EXAFS data treatment is still under progress.

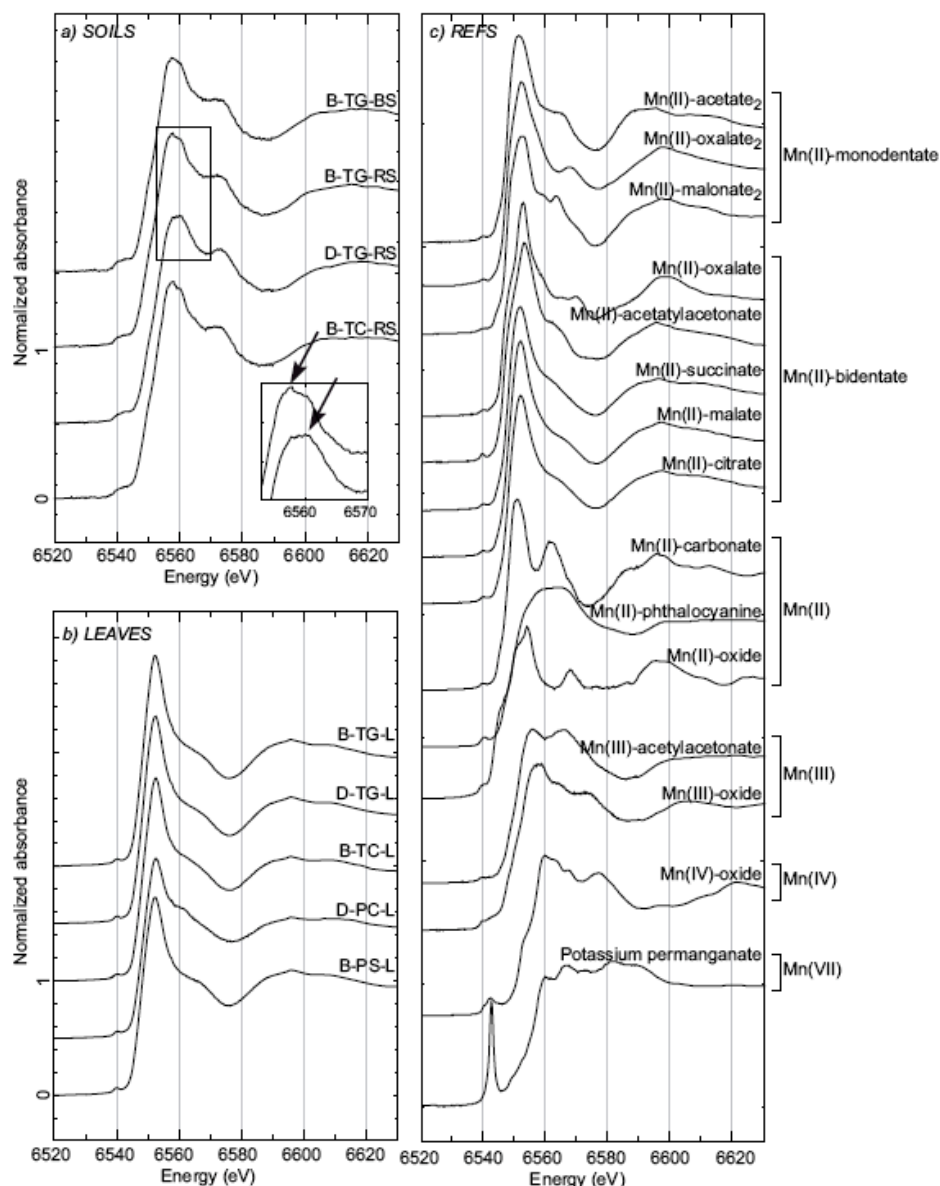


Figure 1: Mn-K edge normalized XANES spectra of a) soil samples, b) leaf samples, and c) reference compounds

Type	Sample	Compound 1 % Compound 1 % + Compound 2 %	R_factor	Decrease of R_factor
SOILS	B-TG-BS	Mn(III)-oxide 100 -	1.17.10 ⁻³	-
	B-TG-RS	Mn(III)-oxide 100 Mn(III)-oxide 100 + Mn(IV)-oxide 1	0.97.10 ⁻³ 0.90.10 ⁻³	8
	B-TC-RS	Mn(III)-oxide 100 -	1.29.10 ⁻³	-
	D-TG-RS	Mn(III)-oxide 100 Mn(III)-oxide 84 + Mn(IV)-oxide 17	2.15.10 ⁻³ 1.15.10 ⁻³	46
LEAVES	B-TG-L	Mn(II)-malate 100 Mn(II)-malate 100 + Mn(II)-oxalate ₂ 3	1.24.10 ⁻³ 0.32.10 ⁻³	74
	D-TG-L	Mn(II)-malate 100 Mn(II)-malate 99 + Mn(II)-oxalate ₂ 4	0.92.10 ⁻³ 0.29.10 ⁻³	68
	B-TC-L	Mn(II)-citrate 100 Mn(II)-citrate 100 + Mn(II)-oxalate ₂ 3	1.18.10 ⁻³ 0.46.10 ⁻³	61
	B-PC-L	Mn(II)-citrate 100 Mn(II)-citrate 99 + Mn(II)-oxalate ₂ 1	4.62.10 ⁻³ 4.62.10 ⁻³	0.1
	B-PS-L	Mn(II)-succinate 100 Mn(II)-succin. 74 + Mn(II)-oxalate ₂ 28	1.20.10 ⁻³ 0.68.10 ⁻³	43

Table 1: One-component and two-component fit results of XANES spectra determined by LCF for the four tested soils between 6 538 eV and 6 614 eV and the five tested leaves between

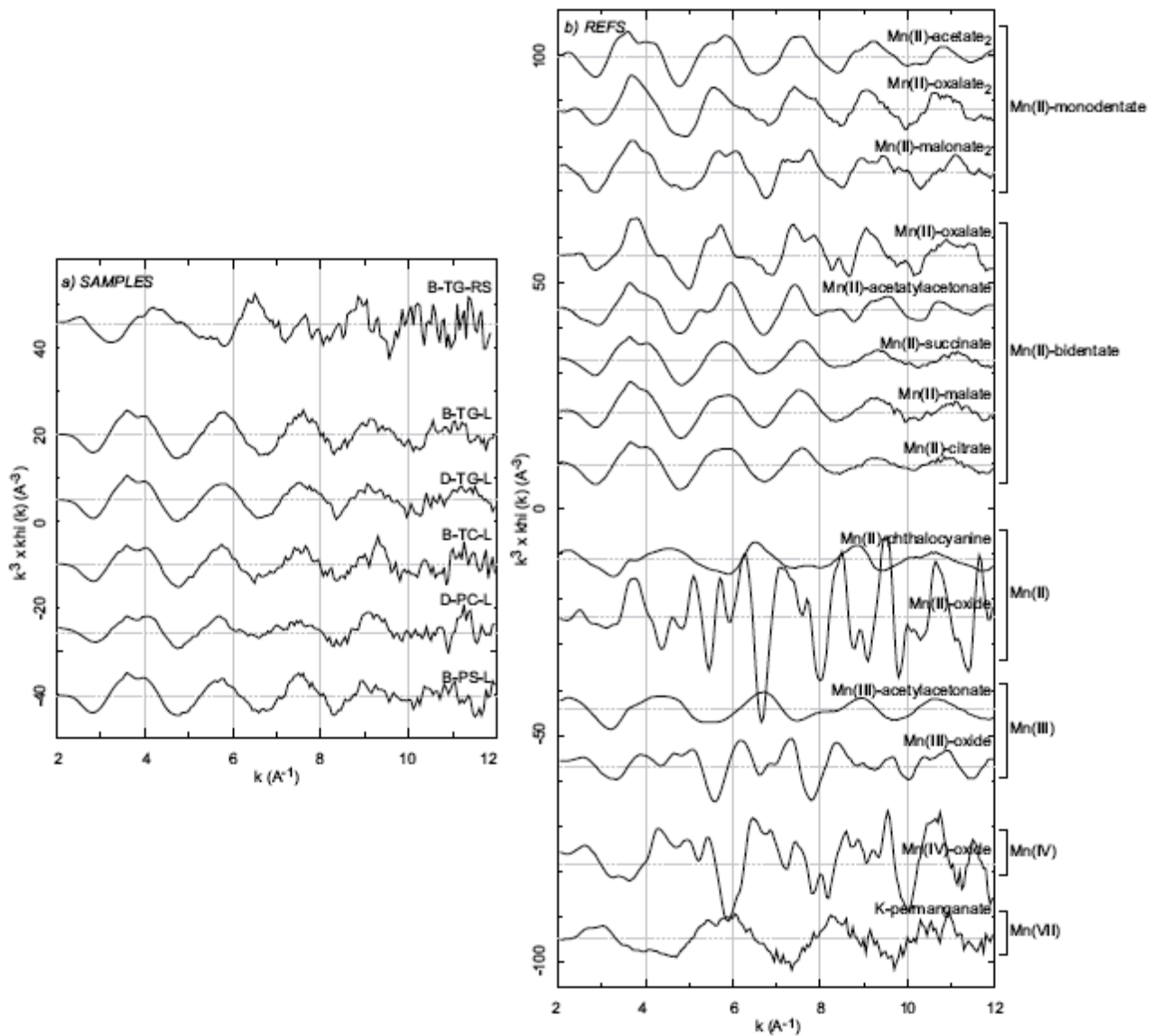


Figure 2 : Mn-K edge $k^3\chi(k)$ EXAFS spectra of a) soil and leaf samples, and b) reference Compounds

References

- [1]: Proctor J. 2003. Vegetation and soil and plant chemistry on ultramafic rocks in the tropical Far East. *Perspectives in Plant Ecology*. 6:1-2, 105-124.
- [2]: Myers N, Mittermeier RA, Mittermeier CG, da Fonseca GAB, Kent J. 2000. Biodiversity hotspots for conservation priorities. *Nature*. 403: 853-858.