	Experiment title: Spéciation of heavy metals (Cr and Ni) in soils from Reunion island : function of « nano-minerals ».	Experiment number: 30-02-664
Beamline: BM30B	Date of experiment: from: 13 July 2004 to: 16 July 2004	Date of report: 15/10/04
Shifts: 9	Local contact(s): Vivian NASSIF (e-mail: nassif@polycnrs-gre.fr)	<i>Received at ESRF:</i>
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Report:

Study of the agronomic and environmental consequences of the spreading of organic wastes (*i.e. all the organic residues and by-products produced by farming: surplus manure, unsold fruit and vegetables, etc.; agrifood industries: agrifood industry sludge, plant, animal and timber processing wastes, etc.; or municipal authorities: garden waste, sewage treatment station sludge and fats, food wastes, green algae, etc.*) is a scientific, technologic and economic challenge.

The environmental impact of such agricultural recycling practices still has to be controlled in order to avoid organic and inorganic contamination of natural resources. This is why the French legislation has set standard threshold values beyond which sewage sludge spreading is unauthorized. These thresholds are based on total sludge and soil heavy metal concentrations. Recently, we investigated the heavy metal content in soils of Réunion (volcanic island in the Indian Ocean) and observed that 60% of the studied samples had a Cr concentration above the threshold set by French legislation. We highlighted the close relationship between heavy metal concentrations in soils and volcanic parent materials. In Réunion, the use of sewage for agricultural applications could be prohibited due to the already high natural soilborne heavy metal concentrations, even though heavy metal concentrations in sewage sludge produced in Réunion are low. It would now be essential to undertake in-depth studies to determine the speciation and mobility of Cr in Réunion soils.

The aim of this project is to characterize the speciation of Cr within an andosol from Réunion. We used a new approach based on physical soil fractionation prior to speciation analyses. The objective was to separate the different minerals and organomineral complexes according to their density. These separations were performed to limit the number of Cr-bearing phases for each fraction and to facilitate the study of Cr speciation.

Experiment was conducted on beam line FAME (07-13/07-16 2004) with a Si (220) monochromator. The spectra were recorded in fluorescence mode using a 13-elements solid-state Ge detector (Canberra) for the least concentrated samples and measured in transmission mode with a diode for Cr-rich samples.

The quality of the data can be checked on Figure 1 for chromite mineral. This spectra was recorded with 2s by point and it clearly shows fine structure until $14,5 \text{ \AA}^{-1}$ thanks to low noise data.

For this study, it was fundamental to register spectra (XANES and EXAFS) Cr model compounds which are representatives of volcanic soils.

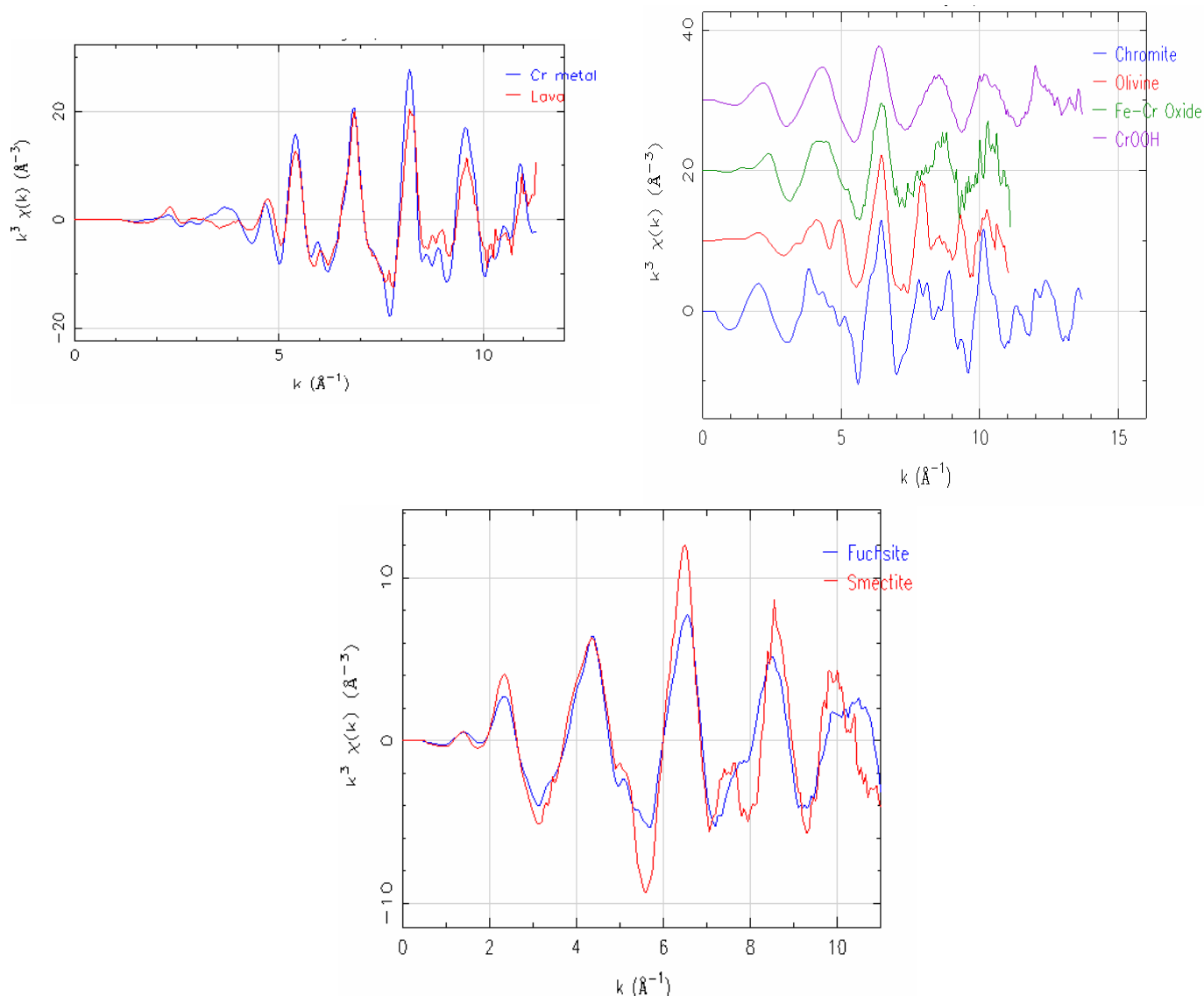


Figure 1 : EXAFS ($k^3\chi(k)$) spectra of mineralogical Cr model compounds.

The library of Cr model compounds consisted in selected minerals and synthetic compounds. The minerals were chromite (FeCr_2O_4), fuchsite ($\text{KCr}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$), stichtite

($\text{Mg}_6\text{Cr}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$), uvarovite ($\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$), eskolaite (Cr_2O_3), and smectite (octahedral substitution of Al for Cr). Fe-Cr oxyhydroxide were synthesized by coprecipitation of mixed 1M $\text{Fe}(\text{NO}_3)_3$ and 0.25M $\text{Cr}(\text{NO}_3)_3$ solutions (cf. Figure 1).

Cr K-edge X-ray absorption spectra of the densimetric soil fractions were recorded at room temperature. At first it is worth noting that the total concentration of chromium in the selected soil from Réunion is quite high (421 $\text{mg}\cdot\text{kg}^{-1}$) concerning the “average” content of Cr in non-contaminated soil, but quite low regarding the sensitivity of synchrotron X-ray beamlines. Moreover, the EXAFS spectrum of the bulk soil was disturbed by the presence of two edges: L_β of Ce and L_α of Nd (Figure 2). The fluorescence detector resolution (200 eV) was not sufficient to separate the fluorescence lines of Cr (5410 eV) with Ce and Nd (around 5200 eV). Nevertheless, the signal/noise ratio is high enough to interpret the data.

The EXAFS spectra of the densimetric soil fractions (Figure 3) are also disturbed by the presence of the two edges (Ce and Nd).

Nevertheless, the Cr-bearing components in the samples (bulk soil and densimetric fractions) are studying by first utilizing a PCA algorithm to determine the minimum number and type of probable components and then quantified from the experimental EXAFS spectra using a least-square linear combination fitting (LCF). This work is facilitated by the good knowledge of the mineralogy of the bulk soil and densimetric fractions.

To conclude, we should mention that it was not possible to study the same samples at K-Ni edge because we did not have enough time. Therefore, we would submit a new proposal to study the speciation of nickel in tropical soils.

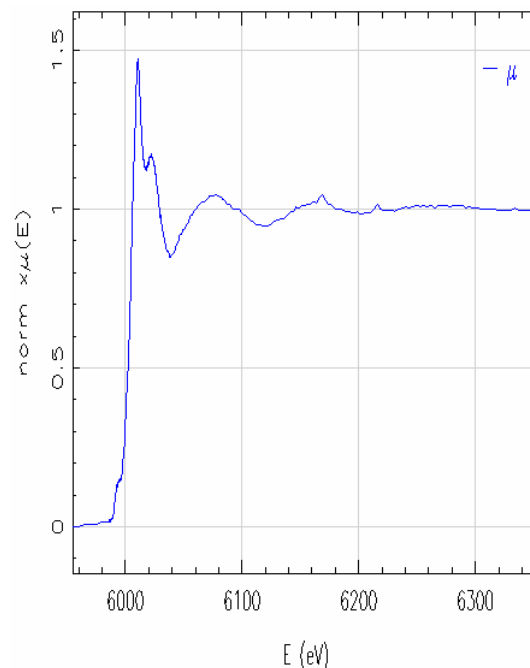


Figure 2 : EXAFS spectrum of the bulk soil

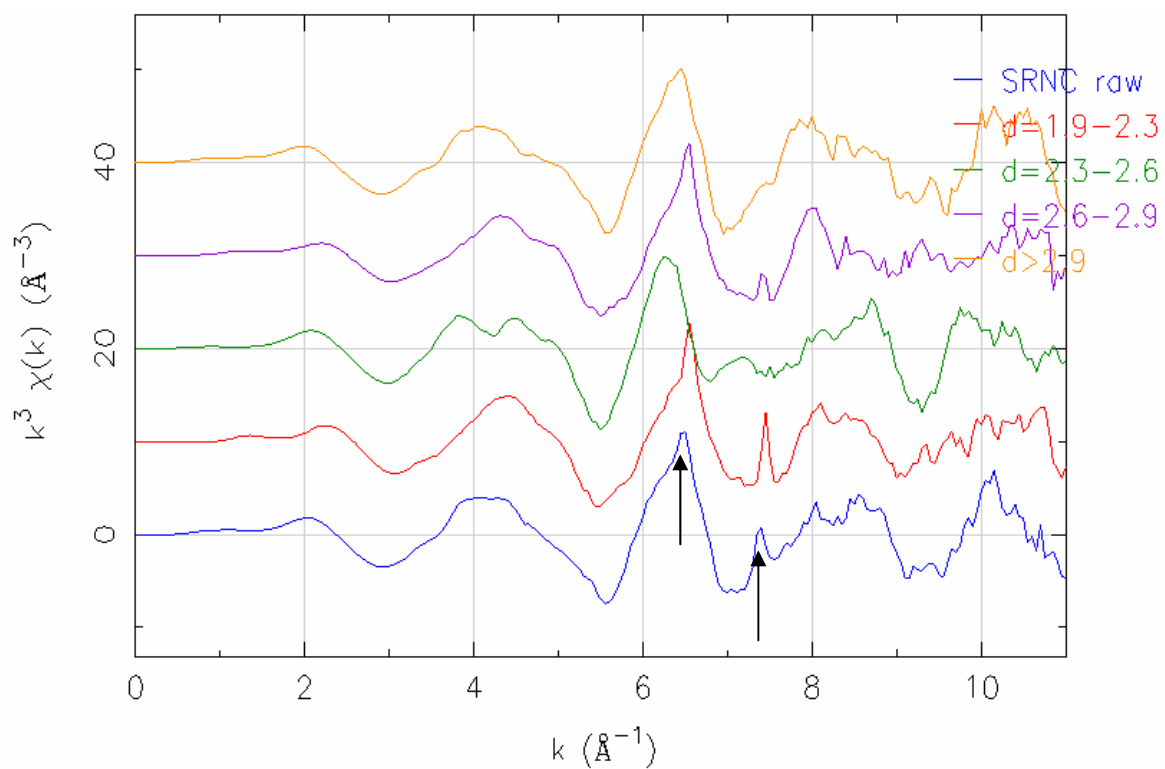


Figure 3 : EXAFS ($k^3\chi(k)$) spectra of bulk soil (SRNC raw) and densimetric soil fractions (d=1.9-2.3 ; d=2.3-2.6 ; d=2.6-2.9 et d>2.9).