



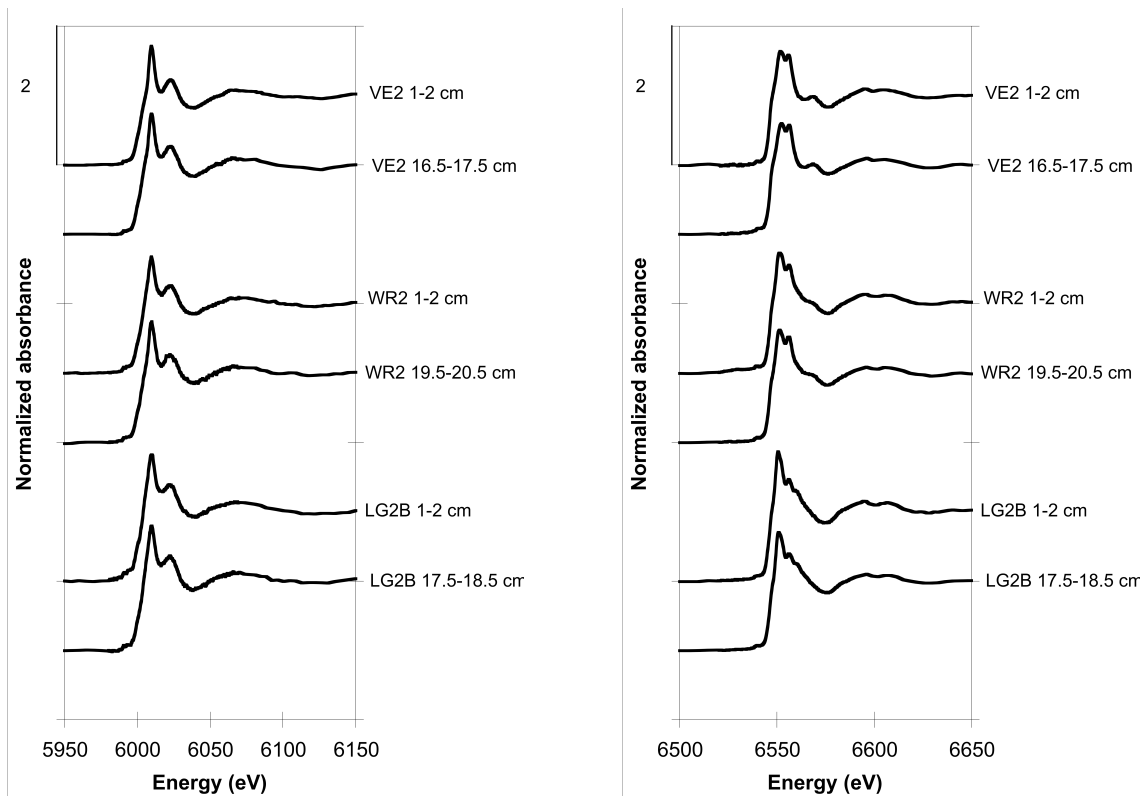
	Experiment title: <b>Nickel speciation and mobility in New Caledonian lagoon sediments</b>	<b>Experiment number:</b> EV-268
<b>Beamline:</b> BM30B	<b>Date of experiment:</b> from: 31 jan 2018 to: 06 février 2018	<b>Date of report:</b> September 4, 2020
<b>Shifts:</b>	<b>Local contact(s):</b> Isabelle Kieffer, Antonio Aguilar	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> <b>Guillaume Morin* IMPMC CNRS ; Jessica Brest* IMPMC CNRS ;</b> <b>Pauline Merrot* IMPMC UPMC, Farid Juillot IMPMC IRD</b>		

## Report:

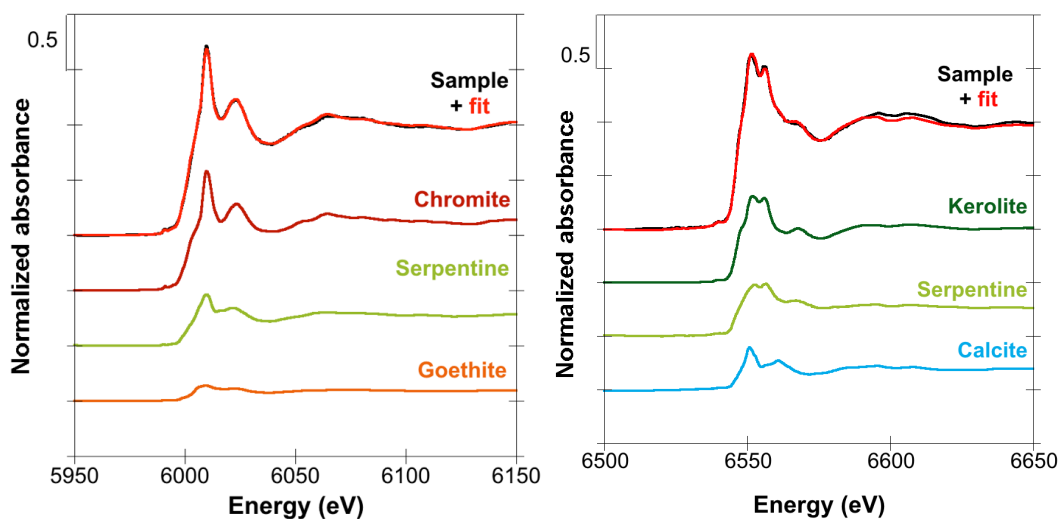
The proposal aimed at determining the bulk speciation of transition metals in sediments of the New Caledonia lagoon that is registered in the registered in UNESCO World Heritage list. Erosion of the massive lateritic Ni ores of New Caledonia represents a source of transition metals to the lagoon, which calls for a comprehensive understanding of the processes that control transition metal dispersion and immobilization in the lagoon ecosystem. Nickel and chromium are particularly addressed because of their potential toxicity. Iron and Manganese are also of interest since Fe and Mn-bearing minerals may be involved in the cycling of trace Ni and Cr metals. Although Ni was initially targeted for this proposal we more focused on Cr and Mn, and to a lesser extent Fe, during this beamtime since Ni data could be collected during another beamtime.

The 18 shifts beamtime on BM30B was a dedicated to the measurement of XAS data at the Mn, Cr and Fe K-edges in a series of samples from 3 sediment cores sampled in the Vavouto bay, located downstream of one of the largest lateritized ultramafic Ni-deposit in New Caledonia that contains up to 5wt% Cr<sub>2</sub>O<sub>3</sub>. We have determined Cr and Mn speciation across a shore-to-reef gradient in these lagoon sediments containing 220-1800 ppm Cr and 310-720 ppm Mn using XANES data collected in fluorescence detection mode at the Cr and Mn K-edges (Figure 1). In order to interpret metal speciation in the natural samples, XANES data were also collected on a large set of reference samples at both the Mn and Cr K-edge. Linear combination fitting (LCF) of Cr K-edge XANES data for the natural sediment samples shows that Cr is present only under its reduced form Cr(III), the less mobile and toxic form, mainly hosted by chromite (FeCr<sub>2</sub>O<sub>4</sub>), and to a lesser extent, by goethite ( $\alpha$ -FeOOH) and serpentine. The evolution of the Cr speciation from the shore to the reef could be interpreted as being due to the alteration of chromite into goethite. LCF analysis of Mn K-edge XANES data shows that this element is mainly present as Mn(II), hosted by phyllosilicates close to the shore and substituting for Ca(II) in marine carbonates when approaching the reef (Figure 2). These results have been submitted to publication in *Journal of Geochemical Exploration* (Merrot et al. submitted).

Part of the beamtime was also dedicated to collect XANES and EXAFS data at the Fe K-edge on a sample from the same lagoon, to complement a previous set of data on Ni and Fe speciation. These results have been included in an article published in *Science of the Total Environment* (Merrot et al. 2019).



**Figure 1.** Chromium and Manganese K-edge spectra of lagoon sediment core samples across a shore to reef transect (top – down in the figure) (From Merrot et al. submitted to *JGR* and Merrot PhD thesis)



**Figure 2.** Example of LCF fit of a Cr K-edge (left) and a Mn K-edge XANES spectrum of a sediment sample showing the dominant chromite contribution in Cr speciation and the dominant clay contribution in Mn speciation (From Merrot et al. submitted to *JGR* and Merrot PhD thesis).

## Publications :

Merrot P., Juillot F., Le Pape P., Lefebvre P., Brest J., Kieffer I., Menguy N., Viollier E., Fernandez J-M., Moreton B., Morin G. Comparative Cr and Mn speciation across a shore-to-reef gradient in lagoon sediments downstream of Cr-rich Ferralsols upon ultramafic rocks in New Caledonia. Submitted to *Journal of Geochemical Exploration*.

Merrot P., Juillot F., Noël V., Lefebvre P., Brest J., Menguy N., Guigner J.M., Blondeau M., Viollier E., Fernandez J.M., Moreton B., Bargar J.R., Morin G. (2019) Nickel and iron partitioning between clay minerals, Fe-oxides and Fe-sulfides in lagoon sediments from New Caledonia. *Science of the Total Environment* 689, 1212–1227. DOI: 10.1016/j.scitotenv.2019.06.274