

# REPORT ON PROJECT 30-02-899

## Crystal chemistry of chromium upon weathering of ultramafic rocks in New Caledonia: Speciation in the suspended matter of rivers

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This project was divided in two parts aimed at improving our understanding of the behavior of chromium upon weathering of ultramafic rocks in New Caledonia. The first objective was to assess the speciation of chromium in the suspended matter of a river related to a weathered lateritic profile where precedent spectroscopic investigations evidenced significant amounts of  $\text{Cr}^{6+}$  (up to 20 wt% of total chromium) in Mn-rich areas whereas no oxidized chromium could be detected in Mn-poor areas (Fandeur et al., 2008; 2009). The aim of this first part was to try to characterize the mechanisms of chromium solid transport (sorbed on vs. co-precipitated with mineral species, complexed to organic matter, ...) along the hydrographic network of the studied watershed. The second objective was focused on the identification of the crystal-chemistry of Cr after oxidation of  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$  by Mn-oxides. The aim of this second part was to try to emphasize the preferential sorption of  $\text{Cr}^{6+}$  onto Fe-oxides surfaces after oxidation of  $\text{Cr}^{3+}$  by Mn-oxides, which has been suspected on the basis of precedent spectroscopic investigations of samples from the weathered lateritic samples.

### Materials and methods

The samples analysed during the first part of the project are natural samples, which were collected along the flow path of the selected river. Although the chromium concentration of these samples (between 300 and 1500 mg/kg) was enough to register good quality EXAFS data, their very low amounts (around 15 mg) lead to a significant dilution within cellulose in order to prepare pellets thick enough to be handled. Consequently, only two of these samples of suspended matter could be analysed during these experiments.

The samples analysed during the second part of the project were obtained by reacting aqueous  $\text{Cr}^{3+}$  at pH 5 either with birnessite alone or with a mixture of 50wt% birnessite + 50wt% goethite during various length of time (from 7 minutes to 24 hours). The concentration of chromium in the reacting suspensions was  $10^{-5}$  mol.L<sup>-1</sup> and the mass of solid (either birnessite or birnessite+goethite in equal amounts) was 250 mg for each experiment. After the selected reacting time for each experiment, the solid and the supernatant were separated by ultra-centrifugation at 10,000 g during 30 minutes. The supernatant was conserved for ICP-AES analyses and the solid was washed three times with double-deionised water, at pH 5 to avoid desorption. Washed solid samples were air-dried and pressed as pellets for XAS experiments.

XANES and EXAFS experiments were performed at room temperature in fluorescence mode with a 30 elements solid-state Ge detector. The energy of the incident beam was monitored with a Si(220) double-crystal monochromator. The number of EXAFS scans ranged from 2 to 14 for the most dilute sample, and at least 2 XANES scans were collected for each sample.

### Results on the speciation of chromium in the suspended matter of a river related to a tropical weathered profile

A first comparison of the EXAFS spectra of the two analysed samples shows some differences, especially in the 8-10 Å<sup>-1</sup> k region (Figure 1). This first result indicates that chromium speciation in the suspended matter of the river changes along its flow path. Comparison of the EXAFS spectra of these two samples with those of samples from various depth in the lateritic weathered profile related to the river indicates that chromium speciation in the "upstream sample" is similar to that found around 41 meters depth in the profile (mainly Cr in Fe-oxides), whereas chromium speciation in the "downstream sample" is closer from the one found in the bedrock sample of the profile (Cr in silicates). These associations strongly suggest that the speciation of chromium in the suspended matter of the river is directly connected to the actual nature of the geological setting crossed by the river (more or less weathered ultramafic rocks). Such an hypothesis indicates that the speciation of chromium in the suspended matter of the river is mainly controlled by erosion processes.

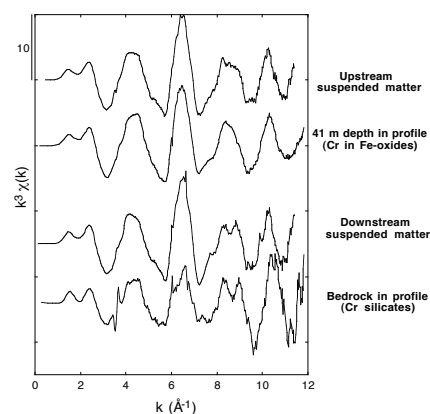


Figure 1: EXAFS spectra of the two samples of suspended matter compared to two samples from the lateritic weathered profile (i.e. the bedrock sample collected at 65meters depth and a sample collected at 41 meters depth).

## Results on the crystal-chemistry of $\text{Cr}^{6+}$ after oxidation by Mn-oxides

### Photon-induced redox reactions

XANES spectra obtained on  $\text{Cr}^{3+}$  or  $\text{Cr}^{6+}$  sorbed goethite or birnessite model compounds after various exposure times under the photon beam indicated some photon-induced redox reactions.

Comparison of the XANES spectrum of  $\text{Cr}^{6+}$  sorbed on goethite after immediate exposure to the photon beam or after 1 hour exposure shows a strong diminution of the pre-edge peak around 5993 eV, which is indicative of  $\text{Cr}^{6+}$  (Figure 2A). This strong diminution indicates that almost all initial  $\text{Cr}^{6+}$  has been reduced to  $\text{Cr}^{3+}$ . The kinetics of this photon-induced reduction has been followed by measuring the fluorescence intensity at 5993 eV on a non-exposed area during 1 hour (Figure 2B). The result of this experiment shows a 50% decrease of the fluorescence intensity within the first 800 seconds, which indicates a strong reduction of  $\text{Cr}^{6+}$  during this set of time. The stabilization of the fluorescence intensity at the end of the experiment (1 hour) suggests either that  $\text{Cr}^{6+}$  reduction has stopped (passivation mechanism ?) or that there is no more  $\text{Cr}^{6+}$  to be reduced.

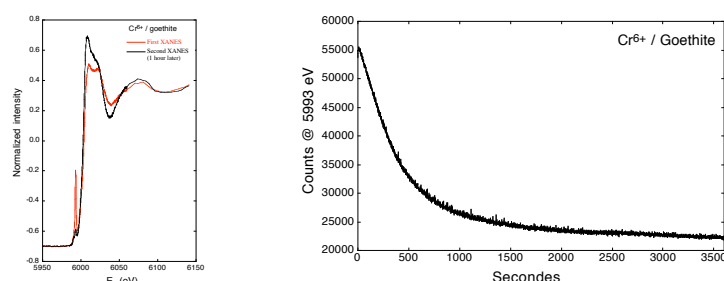


Figure 2: Kinetics of the photon-induced reduction of  $\text{Cr}^{6+}$  when sorbed on goethite.

Although this first kinetics experiment indicated a photon-induced reduction of  $\text{Cr}^{6+}$  sorbed on goethite, an opposite photon-induced oxidation has been evidenced for  $\text{Cr}^{6+}$  sorbed on birnessite. The kinetics of this photon-oxidation is displayed in Figure 3. It shows that the amount of oxidation within the first 800 seconds is lower than 5% of initial  $\text{Cr}^{6+}$ , which is much less than the 50% reduction observed for  $\text{Cr}^{6+}$  sorbed on goethite (Figure 2B).

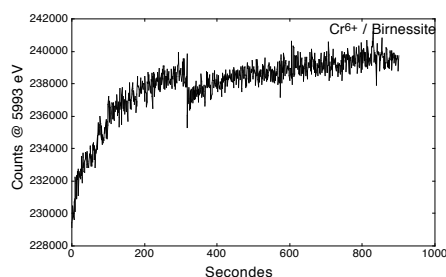


Figure 3: Kinetics of the photon-induced oxidation of  $\text{Cr}^{6+}$  when sorbed on birnessite.

A similar photon-induced oxidation has also been observed for  $\text{Cr}^{3+}$  sorbed on goethite, as indicated by the slight increase of the pre-edge peak at 5993 eV on the XANES spectrum of this model compound after immediate exposure to the photon beam or after 1 hour exposure (Figure 4A). However, as for  $\text{Cr}^{6+}$  sorbed on birnessite, the kinetics of this photon-induced oxidation displayed on Figure 4B shows that the amount of oxidation within the first 800 seconds is quite low (below 10% of initial  $\text{Cr}^{6+}$ ).

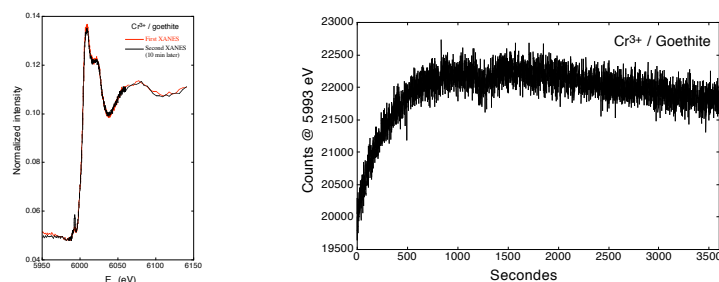


Figure 4: Kinetics of the photon-induced oxidation of  $\text{Cr}^{3+}$  when sorbed on goethite.

The amounts and kinetics of all these photon-induced redox reactions has been considered for the collection of XANES and EXAFS spectra of natural or experimental samples.

#### *Behavior of $\text{Cr}^{6+}$ after oxidation of $\text{Cr}^{3+}$ by Mn-oxides*

The XANES spectra of the solid samples obtained by reacting aqueous  $\text{Cr}^{3+}$  either with birnessite alone or with a mixture of 50wt% birnessite + 50wt% goethite during 7 minutes, 1 hour and 24 hours are displayed on Figure 5A and 5B, respectively. The pre-edge peak around 5993 eV on the XANES spectra of these solid samples indicates the occurrence of  $\text{Cr}^{6+}$ . Since chromium originally occurred as  $\text{Cr}^{3+}$  in these experiments, this result confirms the oxidation of  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$  by birnessite already reported in several studies (Manceau and Charlet, 1992; Fendorf, 1995; Feng et al., 2006; Weaver and Hochella, 2003; Oze and Fendorf, 2007).

Comparison with the XANES spectra of model compounds of  $\text{Cr}^{3+}$  or  $\text{Cr}^{6+}$  sorbed at the surface of birnessite or goethite (Figure 5C) indicates a different behavior for chromium in these two sets of experiments. In the case of birnessite alone, XANES spectra are very close to those of  $\text{Cr}^{3+}$  or  $\text{Cr}^{6+}$  sorbed at the surface of birnessite. In the case of the mixture of 50wt% birnessite + 50wt% goethite, XANES spectra are very close to those of  $\text{Cr}^{3+}$  sorbed at the surface of goethite.

These XANES spectra will be further analysed with a linear combination fitting procedure in order to explain the variations in the intensity of the pre-edge peak after various length of time.

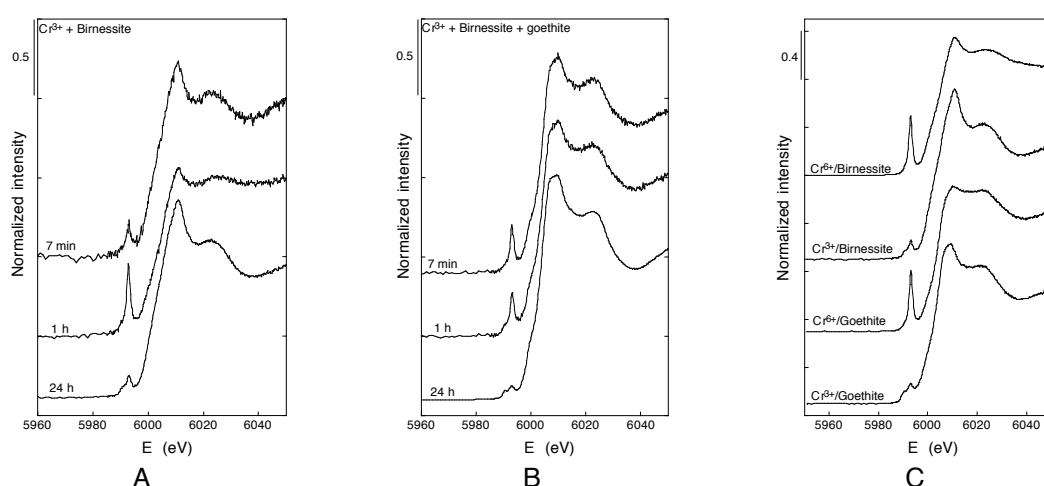


Figure 5 : XANES spectra of solid samples obtained after reacting aqueous  $\text{Cr}^{3+}$  with birnessite alone (A) or with a mixture of 50wt% birnessite + 50wt% goethite and comparison with XANES spectra of model compounds (C).

The EXAFS spectra of the solid samples obtained by reacting aqueous  $\text{Cr}^{3+}$  either with birnessite alone or with 50wt% birnessite + 50wt% goethite during 7 minutes, 1 hour and 24 hours are displayed in Figure 6A and 6B, together with those of  $\text{Cr}^{3+}$  sorbed on goethite and  $\text{Cr}^{6+}$  sorbed on birnessite (Figure 6C). The EXAFS spectrum of  $\text{Cr}^{6+}$  sorbed on goethite could not be registered because of the photon-induced reduction

of  $\text{Cr}^{6+}$  (Figure 2) and the model compounds of  $\text{Cr}^{3+}$  sorbed on birnessite could not be synthesized because of the rapid oxidation of  $\text{Cr}^{3+}$  at the surface of birnessite.

Comparison between these samples confirms the differences already mentioned on XANES data. All the EXAFS spectra will be analysed with a linear combination fitting procedure in order to depict the actual speciation of chromium in these various samples.

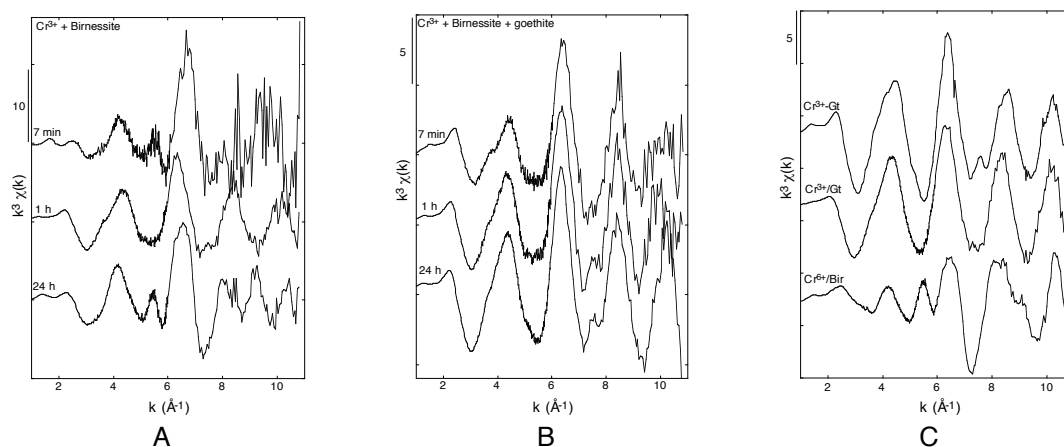


Figure 6 : EXAFS spectra of solid samples obtained after reacting aqueous  $\text{Cr}^{3+}$  with birnessite alone (A) or with a mixture of 50wt% birnessite + 50wt% goethite and comparison with EXAFS spectra of model compounds (C).

## References

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