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Synchrotron-based speciation of chromium in an Oxisol from New Caledonia: Importance of secondary Fe-oxyhydroxides

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Abstract

In New Caledonia, the weathering of ultamafic rocks under a tropical climate has led to the residual accumulation of trace elements in lateritic soils widely dominated by Fe-oxyhydroxides. The speciation of trace elements, such as Cr, Ni, and Co, in these Oxisols remains a major subject of interest regarding mining and environmental issues. We have assessed the speciation of chromium in the upper part of an Oxisol, by combining bulk and spatially resolved chemical analyses (EPMA and SEM-EDS) with synchrotron-based spectroscopic data (EXAFS and XANES). EPMA indicates that the main hosts for chromium in the bedrock sample are the silicates forsterite, enstatite, and lizardite. Hosting of chromium in these easily weatherable mineral species could lead to a significant loss of this element upon weathering. However, total analyses of major elements indicate only a slight depletion of Cr, together with an immobility of Fe and Al and drastic losses of Si and Mg, after the weathering of the bedrock. Such a low mobility of chromium is likely related to its significant incorporation in goethite and hematite formed after the weathering of Fe^{2+}-bearing primary silicates. This efficiency of secondary Fe-oxyhydroxides at immobilizing chromium is demonstrated by quantitative analysis of EXAFS data that indicates that these mineral species host between 67 and 75 wt% of total Cr (compared to the 18 to 22 wt% of total Cr hosted by chromite). In addition, SEM observation and SEM-EDS analyses performed on the Oxisol samples also show some evidence for chemical weathering of chromite. Chromite could then represent a past and/or present source of chromium upon extended tropical weathering of the studied Oxisol, rather than a stable host. These results emphasize the importance of secondary Fe-oxyhydroxides, compared to Cr-spinels, on chromium hosting in Oxisols developed upon tropical weathering of ultramafic rocks. Although the trapping mechanism of chromium mainly corresponds to incorporation within the structural network of goethite and hematite, sorption reactions at the surface of these mineral species could also be involved in such a process. In addition, considering their potential oxidative reactivity that can generate Cr^{6+} or enhance the chemical weathering of chromite, the occurrence of Mn oxides could significantly modify the behavior of chromium upon weathering. These considerations indicate that further studies are needed to assess the actual potential of chromium release from Oxisols developed upon weathering of ultramafic rocks under a tropical climate.

Keywords: Chromium, speciation, Oxisol, New Caledonia