

Ce(III) and Ce(IV) distribution and fractionation during lateritisation: Insights from XRF/ XAS

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In the present study, XRF/XAS measurements using the Lucia beamline (SOLEIL synchrotron) were combined with geochemical and mineralogical data to bring some new important insights into the Ce behaviour during tropical weathering. The selected lateritic profile (Madagascar) corresponds to a 2m-thick soil (C-, B- and A-horizons) developed over a homogeneous tonalite that has experienced some earlier low-temperature hydrothermal alteration. Prior to synchrotron measurements, the samples were characterized by XRD, SEM and EMP for determining the mineral phases and the Ce distribution. XANES spectra (at the Ce L_{III}-edge) were acquired on bulk-rock samples as well as on specific lateritic minerals or polymineral zones (in-situ measurements) localized and identified using XRF mapping.

Remarkably, there is a relatively good agreement between the Ce(IV) abundance estimated using XANES or Ce-anomaly. However, in-situ XANES measurement on mineral or polymineral domains reveal that Ce oxidation states and redistribution are heterogeneous at sample scale in the soil. Despite the expected oxidative conditions of superficial weathering in the soil, only the B-horizon unequivocally records Ce(III) oxidation into Ce(IV). There, cerianite precipitation, which commonly accounts for the positive Ce-anomaly in soils, is only observed in pores in the vicinity of Mn-oxide (and other Fe-oxyhydroxides). Cerianite microstructural position suggests for a possible Ce(III) oxidation/scavenging into Ce(IV) by neighbouring oxyhydroxides. In the other weathered horizons (A- and B-), the preservation of the primary Ce(III)/Ce(IV) ratio in bulk-rock and secondary minerals indicates that Ce(IV) and Ce(III) were solubilized, transported and precipitated in secondary phases with no significant Ce fractionation with respect to the other REE. Therefore, Ce-anomaly in rocks or in secondary minerals is not a robust (paleo)redox proxy of the weathering conditions. We suggest that Ce speciation with organic ligands might be a way to solubilize both Ce(III) and Ce(IV) without fractionating them.