Evaluation of selectivity of sequential extraction procedure for REE speciation in laterite

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To understand rare earth elements (REE) distribution in ore deposits is of prime importance for determining extraction processes and associated costs. Currently, the most expensive heavy REE are mainly produced by ion-adsorption type deposits, where REE are adsorbed at clay surface and readily leached. Petrological models behind IAD are still controversial. In particular, the conditions favoring preferential REE adsorption and fractionation at the clay surface in regard to adsorption by other secondary phases (Mn-oxides, Fe-oxides, organic matter) and/or structural incorporation in secondary REE-minerals remain unclear.

In laterite rocks, REE speciation is commonly estimated from sequential extraction procedure (SEP). In this study, the reagent selectivity of a relatively classical 5-steps protocol was first evaluated on individual synthetic Ce-material and then applied to a well-characterized lateritic profile developing over a granite bedrock from Madagascar. The synthetic Ce-materials are representative of laterite minerals: Ce-doped oxyhydroxides (Mn-oxide, goethite, hematite, gibbsite), Ce-doped kaolinite, cerianite, Ce-rhabdophane and Ce-bastnäsite. The morphology, specific surface area, Ce sorption concentrations were thoroughly characterized prior to SEP. X-Ray absorption spectroscopy on synthetic material indicates that Ce(III) dominates apart for cerianite and Mn-oxide. The evaluation of the 5-steps scheme shows that reagent selectivity is generally good, but the use of hydroxylamine hydrochloride is strongly discouraged. First, distinction between Ce sorbed at the surface of Mn- and amorphous or crystalline Fe-oxyhydroxides remains ambiguous. Second, Ce-rhabdophane (phosphate) and Ce-bastnäsite (carbonate) dissolve partially with this reagent. These experimental results combined with previous mineralogical and geochemical characterization were fundamental to interpret sequential extraction results in the laterite profile from Madagascar. In three samples taken from the A-, B- and Chorizons, REE mainly distribute in authigenic phosphates and Fe- (and Mn-)oxyhydroxide. In the oxidized B-horizon where REE accumulate, there is a significant LREE/HREE and Ce(IV)/Ce(III) fractionation between laterite minerals. While LREE-Ce mainly concentrated in phosphates (alunite-jarosite supergroup), HREE and Ce(IV) uptake is dominated by oxyhydroxides. In the A- and C-horizons, there is no significant LREE/HREE fractionation in laterite minerals and organic matter. In all horizons, the REE ion exchangeable is negligible, although kaolinite is a main mineral (>30%) of the A- and Bhorizons.