

**Experiment title:**

XAS Study of Sc Mineralogical Residence in Enriched Lateritic Deposits

Experiment**number:**

ES-426

Beamline:

ID21 (C07)

Date of experiment:

from: 03/06/2016 to: 06/06/2016

Date of report:

20/11/2016

Shifts:

12

Local contact(s):

Marine Cotte

*Received at ESRF:***Names and affiliations of applicants (* indicates experimentalists):****Chassé^{1,*}, M., Capobianco^{1,*}, N., Cabaret¹, D., Calas¹, G., Galois¹, L. and Juhin¹, A.**

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Report:

Scandium (Sc) lateritic ores in Australia are about to become the major source of this element, of special interest for its applications in high and 'green' technologies. However, the nature of the phases hosting Sc in lateritic deposits and the way it is associated with them are not yet determined. This knowledge would give a better understanding of the mechanisms forming Sc deposits, essential for future exploration and ore processing. We proposed to conduct the first macro and micro-XAS study of Sc in geological samples. Using μ -XAS at the Sc K-edge, we aimed to get molecular-scale data on Sc with the spatial resolution needed in micro-divided rocks as laterites. In parallel, a unique database of XANES spectra on synthetic analogues to natural phases present in laterites, containing substituted or sorbed Sc, was to be constituted. By comparison with the results on thin-sections, we aimed to determine the mechanisms of Sc trapping.

The first part of the beam time was used to constitute a dataset of Sc K-edge XANES spectra of reference, essential to understand the spectroscopic properties of Sc and interpret spectra on natural samples. This dataset of references gave fundamental tools to determine Sc speciation in natural contexts, essential to constrain poorly documented geochemical and mineralogical behaviour of Sc (**Chassé et al., in prep.**). Sc K-edge XANES spectroscopy was used on synthetic Sc-bearing minerals (eringaite, scandia and kolbeckite) to discuss the influence of the local environment on the features observed on the pre-edge and XANES spectra. When Sc is in O_h symmetry, the pre-edge exhibits two features separated by a crystal field splitting energy, $10D_q$, of ca 1.4 eV. The high energy component can be further split by strong distortion of the site. Hybridization with p orbitals of the ligands is also affecting the intensity of the high energy pre-edge feature. The importance of hybridization depends on the nature and orientation of the second neighbours. The edge of the XANES spectra inform on the degree of organisation of the medium- and long-range environment. These interpretations are applied to synthetic Sc-bearing Fe oxides, known to carry Sc in lateritic contexts, constituting the dataset of references for the study of Sc in natural samples. The spectral features reflects the substitution of Sc^{3+} for Fe^{3+} in Sc-doped Fe oxides. On the other hand, Sc is sorbed on Fe oxides via an octahedral hydration sphere.

These results have been applied to investigated Sc speciation in a world-class lateritic deposit [1]. During the remaining beam time, we mapped Sc concentration along with Fe speciation, the correlation of these mappings along with the use of SEM-EDXS mapping on major elements was essential to identify the nature of the phases hosting Sc. In parallel, μ -XANES spectra have been acquired at the Sc and Fe K-edges in different grains of our finely divided lateritic samples to identify the exact speciation of Sc in the host phases.

By combining these results with X-ray diffraction and microscopic and chemical analyses, we show that Sc-rich volumes are associated with iron oxides. In particular, Sc adsorbed on goethite accounts for ca 80 % of the Sc budget in our samples. The remaining is incorporated in the crystal structure of hematite, substituting for Fe³⁺. Scandium grades reflect the high capacity of goethite to adsorb this element. In contrast, the influence of hematite is limited by the low levels of Sc that its structure can incorporate. These crystal-chemical controls play a major role in lateritic Sc deposits developed over ultramafic–mafic rocks.

Publication:

[1] Chassé, M., Griffin, W.L., O'Reilly, S.Y., and Calas, G. (2017) Scandium Speciation in a World-Class Lateritic Deposit. *Geochemical Perspectives Letters*, 3, 105–114.