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First-Principles Modeling of X-Ray Absorption Spectra Enlightens the Processes of Scandium Sequestration by Iron Oxides

REVISION 1

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Abstract

Scandium is often associated with iron oxides in the environment. Despite the use of scandium as a geochemical tracer and the existence of world-class supergene deposits, uncertainties on speciation obscure the processes governing its sequestration and concentration. Here, we use first-principles approaches to interpret experimental *K*-edge X-ray absorption near-edge structure spectra of scandium either incorporated in or adsorbed on goethite and hematite, at concentrations relevant for the environment. This modeling helps to interpret the characteristic spectral features, providing key information to determine scandium speciation when associated with iron oxides. We show that scandium is substituted into iron oxides at low concentration without modifying the crystal structure.

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22 When scandium is adsorbed onto iron oxide surfaces, the process occurs through outer-sphere
 23 complexation with a reduction in the coordination number of the hydration shell. Considering available
 24 X-ray absorption spectra from laterites, the present results confirm that scandium adsorption onto iron
 25 oxides is the dominant mechanism of sequestration in these geochemical conditions. This speciation
 26 explains efficient scandium recovery through mild metallurgical treatments of supergene lateritic ores.
 27 The specificities of scandium sorption mechanisms are related to the preservation of adsorbed
 28 scandium in million-years old laterites. These results demonstrate the emerging ability to precisely
 29 model fine X-ray absorption spectral features of trace metals associated with mineral phases relevant to
 30 the environment. It opens new perspectives to accurately determine trace metals speciation from high-
 31 resolution spatially-resolved X-ray absorption near-edge structure spectroscopy in order to constrain
 32 the molecular mechanisms controlling their dynamics.

33 **Keywords:** Scandium, XANES, Ab-Initio Calculations, Speciation, Fe oxides, Sorption, Critical Zone.

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Introduction

36 In the critical zone (CZ: the interface between geological, hydrological and atmospheric compartments
 37 where rocks interact with air, water and biota), iron oxides, in particular goethite (α -FeO(OH)) and
 38 hematite (α -Fe₂O₃), are ubiquitous. They affect the biogeochemical cycling of many elements as they
 39 bind through adsorption onto mineral surfaces or incorporate within the crystal structure (Brown and
 40 Calas, 2012). Adsorption can also be followed by diffusive penetration into the interior of mineral
 41 particles through lattice or pore diffusion (Brümmer et al. 2013). Recurring changes of the
 42 biogeochemical conditions within the CZ lead to dynamic dissolution and crystallization of Fe oxides
 43 controlling the fate of trace metals (e.g., Friedrich et al., 2011).
 44 The fate of scandium (Sc) in the CZ is a case in point. Scandium is used as a conservative element to
 45 model mass transfer during weathering (e.g., Eshel et al., 2015). The absence of accessory Sc minerals

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46 in supergene contexts (Samson and Chassé 2016) implies that its sequestration in the CZ depends on
 47 the rock-forming phases present. Scandium association with Fe oxides is well-known (Norman and
 48 Haskin 1968) and illustrated by worldwide findings of Sc-rich laterites (e.g., Aiglsperger et al., 2016;
 49 Chassé et al., 2017; Teitler et al., 2019), expected to become a potential source for this critical metal.
 50 Nonetheless, the processes of Sc trapping in laterites remain elusive. Isomorphous substitution in Fe
 51 oxides or sequestration by adsorption have been invoked in Sc-bearing laterites (Chassé et al. 2017;
 52 Vind et al., 2018; Ulrich et al., 2019), making necessary an accurate determination of Sc speciation to
 53 constrain Sc dynamics in the CZ.

54 In this perspective, the chemical selectivity and high sensitivity of X-ray absorption spectroscopy
 55 proved to be invaluable (Chassé et al. 2017, 2019). The low Sc concentration in natural systems
 56 requires the use of Sc *K*-edge X-ray absorption near-edge structure (XANES) spectroscopy.

57 Nonetheless, a precise analysis of Sc speciation based on XANES spectroscopy requires theoretical
 58 modeling to understand the origin of the spectral features. This has been made for the first time on the
 59 Sc *K*-edge XANES spectra of mineral compounds using first-principles calculations (Chassé et al.,
 60 2018). We apply this density functional theory (DFT) approach to model XANES spectra of Sc trapped
 61 by Fe oxides, stressing the interest of the method to unravel the role of incorporation and sorption
 62 processes on Sc fate in the CZ.

63

64 **Experimental methods and theoretical approach**

65 We studied a Sc-chloride solution (ca. 1 wt%), Sc-substituted (ca. 1 wt%) and Sc-adsorbed (ca. 0.1 wt
 66 %) goethite and hematite, and Sc-adsorbed montmorillonite $((\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O})$,
 67 ca. 1 wt%). The Sc-chloride solution was prepared by dilution of Sc^{3+} chloride hexahydrate powder.
 68 Scandium-substituted goethite was prepared by maintaining a ferrihydrite suspension at 65 °C for two
 69 days after precipitation from Fe^{3+} nitrate at a basic pH in presence of Sc chloride. Scandium-substituted

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70 hematite was obtained by dehydroxylation of goethite through heating. Scandium-adsorbed samples
 71 were prepared by adding a Sc-chloride solution to Sc-free synthetic goethite, hematite or natural
 72 montmorillonite, later separated and dried. Details are given in Supplemental Material.

73 We recorded Sc *K*-edge XANES spectra at the LUCIA beamline (SOLEIL synchrotron) using an
 74 Si(311) double crystal monochromator calibrated against a Sc₂O₃ standard. Measurements were
 75 performed in the energy range (4400–4800) eV with energy steps of (5, 0.2, 0.5 and 1) eV in energy
 76 ranges of (4400–4485) eV, (4485–4534) eV, (4534–4586) eV and (4586–4800) eV, respectively.

77 Spectra were collected at room temperature, under vacuum in XRF mode on pellets obtained from
 78 powdered material and mounted on a holder between two 2 µm thick Ultralene® films, using a four-
 79 element silicon drift detector (SDD). Two spectra were recorded for each reference with a counting
 80 time of ca. 50 s per spectrum. The spectra acquired for each reference were merged before background
 81 subtraction and normalization. Details can be found in Chassé et al. (2017).

82 Theoretical XANES spectra were calculated using the Quantum ESPRESSO plane-wave based DFT
 83 suite of codes (Giannozzi et al. 2009) in the generalized gradient approximation (Perdew–Burke–
 84 Ernzerhof parametrization, Perdew et al., 1996). The charge density is obtained via a relaxation of the
 85 atomic positions and a self-consistent field calculation using the PWscf code. Then, XANES spectra
 86 are computed in a continued fraction approach using the XSpectra code (Taillefumier et al. 2002;
 87 Gougoussis et al. 2009). Computational details are given in Supplemental Material.

88 Charge density calculations were initialized using cell parameters and atomic positions obtained from
 89 structure relaxations of goethite (Ducher et al. 2015) and hematite (Blanchard et al. 2008). Either one
 90 or two adjacent Sc atoms (isolated or paired models, Supplemental Material) were substituted for Fe
 91 atoms into the crystal structure to model Sc-substituted goethite (Fig. 1a) and hematite (Fig. 1b). It
 92 corresponds to ca. 2 wt% and 4 wt% Sc for goethite models and ca. 1 wt% and 2 wt% Sc for hematite
 93 models. Physiosorbed Sc was modeled by a 6-fold coordinated water complex (Rudolph and Pye

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94 2000).

95 **Results and discussion**

96 **Spectral signature of scandium associated with iron oxides**

97 Experimental Sc *K*-edge XANES spectra of Sc-substituted goethite and hematite exhibit four major
 98 features in the main edge (A_0 , A, B and C, Fig. 2a,b), respectively located at ca. 4501 eV, 4508 eV,
 99 4512 eV and 4524 eV. In the pre-edge region, two low-intensity features (P_1 and P_2), observed in
 100 compounds with six-fold coordinated Sc (Lindqvist-Reis et al. 2006; Oberti et al. 2006; Chassé et al.
 101 2018), are present at ca. 4492 eV and 4494 eV. The position, shape and intensity of the main-edge
 102 features are reproduced in the theoretical spectra obtained from structural models of Sc-incorporated
 103 goethite and hematite indicating the robustness of the calculation method and the validity of the
 104 structural models (Fig. 2a,b). In the pre-edge region, the P_2 feature is less intense and split in two
 105 components in the theoretical spectra (close view, Figs. 3 and S1). When Sc atoms are paired in the
 106 model structure of goethite, a feature appears at higher energy (Fig. 3, *).
 107 To interpret the pre-edge spectra, the DOS, correlated to the spectral features, are projected on the
 108 absorbing Sc (Sc^*) and its first neighbors (Fig. 3 and S1). These DOS describe, for each energy level,
 109 the number of empty states available that can be reached with a certain transition probability by the
 110 photoelectron during XANES experiments. The contribution of electric quadrupole (E2) transitions to
 111 the P_1 and P_2 features, corresponding respectively to $1s \rightarrow 3d-t_{2g}$ and $1s \rightarrow 3d-e_g$ transitions is minor
 112 (Figs. 3 and S1). Electric dipole (E1) transitions $1s \rightarrow 4p$ dominate the P features. They reflect local
 113 transitions due to $4p-3d$ hybridization of Sc^* , observed for non-centrosymmetric sites, such as
 114 tetrahedra (Knoll et al. 2014) or distorted octahedra (Chassé et al. 2018). Non-local transitions also
 115 contribute to E1 transitions and result from orbital mixing between the $4p$ orbitals of Sc^* and $3d$
 116 orbitals of its nearest Fe neighbors *via* the empty $2p$ orbitals of the oxygen ligands. This orbital mixing
 117 of Sc^* is documented for Sc-bearing compounds exhibiting $3d$ neighbors (Chassé et al. 2018). The

DOS show that the energy difference between $3d-t_{2g}$ and $3d-e_g$ orbitals, i.e. the crystal field splitting energy ($10Dq$), is greater for Sc than for Fe, inducing the splitting of the P_2 feature. The $10Dq$ value for Fe tends to be underestimated compared to experiments (Ducher et al. 2016). A higher $10Dq$ would lead to the superimposition of the theoretical P_2 features, matching experimental spectra. When Sc atoms are paired in the model structure of goethite and hematite, non-local E1 transitions may also arise from orbital mixing with $3d$ orbitals of the adjacent Sc ions. Due to the absence of core hole on these neighbors, the position of the $3d$ orbitals is at higher energies, leading to additional features on the calculated pre-edge (Figs. 3 and S1, shown as *, at ca. 4497 eV for goethite and at ca. 4496 eV and 4498 eV for hematite), absent from experimental spectra. This additional feature is unambiguous in the hematite spectrum when plotting the different polarization dependent components of the isotropic spectrum (Fig. S2). Such additional pre-edge features are also observed for Sc oxides (Chassé et al. 2018) and for other $3d$ ions in oxides such as Ti^{4+} (Cabaret et al. 2010) and Cr^{3+} ions (Verger et al. 2016) accounting for the presence of neighbors with the same nature as the absorbing atom.

Atomic environment of scandium associated to iron oxides

The agreement between experimental and theoretical spectra in the main edge confirms the structural incorporation of Sc in the synthesized Fe oxides. Despite small discrepancies in the energy and intensity of some transitions, inherent to the limitation of DFT-based methods to model the core-hole electron interaction and the $3d$ electron-electron repulsion (Cabaret et al. 2010), the transitions observed in the pre-edge are reproduced and interpreted from the projected DOS. The absence of the feature diagnostic of Sc pairing (Figs. 3 and S1, *) in experimental spectra of goethite and hematite indicates that substituted Sc sites are isolated. A correct modeling of the spectra does not require volume-cell relaxation. At low Sc concentrations, below a few wt%, the structure of these Fe oxides accommodates Sc substitution without significant changes in the cell volume, the changes in Sc–O

distances relative to Fe–O distances remaining low (< 7 %, Supplemental Table S1). When Sc is structurally incorporated, it is dispersed at low concentration, without modifying the Fe-oxides cell volume.

Scandium *K*-edge XANES spectra of Sc-adsorbed goethite and hematite are similar and alike that of Sc adsorbed on Fe-free clay surfaces (Fig. 2c). Specific affinity for a given site of Fe-oxide surfaces and adsorption through covalent bonding is thus excluded. Scandium binding must occur through outer sphere complexes. Comparison with such Sc complexes indicates that the splitting of the pre-edge associated with the low intensity of the main edge is consistent with six-fold coordinated complexes but incompatible with higher coordination numbers (Fig. 2c, Sc-chloride solution and Lindqvist-Reis et al., 2006; Yamaguchi et al., 1997). A theoretical spectrum is calculated using an isolated 6-fold coordinated $[\text{Sc}(\text{H}_2\text{O})_4(\text{OH})_2]^+$ complex, $\text{Sc}(\text{OH})_2^+$ being the dominant species at the slightly acidic pH of adsorption experiments (Wood and Samson 2006). The calculated spectrum reproduces the major features exhibited by experimental spectra (A and B, Fig. 2c). The splitting of the pre-edge and the relative intensity of the two features is reproduced (P_1 and P_2 , Fig. 2c). Despite discrepancies in this region arising from the simpleness of the model, the closeness between the calculated spectrum and the experimental spectra of adsorbed Sc indicates that adsorption results in a reduction of the coordination number of the Sc^{3+} complex. This complex is seven- to nine-fold coordinated in solution (Vchirawongkwin et al. 2012, illustrated by the spectrum of the Sc-chloride solution, Fig. 2c) and six-fold coordinated at the surface of Fe oxides (illustrated by the spectrum of Sc-adsorbed goethite and hematite, Fig. 2c). The lability of the Sc^{3+} hydration shell supports this observation (Migliorati and D'Angelo 2016).

Mechanisms of scandium sequestration by iron oxides in the critical zone

First-principles calculations do not show significant difference of affinity for Sc substitution in goethite

166 or hematite ($\Delta E_{\text{Gt-Hem}} = 0.33$ eV, Supplemental Material and Table S2). Preferential incorporation into
167 goethite (Ulrich et al. 2019) or hematite (Vind et al., 2018) must reflect the role of the conditions of
168 formation in determining the nature of the phase incorporating Sc, as shown for lutetium (Yokosawa et
169 al. 2019). In particular, differences in specific surface area or distinct precursor phases during Fe oxides
170 crystallization can explain variations in affinity for Sc. Sorption to goethite in lateritic Fe oxide-rich
171 horizons plays a major role in Sc trapping and concentration processes (Chassé et al. 2019). The
172 theoretical modeling of the spectra of outer-sphere Sc complexes exhibit features for which the
173 position, intensity and shape are comparable to experimental spectra of Sc-adsorbed species and bulk
174 lateritic samples (Fig. 2c). The agreement with experimental spectra of Sc-substituted goethite and
175 hematite excludes trapping by structural incorporation within crystallized Fe oxides in supergene
176 contexts, despite the existence of a solid solution $\text{Fe}_x\text{Sc}_{(1-x)}\text{O}(\text{OH})$ in mild hydrothermal conditions (70
177 °C, Levard et al., 2018). Subtle differences between spectra of lateritic samples and Sc-adsorbed Fe
178 oxides (Fig. 2c, +), close to major features observed in Sc-substituted reference spectra, indicate minor
179 incorporation. With aging, as other metallic ions (Brümmer et al., 2013), Sc could penetrate Fe oxides
180 following adsorption processes enhanced by nanoporosity or lattice diffusion. The physico-chemical
181 parameters and growth kinetics are key determinants of the mechanism of Sc sorption. At increasing
182 metal concentration in solution, the process of adsorption through complexation at goethite surface may
183 be replaced by the formation of surface precipitates and structural incorporation, such as is the case for
184 nickel (Ugwu et al. 2019). At environmental conditions, with low Sc concentrations (< a few tenth
185 of wt%) and room temperature (ca. 30 °C on average under tropical climates), the surface complexation
186 process and slow kinetics must favor Sc adsorption onto goethite at the expense of structural
187 incorporation. In particular, the kinetics of this process in competition with successive dissolution and
188 crystallization processes may lead to the preservation of Sc complexes during the formation and
189 evolution of lateritic profiles.

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Implications

192 **A speciation explaining mineral processing results.** The speciation of critical metals has direct
193 implications for ore processing. For instance, cobalt sorption to goethite is mainly irreversible when
194 forming monodentate complexes while leaching remains efficient when polydentate polynuclear
195 complexes form (Ugwu and Sherman, 2017). The preservation of Sc sorbed onto Fe oxides surfaces in
196 laterites explains why Sc is efficiently recovered from lateritic ores using ion exchange (79 % recovery,
197 Williams-Jones and Vasyukova, 2018) or high-pressure acid leaching processes (94 % recovery with
198 limited Fe-oxides dissolution, Wang et al., 2011).

199 **An original sorption process controlling Sc fate in the critical zone.** The nature of the adsorption
200 process may be of importance to the stability of Sc sorption after aging. The exchange of water
201 molecules inside the solvation shell of Sc with the solvent is eased by the existence of a far-coordinated
202 water molecule capping the complex (Migliorati and D'Angelo 2016), facilitating geometric changes
203 required for Sc adsorption and stabilizing the six-fold coordinated complex. The persistence of
204 adsorbed Sc species in million-years old laterites may result from this original sorption mechanism.

205 **A promising tool to study the speciation of trace metals in the critical zone.** This study
206 demonstrates that state-of-the-art first-principles calculations can reproduce XANES spectra of metals
207 associated with phases ubiquitous in the CZ. The complexity of the pathways leading to Sc trapping in
208 the CZ and their dependence to varying environmental conditions are evidenced. As for other trace
209 metals, experimental sequestration on model systems prepared in diverse but controlled conditions are
210 required as references to determine speciation in natural contexts. This theoretical tool, combined to
211 XANES, offers a new opportunity to make the link between experiments and natural environments to
212 obtain direct information on the molecular environment of trapping at trace concentration.

213 **Future directions for first-principles-assisted investigation in environmental mineralogy.** X-ray

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214 absorption spectroscopy has become a central tool in environmental sciences (Brown and Calas 2012).
215 In the case of transition elements, the pre-edge features are used to determine element speciation but
216 their understanding is still complicated by the limitation of DFT-based approaches in this region. A
217 better modeling of the core-hole effects and of electron-electron interactions in DFT-based software is
218 developed (e.g., Cabaret et al. 2010) and will further improve the agreement between experimental and
219 calculated pre-edge spectra. Another direction, specific to adsorbed elements, would be to combine
220 DFT-based calculations of X-ray absorption spectra with DFT-based molecular dynamic simulations to
221 determine the molecular environments of adsorption and their energies (e.g., Watts et al. 2019).

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List of figures

340

Figure 1 Representations of the supercells of Sc-substituted goethite ($2 \times 1 \times 3$) **(a)** and hematite

341

($2 \times 2 \times 1$) **(b)**, and of the $[\text{Sc}(\text{H}_2\text{O})_4(\text{OH})_2]^+$ model complex **(c)** considered in the present study. The

342

two-tone sites can either be occupied by Fe (isolated model) or by Sc (paired model).

343

Figure 2 Comparison between experimental (red) and calculated (black) normalized Sc *K*-edge

344

XANES spectra for Sc-substituted goethite **(a)** and hematite **(b)** and Sc-adsorbed goethite and hematite

345

(c). Additional reference spectra of a ScCl_3 solution (ca. 1 wt% Sc), Sc-adsorbed montmorillonite

346

(ca. 1 wt% Sc) and from a lateritic sample (ca. 750 ppm Sc, Chassé et al. 2017) are given for

347

comparison in **(c)**. Calculated spectra are shifted in energy to match the experimental A feature. The

348

symbols + indicate features discussed in the paper.

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Figure 3 Experimental and calculated pre-edge regions of Sc *K*-edge XANES spectra of Sc-substituted

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goethite: **(a)** isolated structural model; **(b)** paired structural model. The calculated electric dipole (E1)

351

and quadrupole (E2) contributions are displayed. The partial densities of the absorbing Sc (Sc^*) 4*p* and

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3*d* states, of the first six O neighbors 2*p* states, of the first Fe and Sc neighbors 3*d* states are shown.

353

The energy scale of the experimental spectra is shifted to match calculated spectra. The vertical line

354

indicates the Fermi level (E_F). The * symbol indicate features discussed in the paper.

Feuille1

Goethite			
Interatomic distances (Å)			
Oxygen neighbor	Fe–O	Sc–O (isolated)	Difference relative to Fe–O distances (%)
O1	1.90	2.03	6.84
O2	1.98	2.07	4.55
O3	1.98	2.07	4.55
O4	2.12	2.16	1.89
O5	2.12	2.16	1.89
O6	2.14	2.15	0.47
Hematite			
Interatomic distances (Å)			
Oxygen neighbor	Fe–O	Sc–O (isolated)	Difference relative to Fe–O distances (%)
O1	1.93	2.04	5.70
O2	1.93	2.04	5.70
O3	1.93	2.04	5.70
O4	2.14	2.17	1.40
O5	2.14	2.17	1.40
O6	2.14	2.17	1.40

Table S1

Feuille1

Sc–O (paired)	Difference relative to Fe–O distances (%)
2.03	6.40
2.04	2.94
2.08	4.81
2.16	1.85
2.16	1.85
2.15	0.47

Sc–O (paired)	Difference relative to Fe–O distances (%)
2.03	5.18
2.03	5.18
2.03	5.18
2.19	2.34
2.19	2.34
2.19	2.34

Feuille1

Total energy (eV)		
Goethite	Sc-substituted goethite (isolated)	Sc-substituted goethite (paired)
39459.87	40037.77	40615.77
Hematite	Sc-substituted hematite (isolated)	Sc-substituted hematite (paired)
67718.57	68296.14	68873.69

Table S2

Figure 1

a

b

c

Figure 2

Figure 3