Adsorption of rare earth elements in regolith-hosted clay deposits

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Global resources of heavy Rare Earth Elements (REE) are dominantly sourced from Chinese regolith-hosted ion-adsorption deposits in which the REE are inferred to be weakly adsorbed onto clay minerals. Similar deposits elsewhere might provide alternative supply for these high-tech metals, but the adsorption mechanisms remain unclear and the adsorbed state of REE to clays has never been demonstrated in situ. This study compares the mineralogy and speciation of REE in economic weathering profiles from China to prospective regoliths developed on peralkaline rocks from Madagascar. We use synchrotron X-ray absorption spectroscopy to study the distribution and local bonding environment of Y and Nd, as proxies for heavy and light REE, in the deposits. Our results show that REE are truly adsorbed as easily leachable 8- to 9-coordinated outer-sphere hydrated complexes, dominantly onto kaolinite. Hence, at the atomic level, the Malagasy clays are genuine mineralogical analogues to those currently exploited in China.
Regolith-hosted ion-adsorption deposits (IADs), formed by subtropical weathering of igneous rocks, are the world’s primary source for heavy rare earth elements (HREEs, Gd-Lu and Y)\textsuperscript{1,2}. These elements, along with some of the other rare earth elements (REEs), are considered critical to society because of their ubiquitous use in modern technologies and renewable energy solutions, and because limits on supply would hinder global economic and technological development\textsuperscript{3-5}. Regolith-hosted IADs, also referred to as ion-adsorption clays, weathering crust elution- or laterite-hosted rare earth deposits\textsuperscript{6-9}, readily liberate the metals following mild acidification during addition of ammonium sulfate leach solutions\textsuperscript{10}. In such deposits, the REEs are inferred to be weakly adsorbed onto clay minerals (dominantly kaolinite and halloysite), as well as oxides, at a range of structural sites, including broken edge sites, charged aluminol or siloxane groups at defects and isomorphous substitutions (e.g. \(\text{Al}^{3+}\) for \(\text{Si}^{4+}\), \(\text{Fe}^{3+}\) for \(\text{Al}^{3+}\)), the hydration shells of exchangeable cations or by direct substitution of exchangeable cations\textsuperscript{11,12}. However, such behaviour is also consistent with the dissolution of nanoparticulate secondary REE-bearing phosphates, (fluor)carbonates, or colloidal particles\textsuperscript{13}. Based on the assumption that the exchangeable REEs are clay adsorbed, the term IAD is ubiquitously used in the literature to describe easily leachable REE deposits associated with lateritic weathering. However, despite their global economic and scientific importance, the adsorption mechanisms of REEs in laterite deposits of commercial value remain poorly understood and the coordination of REEs in such deposits has never been measured in situ.

The majority of economically exploited IADs occur in Southern China, where the REEs are hosted in the weathered crusts of igneous, mostly granitic, bedrock\textsuperscript{7,8,12}. They account for c. 35% of China’s total REE production and roughly 80% of global HREE supplies\textsuperscript{6,6}, despite being low grade (0.05–0.2 wt% total \(\text{RE}_2\text{O}_3\), incl. \(\text{Y}_2\text{O}_3\)) and relatively low tonnage compared to hard-rock REE deposits associated with carbonatites and alkaline igneous rocks\textsuperscript{1,14}. Economic exploitation of IADs is viable through REE deposits associated with carbonatites and alkaline igneous rocks\textsuperscript{11,12}. However, such behaviour is also consistent with the dissolution of nanoparticulate secondary REE-bearing phosphates, (fluor)carbonates, or colloidal particles\textsuperscript{13}. Based on the assumption that the exchangeable REEs are clay adsorbed, the term IAD is ubiquitously used in the literature to describe easily leachable REE deposits associated with lateritic weathering. However, despite their global economic and scientific importance, the adsorption mechanisms of REEs in laterite deposits of commercial value remain poorly understood and the coordination of REEs in such deposits has never been measured in situ.

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Weathering profiles developed on prototholiths with a primary enrichment in the mid and HREEs. XAS was also used to study the speciation of Sc in laterite profiles of ultra-mafic rocks, where Sc was found to be adsorbed dominantly on iron oxides\textsuperscript{12}. Although these studies provide important insights into the geochemical behaviour and deportment of Ce and Sc during weathering, they do not constrain the distribution and speciation of the economically significant elements HREE and Nd in association with lateritic clays developed on rare earth bearing igneous protoliths. Here, we measure Y K-edge and Nd L\(_3\)-edge X-ray absorption spectra, as proxies for HREE and light REE, respectively, from regolith samples and leachates to quantify the structural state of REEs associated with clay minerals as well as relict phases. Our results provide novel constraints on the speciation and coordination of these elements in regoliths of economic interest, and demonstrate that the rare earths are genuinely adsorbed to clay minerals.

**Results**

**Locality descriptions.** Regolith profiles in the Zhaibei region, southern Jiangxi province, developed through subtropical weathering of Jurassic peraluminous biotite and muscovite granites (188 ± 0.6 Ma)\textsuperscript{17}. The laterites range in thickness between 30 m\textsuperscript{26}. The Zhaibei granite is dominantly composed of quartz, K-feldspar, plagioclase and biotite, with small quantities of muscovite and amphibole. The REEs are dominantly hosted in the micas and amphibole, as well as accessory phases, such as zircon, monazite, Ca-REE fluorocarbonates, fergusonite-(Y), aeschynite-(Y), xenotime, titanite, rutile, ilmenite and fluorapatite\textsuperscript{17,26}. Samples were obtained from surface-exposed profiles in a 12-m-thick mineralised laterite (LJ316, Fig. 2). The exchangeable fraction of REEs in the LJ316 profile demonstrates a moderate LREE enrichment and negative Ce and Eu anomalies (Supplementary Fig. 1), containing up to 29–44% HREEs (Supplementary Fig. 2).

The Malagasy regolith profiles developed on highly heterogeneous bedrock comprising silica-saturated and -under-saturated syenites, peralkaline granites and pegmatites, as well as volcanic lithologies belonging to the Cenozoic Ambohimahavavy subvolcanic ring complex (c. 23 Ma)\textsuperscript{27-29,33,34}. The country rocks (Mesozoic marl, limestone and mudstone) and the main syenites have low abundances of primary REE-bearing minerals, whereas the peralkaline granite, nepheline syenite and pegmatite dykes contain a wide range of REE-rich minerals, including REE fluorocarbonates, zirconosilicates, silicates, oxides and minor phosphates. Many of these comprise a secondary paragenesis formed through late-magmatic hydrothermal alteration of primary igneous phases, such as eudialyte-group minerals (EGMs) (Na-Ca-zirconosilicates)\textsuperscript{35}, alongside Nb minerals, such as members of the pyrochlore group and aeschynite-(Y)\textsuperscript{28,34}. The Malagasy regolith profile is up to 30 m thick and comprises, from the bottom up: unaltered bedrock, saprock, saprolite and a pedolith made up of a mottled zone, a ferruginous zone and a topsoil (Fig. 2). The superegene mineralogy includes gibbsite, Mn and Fe oxhydroxides and clay minerals, primarily kaolinite, minor halloysite (both 7 and 10 Å) and illite\textsuperscript{38}.

**Sample characterisation.** The Zhaibei pedolith sample chosen for XAS analyses was taken from the upper 2 m of the LJ316 laterite profile, which had the highest exchangeable REE fraction (1000.9 mg kg\textsuperscript{-1}, 37% HREEs; Supplementary Figs. 1 and 2; Supplementary Table 1). SEM analyses show the mineralogy to be dominantly kaolinite, K-feldspar, quartz and iron oxides, with minor illite, micron-sized zircon and rutile-bearing pseudomorphs after titanite (Fig. 3a, b). X-ray diffraction (XRD) of the sub-2-μm fraction as oriented powders indicates that kaolinite (Al\(_2\)Si\(_2\)O\(_5\))(OH)\(_4\)) is the dominant clay mineral, with minor
Global distribution of rare earth element deposits

Ambohimirahavavy
Ion-adsorption type REE deposits (Alkaline complex-hosted REE deposits Carbonatite-hosted REE deposits
Zhaibei, Araxa, Catalão Ilímaussaq, Kangankunde, Songwe Hill Norra Kärr, Bayan Obo, Phuketö Strange Lake, Thor Lake Mountain Pass, Bear Lodge Pitinga, Mulanje Palling, Catalão Serra Verde, Kipawa Strange Lake, Khibiny, Lovozero, Khibiny, Norra Kärr Southern China Deposits e.g. Zudong, Longnan, Dingbian, Datian, Heling

Fig. 1 Global distribution of rare earth element deposits. Regolith-hosted ion-adsorption-type REE deposits (shown in white circles) dominantly occur in the tropics and subtropics and currently provide most of the world’s heavy REE supply. The majority of economically exploited regolith-hosted REE deposits occur in China, where REEs are associated with clay minerals in granitic weathering profiles. The two localities studied here are marked in orange: the Ambohimirahavavy complex in Madagascar and the Zhaibei granite in China. Other economically significant rare earth prospects are dominantly hard-rock deposits associated with alkaline igneous rocks and carbonatites, some are shown as grey pentagons and black triangles, respectively.

Fig. 2 Schematic regolith profile and studied samples. a Schematic regolith profile indicating leaching in the top of the weathering profile (pedolith) and accumulation of rare earth elements (REEs) in the saprolite, in which REEs are inferred to be adsorbed to clay minerals. The presence of Ce$^{4+}$ in the leached and oxidised top zone of the pedolith, hosted in insoluble cerianite-(Ce), commonly leads to positive Ce anomalies, whereas complementary negative Ce anomalies are recorded in the REE-accumulation zone (saprolite). The saprolite is underlain by weakly weathered bedrock (saprock) and unaltered bedrock. b Thin section photographs of the rare earth-rich lower pedolith and saprolite samples from Madagascar. White scale bars are 1 cm. c Photograph of the resin mount from the pedolith sample from China. Scale bar is 1 cm. d List of supergene and relict mineral phases identified in the regolith samples.
Fig. 3 Petrography of the studied samples. a, b Backscatter electron images of relict grains of alkali feldspar (ksp) and quartz (qtz) in a fine-grained matrix of kaolinite (kln), minor illite (ill) and Mn and Fe oxyhydroxides (Mn-Fe ox) in the Zhaibei pedolith sample. Refractory magmatic phases containing appreciable high field strength elements (HFSEs), including Zr, Ti, Nb and rare earth elements (REEs), include zircon (zrc), ilmenite (ilm) and lozenge-shaped pseudomorphs containing rutile (rt), likely after magmatic titanite (tit). c-f Malagasy samples contain alkali feldspar (ksp, ab), quartz, gibbsite (gbs), kaolinite, minor halloysite (hly) and goethite (gth). Dominant HFSE-bearing phases include zircon (zrc), zirconolite (zcl) and aeschynite-(Y) (aes-Y), which occur in pseudomorphs after eudialyte, as well as pyrochlore (pcl), which shows late-magmatic alteration to Pb-rich pyrochlore (Pb-pcl) and REE fluorocarbonates.

gibbsite and no discernible halloysite-10 Å (Supplementary Fig. 3). Since halloysite-10 Å (Al₂Si₂O₅(OH)₄·2H₂O) can readily dehydrate to halloysite-7 Å (Al₂Si₂O₅(OH)₄), some halloysite-7 Å may be present, but this is difficult to quantify or distinguish from kaolinite using XRD.

Selected samples from the Ambohimirahavavy complex include pedoliths and saprolites from a hand-dug pit in a regolith profile inferred to overlie a Si-undersaturated syenite, and drill cores of regolith profiles on REE mineralised peralkaline granite and pegmatite dykes (Supplementary Data 1). Samples analysed by XAS were chosen to re

4 and 9 m depth, respectively, in a drill core directly over REE mineralised granitic pegmatite dykes. The former has an exchangeable REE fraction of 783.43 p.p.m. (17% HREEs) and is dominantly composed of kaolinite, quartz and iron oxides with microscopic grains of refractory zircon (Fig. 3c). Saprolite sample MAD238 was taken where REE mineralised peralkaline dykes cut mudstone. The dyke material is composed of albite, K-feldspar and quartz with minor amounts of zircon, Ca-REE fluorocarbonates, pyrochlore-group minerals and aeschynite-(Y), occurring interstitially between clays and within pseudomorphs after a primary Na-Ca-HFSE phase, inferred to be an EGM (Fig. 3d). Some REE fluorocarbonates are associated with partially decomposed pyrochlore-group minerals with late-magmatic or hydrothermal alteration zones enriched in Pb (Fig. 3e, f). Although clearly REE mineralised, MAD238 has the lowest concentration of exchangeable REEs (484 p.p.m., 27% HREEs; Supplementary Fig. 2, Supplementary Table 1), consistent with most REEs being hosted in refractory REE phases. Sample MAD340 (634 p.p.m., 32% HREEs) is a saprolite sample collected from a surface road cut within the syenite ring dyke of the complex. It is dominantly composed of kaolinite with accessory zircon and rutile (Fig. 4g).

Element mapping. µXRF mapping was used to visualise the microscale distribution of Y associated with clays, Fe-Mn oxides and other supergene or relict mineral phases at both sites.
Different REE-bearing phases identified in the element maps were targeted for Y K-edge and Nd L$_2$-edge XANES and EXAFS analyses. Representative element maps are shown in Fig. 4. µXRF maps of the Zhaibei pedolith demonstrate localised enrichments of Y in and around clay minerals, as well as Fe-Mn-rich areas containing haematite, goethite and Mn oxyhydroxides (Fig. 4a, b). The hotspots of Y associated with clay minerals occur where no distinct bright REE-rich phases are identified in backscatter and by SEM-based energy-dispersive X-ray (EDX) analyses, and may represent nanoscopic REE phases or heterogeneously adsorbed Y. Element maps for the Malagasy samples with the highest leachable HREE fractions show similar elemental distributions, with Y visibly enriched along the margins of clay aggregates, possibly correlating with areas of finer crystal sizes and higher porosity. Within saprolites MAD238 and MAD340, a significant portion of the Y is associated with relict bedrock phases of zircon, pyrochlore, zirconolite or aeschynite-(Ce) as identified by SEM analyses (Figs. 3d–f, 4g, h). In lower pedolith sample MAD217, most Y is hosted in <30-μm-sized grains of zircon (Fig. 3c), while the clays show no particular enrichments in Y (Fig. 4i, j). This is consistent with the relatively low leachable HREE fraction (17%) in this sample. X-ray absorption spectra were collected from all identified phases with variable Y concentrations to determine whether localised Y enrichments represent nanoparticles of primary or secondary REE-rich phases, such as zircon, pyrochlore-group minerals or Ca-REE fluorocarbonates within the clays, or are adsorbed to clay surfaces.

**Yttrium X-ray absorption spectra.** Normalised Y K-edge XANES spectra from the samples and standards are shown in Fig. 5. The standards were measured to demonstrate a range of REE coordination states and point symmetries, allowing for a qualitative comparison with the Y K-edge XANES obtained from the regolith samples. Mineral standards in which Y occupies low point-symmetry sites, that is, parsite-(Ce), bastnäsite-(Ce) (CN = 9) and vitusite-(Ce) (CN = 6), as well as Y$^{3+}$ in aqueous solution (CN = 8), demonstrate relatively featureless Y XANES spectra with sharp white lines at 17056 eV and a broad peak ~17,104 eV (Feature C, Fig. 5a). XANES result from atom-to-atom resonances that are promoted by elements occupying sites with high point symmetry. Hence, higher symmetry minerals in which REEs occupy higher point-symmetry sites show more pronounced XANES features. For example, Y-doped NdPO$_4$ (monazite structure, CN = 9), zircon and xenotime (both natural and synthetic Nd-doped YPO$_4$, CN = 8) have a characteristic bump at 17,064 eV on the shoulder of the main XANES peak (Feature B, Fig. 5a). This feature is visible also in rinkite and nacrenarniosite-(Ce) (Nb-Ti disilicates) in which REEs occupy seven-coordinated M$^4+$ and A$^8$ sites$^{37,38}$. Spectra for Y$_2$O$_3$ (CN = 6) show a second peak at 17,064 eV (Feature B) that is as prominent as the main peak at 17,056 eV, comparing well to published Y K-edge XANES spectra for cubic Y$_2$O$_3^{39}$. EGMs are characterised by a double-peeked XANES with a minor peak at 17,053 eV (Feature A) and a broad maximum between A and B at 17,061 eV$^{40}$. The spectra show a systematic shift in the position and shape of the broad peak around 17,104 eV (Feature C), shifting to higher energy with decreasing coordination numbers (CNs) (from 17,104 eV for Y in low symmetry 11- to 8-fold sites, to 17,110 eV for phases with Y in six-coordinated sites$^{40}$).

Figure 5b, c shows Y XANES for relict minerals and supergene phases in the laterite samples. In both the Madagascar and Chinese samples, Y XANES measured on kaolinite with medium to high Y concentrations are identical (Fig. 5b, c). They compare most closely to Y XANES of parsite-(Ce) and Y in standard

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**Fig. 4 Mineralogy and synchrotron element maps.** Backscatter electron images of studied regolith samples with accompanying synchrotron micro-X-ray fluorescence maps to show the distribution of Y (red), Fe (green) and Mn (blue) in different mineral phases. a Backscatter image of the Zhaibei pedolith sample containing relict quartz (qtz) and alkali feldspar in a matrix of kaolinite (kln) and grains of goethite and Fe-Mn oxyhydroxides (Fe-Mn ox). White box indicates location of Y-Fe-Mn element map shown in b showing heterogeneous enrichment of Y (red) with localised hotspots in the kaolinite matrix. c-f Malagasy pedolith sample containing goethite (gth) and Mn oxyhydroxides with traces of cerianite-Ce (cer) in a matrix of kaolinite (kln) and halloysite (hly). White boxes in c, e correspond to Y-Fe-Mn element maps in d, f, respectively, both showing strong local enrichments of Y along the margins of clay minerals. g Strongly weathered saprolite sample from Madagascar showing h medium clay-hosted Y enrichment and localised Y hotspots associated with microscopic grains of relict zircon (zrc). i Fine-grained gibbsite (gbs) and goethite-rich pedolith sample with j low concentrations of clay-hosted Y and local Y enrichments associated with relict zircon.
solution, in which Y occupies 9- and 8-fold coordinated sites, respectively. Specifically, the position of feature C in the medium to high Y kaolinite XANES lies at 17,104 eV, comparable to the low point-symmetry standards with Y in 8- to 9-fold sites (Fig. 5a).

Notably different are the XANES spectra measured on kaolinite areas with background to low concentrations of Y (PIT2, Fig. 5b) which demonstrate a peak at lower energy and a shoulder at Feature B, similar to the XANES of laterite-hosted zircon and zirconolite spectra (below). Yttrium XANES from goethite grains

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**Fig. 5 Yttrium X-ray absorption spectra.** a) Yttrium K-edge X-ray absorption near-edge structure (XANES) spectra for rare earth element-bearing mineral standards and solution, vertically arranged by decreasing coordination number of the rare earth site (CN). b) Y XANES for supergene and relict mineral phases in Madagascar samples. c) Y XANES for supergene and relict minerals in the Chinese sample. In all panels, the main adsorption features are indicated by grey lines at 17,056 eV (Y³⁺, main peak), 17,053 eV (Feature A), 17,064 eV (Feature B), and 17,104 eV (Feature C). Details on mineral standards are provided in Supplementary Data 1 and X-ray absorption data provided in Supplementary Data 2.
in sample LJ316 and PIT2 (Fig. 4b, d) are comparable to the clay-hosted Y XANES, suggesting a similar structural state for REEs adsorbed to goethite (Fig. 5b, c) and clay at low concentrations. A XANES spectrum from the Mn-rich area (blue area in Fig. 4d), in which SEM suggests the presence of MnO(OH) with traces of cerianite-(Ce), yields noisy Y XANES reflecting low Y concentrations (Fig. 5c).

Yttrium hotspots in the µSXRF maps of the Zhaibei regolith (Fig. 4b) are confirmed by SEM analyses to correspond to microscopic grains of zircon, as the only significant relic REE-bearing phase. These grains yield Y XANES spectra that, although noisy, are markedly different from the clay-hosted Y XANES. Refractory REE phases identified by SEM in the Madagascar saprolites and pedoliths (i.e. the Y hotspots in µSXRF maps) include zircon, pyrochlore-group minerals, aegirine-(Y) and zirconolite as confirmed by SEM (Fig. 5c). Merged XANES spectra from relic grains of zircon in MAD340 and MAD217 compare well to the Y XANES of 8-fold coordinated high symmetry Y standards (zircon and xenotime), which show pronounced features at 17.056 eV (Feature B) and a double peak 17–17.104 eV (Feature C), indicating Y is hosted in the zircon lattice. It is of note that µSXRF mapping of Malagasy samples by Ram et al. demonstrated a positive correlation of REE + Y with Zr associated with clay minerals in samples containing no relic zircon, indicating local co-sorption of Zr⁴⁺ with REE³⁺ in the most strongly weathered samples. No XAFS data are currently available for Zr in these profiles to confirm sorption of Zr to clay surfaces. Aegirine-(Y), a Y-Ti-Nb oxide in which REEs occupy 8-fold sites⁴¹, and zirconolite (CaZrTi₅O₁⁷) in which REE substitute for 8-fold Ca⁴², show similar XANES spectra to zircon and xenotime standards. Both phases occur within fine-grained pseudomorphs after EGMs in the MAD238 saprolite (Fig. 3d). XANES spectra from relic pyrochlore-group minerals in the same sample (both Pb-poor and Pb-rich zones, Fig. 3e) demonstrate a lower white line and less pronounced XANES features. Yttrium enrichments in µSXRF maps near the margins of the pyrochlore grains are interpreted as micron-sized secondary REE fluorocarbonates (Fig. 3e) formed by the breakdown of primary pyrochlore, and yield a somewhat noisy but broad Y XANES that is comparable to the fluorocarbonate standards.

Neodymium X-ray absorption spectra. Normalised Nd L₃-edge XANES spectra for the samples and standards are shown in Fig. 6. All minerals show sharp white lines at 6215 eV with narrow peaks and minor variations in the relative heights and positions of Features A and B (grey lines in Fig. 6). Despite tight windowing of the secondary X-rays, absorption features at the Ce L₂-edge are visible in the Nd pre-edge region for all natural standards and samples. Relative variations in height of the Ce³⁺ and Ce⁴⁺ absorption peaks reflect natural variations in Ce oxidation state associated with different phases³⁰. Cerium peaks observed in the pre-edges of the clay-hosted Nd XANES from both Madagascar and China demonstrate the presence of Ce, which is dominated by Ce³⁺ with variable Ce⁴⁺. Peaks for Ce⁴⁺ (at 6179 eV) are most prominent in zircon and MnO(OH)-rich areas from the Malagasy laterites, consistent with the presence of cerianite (CeO₂) as determined by SEM (Fig. 4c, d) and the formation of secondary zircon under oxidising conditions. The deportment of Ce with Fe/Mn oxides was previously noted in the Malagasy profiles²⁸,3⁰,3¹ and is a common feature in regolith profiles globally¹²,1⁸, reflecting the effective oxidation of Ce³⁺ to Ce⁴⁺ by Fe and Mn oxhydroxides, leading to characteristic positive Ce anomalies in the oxidised REE-leaching zones and negative Ce anomalies in the REE-accumulation zones¹²,3⁰,4³,4⁴. We note that Ce adsorption features are higher in the XANES spectra of supergene phases with lower Y concentrations (Fig. 6b), demonstrating heterogeneous distribution of Y/Ce in the Malagasy PIT2 sample. The relative height of the Ce adsorption peaks, as well as the Ce³⁺/Ce⁴⁺ ratios, with respect to Nd and Y are more consistent in the Zhaiabe sample.

The clay- and oxide-hosted Nd XANES are identical within individual laterite samples, but the Chinese spectra slightly vary from those of Madagascar, with Feature B (6286 eV) being more prominent in spectra from the Malagasy PIT2 sample than in those from the Zhaiabe sample. With exception of Feature B in PIT2, the clay-hosted Nd XANES most closely resemble spectra of the fluorocarbonates, NdPO₄, steenstrupine and allanite. Noisier Nd spectra for the goethite and Mn oxhydroxide/cerianite-(Ce) reflect relatively low concentrations of Nd associated with those phases. Standards in which LREEs are inferred to occupy higher symmetry sites (yttriofluorite, xenotime (YPO₄-Nd), Nd₂O₃) show more pronounced Nd XANES features (several or higher peaks at Feature A, or a stronger Feature B, Fig. 6a) and higher white lines than XANES of minerals in which LREEs occupy lower symmetry, or multiple sites⁴⁰. XANES for Nd in aqueous solution (in weak HNO₃) demonstrates the highest white line among the standards, and additional features that are not observed in the other spectra (Fig. 6a). From this we infer that Nd in aqueous solution occurs as highly ordered and symmetric hydrated NdOH complexes. Unlike the Y K-edge XANES, no systematic variations are observed in the height of Y XANES in the standards. Hence, we infer that the Nd L₃-XANES is dominated more by the point symmetry of the site and, compared to Y, is relatively insensitive to the CN.

Coordination of yttrium. The local atomic structure of Y associated with clay minerals in the Chinese and Malagasy laterites is further constrained by fitting the Y K-edge EXAFS spectra. EXAFS signals for the clay-hosted Y were merged to improve signal-to-noise ratios and fitted to a theoretical scattering path of nearest-neighbour oxygens to constrain the local structure around the absorbing Y atom (e.g. CN and bond distances). From samples MAD217 and MAD238 only two and three spectra, respectively, were useable for quantitative analyses and were therefore merged together. The k²-weighted EXAFS oscillations and phase-corrected radial distribution functions of the merged spectra and their fits are shown in Fig. 7. All radial distribution functions (Fig. 7b) demonstrate a single peak, representing the first coordination sphere of scattering atoms surrounding Y at an average distance of 2.4 Å. These can be attributed to the oxygen of water molecules, or the hydroxides and oxygens within the structural framework of the clay mineral (Fig. 7b). No further peaks are visible beyond the first shell of oxygens, which might indicate longer-range order, such as nearby Al or Si atoms within the structure of the clay or other crystalline solids. Refined parameters from the EXAFS curve-fitting analysis of the standards and samples are listed in Tables 1 and 2, respectively. Details of the fitting procedures are described in the “Methods”.

Discussion
The clay fractions in the studied laterite samples are dominated by kaolinite, and in the case of Madagascar, minor halloysite
(10 Å and possibly 7 Å)\textsuperscript{28,31}. Other supergene phases include gibbsite, goethite, Mn oxyhydroxides and cerianite-(Ce). SXRF element mapping of the Zhaibei and Ambohimahavavy pedolith samples with the highest concentrations of exchangeable REEs show that REEs are dominantly associated with clay minerals. In the saprolite samples from Madagascar, a significant portion of REEs are hosted in refractory mineral phases, such as zircon, pyrochlore, zirconolite, aeschynite-(Y) and REE fluorocarbonates. XANES of the clay-hosted Y and Nd from both Madagascar and China are similar to XANES spectra of REE elements (La-Eu) favour 9-fold coordination \cite{47}. The similarity between clay-hosted Y and Nd XANES, those of fluorocarbonates and REEs in aqueous solution, suggest a similar 8- or 9-fold coordination sphere for the REEs associated with kaolinite and halloysite. EXAFS analysis further constrains the local atomic structure of Y hosted in clay minerals to be surrounded by 7.9 to 8.3 ± 0.9 oxygens at a radial distance of 2.35 – 2.38 ± 0.01 Å, and without further scattering of atoms up to a radial distance of 5 Å. This indicates a coordination sphere within error of that obtained for Y\textsuperscript{3+} in aqueous solution (Table 1, Fig. 7).

To further interpret these EXAFS results, we briefly review the structure and metal sorption mechanisms of kaolinite-group minerals. Metal sorption on kaolinite and halloysite, as 1:1 layer clays, can take place either at charged edge sites or at neutral or charged basal surfaces\textsuperscript{11,50}. Permanent charge resulting from interlayer ion exchange due to relatively strong bonding between 1:1 layers\textsuperscript{11}. This typically gives neutral siloxane (Si-O) surfaces at the tetrahedral layer\textsuperscript{51}, and precludes significant adsorption of hydrated ions or hydroxyl complexes on the siloxane surfaces\textsuperscript{52,53}. Instead, most charge in kaolinite-group minerals is typically much lower than that of 2:1 layer clays, such as smectite and illite, which exhibit a much wider range of substitutions\textsuperscript{50}. Nevertheless, kaolinite and halloysite are the dominant clay minerals in regolith-hosted REE deposits and

| Standards                  | Samples                      |
|----------------------------|------------------------------|
| Standards                  | Madagascar                   |
| Catapleite, 6              | Kaolinite, high Y            |
| Euclayite, 6               | Kaolinite, medium Y          |
| Fluorapatite, 6–7          | Kaolinite, low Y             |
| Nacacenobiste-(Ce), 7      | Goethite, Fe phase           |
| Nd\textsubscript{2}O\textsubscript{3}, 7 | MnO(OH)\textsuperscript{-}cerianite, medium Y |
| Yttrfluorite, 8            | Zircon, high Y               |
| Zircon, 8                  | China                        |
| YPO\textsubscript{4}-(Nd), 8 | Kaolinite, high Y            |
| Nd solution, 9             | Kaolinite, medium Y          |
| NdPO\textsubscript{4}-(Y), 9 | Kaolinite, low Y             |
| Bastnasite-(Ce), 9         |                              |
| Parisite-(Ce), 9           |                              |
| Steenstrupine-(Ce), 10     |                              |
| Allanite-(Ce), 9–11        |                              |

Fig. 6 Neodymium X-ray absorption spectra. a Neodymium L\textsubscript{2}-edge X-ray absorption near-edge structure (XANES) for mineral standards and Nd in solution, vertically arranged by decreasing coordination number (CN). Cerium L\textsubscript{2}-edges observed in the Nd pre-edge demonstrate variable Ce oxidation states (Ce\textsuperscript{3+} at 6168 eV and Ce\textsuperscript{4+} at 6179 eV) in the natural mineral standards. The main Nd absorption features are marked by grey lines at 6215 eV (Nd\textsuperscript{3+}, main peak), at 6248 eV (Feature A) and 6286 eV (Feature B). b Nd XANES spectra for clays and relict minerals in the Chinese and Malagasy samples. Kaolinite spectra from both sites demonstrate variable peaks for Ce\textsuperscript{3+} and minor Ce\textsuperscript{4+}. Absorption of Ce\textsuperscript{4+} (6179 eV) is most prominent in the zircon and the Mn oxyhydroxide, the latter containing traces of cerianite-(Ce). Grey lines are as in a.
their respective roles in adsorbing and fractionating REE within lateritic weathering profiles have been highlighted in numerous recent studies, for example, refs. 12,16,35–58.

In addition to physicochemical and microstructural properties, such as particle size, morphology, crystallinity, composition and purity,36,50,55, the cation adsorption capacity of kaolinite and halloysite strongly depends on the pH and ionic strength of the weathering solutions in which they occur.32,58. For example, these determine whether metal ion complexes are adsorbed onto the clay surfaces as outer-sphere complexes or as inner-sphere complexes.32,39. Outer-sphere complexes retain a full hydration sphere and are loosely adsorbed to the basal surface via electrostatic attraction, whereas inner-sphere complexes are partially desolvated such that the metal bonds directly with Al-O or Si-O groups on the aluminol or siloxane surfaces, or edge sites of clay particles, as illustrated in Fig. 8. This distinction is important as outer-sphere complexes are more easily leachable than inner-sphere ones. Peacock and Sherman60 and O’Day et al.61 showed that divalent cations (Cu²⁺ and Co²⁺, respectively) provided EXAFS with features related to a second shell of Al (or Si) atoms, consistent with inner-sphere adsorption via one or two bridging oxygens. A second shell of Al/Si atoms expected between 3 and 4 Å is not visible in our EXAFS results. Surface complexes on the aluminol basal surface will therefore be of the form [≡Al-O-Ln(H₂O)₇₋₈]⁺, representing a total coordination sphere of 8–9 (Fig. 8). With increasing pH, inner-sphere complexation becomes more dominant due to hydrolysis of edge and basal hydroxyl groups in the clay structure.32,61. Inner-sphere complexes for trivalent ions generally maintain a similar coordination sphere in the first shell, but are distinguishable from outer-sphere complexes using EXAFS data by showing evidence for a second shell of Al and/or Si atoms in the tetrahedral and octahedral sheets.39,61,62. The close comparison of the clay-hosted EXAFS fitting results with that of Y in aqueous solution, combined with the absence of a second shell in our EXAFS data, indicates that the majority of Y retains a first shell, similar to that measured for Y³⁺ in aqueous solution. References for crystal structures of the standards are provided in Supplementary Data 1.
The presence of hydrated Ln3 ions may lead to the formation of inner-sphere complexes in aqueous solution. However, Malagasy pore waters measured during fieldwork start to form at pH 6 (and less for HREEs) and possibly as low as 5. At higher pH, and at higher ionic strength, desolvation of low ionic strength, REEs are likely to be present as eight- and nine-coordinated hydrated outer-sphere complexes. This is critical in the ease of leaching and hence the economics of these deposits. Notably, the EXAFS data show that the coordination state of Y3+ is identical within the Chinese and Malagasy laterite deposits. Notably, the EXAFS data show that the coordination state of Y3+ is identical within the Chinese and Malagasy laterite deposits. However, the EXAFS data show that the coordination state of Y3+ is identical within the Chinese and Malagasy laterite deposits. The respective roles of halloysite and kaolinite in the regolith samples.

### Table 1 EXAFS fitting results for the coordination state of Y in selected mineral standards and aqueous solution.

| Standard     | Origin                          | Shell | Path | CN | $R$ (Å) | $\sigma^2$ (Å$^{-2}$) | $\Delta E_0$ (eV) | $S_0^2$ | $\chi^2$ | R-factor | Ref. |
|--------------|---------------------------------|-------|------|----|---------|------------------------|------------------|---------|---------|---------|------|
| Y-aqueous    | Synthetic, Inorganic Ventures   | 1st   | Y-O  | 8.2 (4) | 2.37 (1) | 0.005 | -1.7 | 1 | 656 | 0.016 | 1 |
| Y$_3$O$_3$   | Synthetic, Johnsen Matthey      | 2nd   | Y-Y  | 6 | 3.53 (0) | 0.003 (0) | 2.4 (1.1) | 1.2 (1) | 995 | 0.047 | 3 |
| YPO$_4$-Nd   | Synthetic, ORNL                | 1st   | Y-O  | 4 | 2.33 (1) | 0.004 | 2.4 (1.1) | 1.2 (1) | 995 | 0.047 | 3 |
| Eudialyte    | Kringlerne, Ilimaussaq, Greenland | 1st   | Y-O  | 2 | 2.24 (1) | 0.004 (1) | 1.2 | 1 | 33.4 | 0.017 | 4,5 |
|              |                                 | 2nd   | Y-O  | 4 | 2.30 (1) | 0.004 (1) | 1.2 | 1 | 33.4 | 0.017 | 4,5 |

EXAFS fits based on crystal structures from (1) Ni et al., (2) Santos et al., (3) Ni et al., (4) Johnsen, (5) Borst et al. CN is coordination number. R is radial distance in Ångström. Definitions of other fit parameters listed in this table are provided in the ‘Data Processing’ section of the methods. Errors shown within parentheses are on last digit of the fitted variable. Values without errors were fixed in the final fit.

### Table 2 EXAFS fitting results for the coordination state of clay-hosted Y in the regolith samples.

| Sample       | Depth | Shell | Path | CN | $R$ (Å) | $\sigma^2$ (Å$^{-2}$) | $\Delta E_0$ (eV) | $S_0^2$ | $\chi^2$ | R-factor | n |
|--------------|-------|-------|------|----|---------|------------------------|------------------|---------|---------|---------|---|
| Zhaibei, China |       |       | Y-O  | 8.3 (9) | 2.38 (1) | 0.007 (2) | -1.5 | 1 | 317 | 0.017 | 16 |
| LJ316        | 2 m   | 1st   | Y-O  | 7.9 (8) | 2.37 (1) | 0.007 (2) | -1.5 | 1 | 120 | 0.013 | 14 |
| PIT2         | 4.8 m | 1st   | Y-O  | 8.1 (5) | 2.35 (1) | 0.008 (2) | 0 | 1 | 11 | 0.018 | 5 |
| MAD238-217   | 9 m, 4 m | 1st | Y-O  | 8.1 (8) | 2.35 (1) | 0.008 (2) | 0 | 1 | 11 | 0.018 | 5 |

CN is coordination number. R is radial distance in Ångström. n is number of merged spectra. Definitions of other fit parameters listed in this table are provided in the ‘Data Processing’ section of the methods. Errors shown within parentheses are on last digit of the fitted variable. Values without errors were fixed in the final fit.

Siloxane complexes (\[\equiv Al-O-Ln^3+\] and \[\equiv Al-O-Ln(OH)_2^2-\]) would start to form at pH 6 (and less for HREEs) and possibly as low as pH 5. However, Malagasy pore waters measured during fieldwork range from pH 6.98 to 8, and hence, at close to neutral pH and low ionic strength, REEs are likely to be present as eight- and nine-coordinated hydrated outer-sphere basal surface complexes (Fig. 8). At higher pH, and at higher ionic strength, desolvation of the Ln3+ ions may lead to the formation of inner-sphere complexes, either on the aluminol or siloxane surfaces or terminal OH groups. This finding is significant as the lack of hydrolysis and the presence of hydrated Ln3+ ions adsorbed to the clay surface is critical in the ease of leaching and hence the economics of these deposits. Notably, the EXAFS data show that the coordination state of Y3+ is identical within the Chinese and Malagasy laterite samples that are rich in exchangeable HREEs, and hence we infer a common REE adsorption mechanism across the deposits.

Our data do not clearly differentiate between kaolinite and halloysite, but previous studies suggest that halloysite has an enhanced REE adsorption capacity within weathering profiles. Given that kaolinite is dominant over halloysite in the Malagasy samples, and halloysite (10 Å) is not typically has a higher porosity and specific surface area than kaolinite, recent experiments by Yang et al. have shown that halloysite has a lower specific surface area normalised adsorption capacity for the REEs than kaolinite under the same conditions of pH and ionic strength. This may be because the variable charge aluminol surfaces on which REE 3+ adsorption is inferred to take place is inside the halloysite tubes rather than on the outer surface. The respective roles of halloysite and kaolinite within regolith-hosted REE deposits and their progressive transformation during weathering are still not fully understood and remain an important subject of further study.
Of additional importance for understanding both deposit genesis and development of REE-leaching strategies for laterite deposits is that our XANES and EXAFS studies capture the easily leachable fraction of the REEs. To ensure that we have measured the easily leachable REE fraction associated with clay minerals in our samples, we also measured Y K-edge XANES of bulk powders prepared from the laterite samples, pre- and post-leaching with (NH4)2SO4 (Supplementary Data 2), and compared these to leachates of an IMERYS kaolinite standard doped in synthetic REE solutions (Supplementary Figs. 5–7, Supplementary Table 2). This also allowed us to test for changes in the structural state of REEs during sample processing to produce polished thin sections. The XANES spectra for the bulk powders are shown unnormalised in Supplementary Fig. 6 to illustrate the reduction in Y K-edge absorption intensity before and after leaching. The markedly lower absorption of the post-leach material demonstrates that the XANES acquired for the pre-leach material are characteristic of the REEs in leachable form. We are therefore confident that we are directly characterising the structural state of the leachable; hence, economic fraction of the REEs in this deposit type. Moldoveanu and Papangelakis modelled the desorption behaviour of REEs during leaching as substitution of dehydrated monovalent cations for the hydrated Ln$^{3+}$ at the clay surface. Because monovalent cations can dehydrate completely at ambient temperature, they form a strong ionic bond with the clay surface, compared to the weak adsorption of the hydrated lanthanides. Our data are fully consistent with this model and support further development of simple, environmentally friendly, leach solutions based on this mechanism. Supplementary Figure 7 also shows the normalised XANES of the prepared clay samples pre- and post leaching. The post-leach XANES demonstrate a minor peak at 17,065 eV (Feature B), which resembles spectral features of the high point-symmetry standards (e.g. zircon, Fig. 5). These features, typical of high symmetry site occupations, are consistent with the non-leachable REEs being structurally bound to kaolinite, in interlayer positions or as partially desolvated inner-sphere complexes. Inner-sphere complexation may also explain the anomalous XANES for kaolinite with low or background Y concentrations in the Malagasy PIT2 pedolith sample (Fig. 5b), which shows similar spectral features as the post-leach XANES spectrum (Supplementary Fig. 7).

Fig. 8 Schematic adsorption model of rare earth elements onto kaolinite. a Schematic kaolinite structure showing the 1:1 stacking of Al-octahedral (O) and Si-tetrahedral (T) sheets, forming TO layers with aluminol and siloxane external basal surfaces, edge and interlayer surfaces. b Rare earth sorption model associated with Al-octahedral (O) sheets of kaolinite. Light and heavy rare earth element (LREE$^{3+}$ and HREE$^{3+}$) complexes may occur as eight- to nine-coordinated inner-sphere (basal surface or edge) complexes via mono- or bidentate bridging oxygens, or loosely adsorbed as 8- or 9-fold hydrated outer-sphere complexes. Our data demonstrate that Y in the studied ion-adsorption ores are dominantly present as 8-fold hydrated outer-sphere basal surface complexes. The data show no evidence for Al or Si scattering within a distance of 4 Å, thereby excluding the inner-sphere adsorption model. A similar sorption model can be made for halloysite (7 and 10 Å), which typically displays a tubular morphology with the aluminol basal surface on the inside of the tubes. CN coordination number.
Analysis of saprolite and saprock samples in the Madagascar laterite profiles highlights the importance of the primary (magmatic and hydrothermal) REE-hosting phases in the genesis of IADs. The complex controls of bedrock mineralogy in the Ambohimiarahavy complex on the release of REEs into the regolith profile were explored in more detail by Estrade et al. They showed that easily weatherable zirconosilicates, such as EGMs, are dominant primary REE hosts in the bedrock, and that REE enrichment within the pedolith and saprock is correlated to the local occurrence of REE-rich pegmatite veins containing EGMs. In places, late-magmatic hydrothermal breakdown of EGMs resulted in the formation of secondary zircon and zircono-nilite (Fig. 3d), which are more resistant to weathering and subsequently inhibit the mobility and leaching of HREEs into the laterite profile. The latter phases are clearly identifiable by high symmetry Y XANES of microscale Y-rich reaction products. This is consistent with previous studies demonstrating that zircon is resistant to weathering,

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Methods

Sample and standard preparation. Samples were prepared as polished thin sections (Madagascar samples) or as polished resin-mounted regolith mounts (LJ316, China). Thin sections were produced at the British Geological Survey (Keyworth, UK), from either intact blocks of saprock and saprolite or from surface pedolith sampled using soil boxes. Samples were first impregnated with resin and then mounted on spectroscopically pure glass slides prior to polishing with diamond paste, in order to prevent interference on the XANES from trace elements incorporated in the glass slide. Disaggregated materials from Chinese samples were mounted in resin and then also polished. Cerium oxide polishing media were avoided. A powdered fraction of all samples prepared as resin-impregnated polished blocks or sections was also prepared as a pressed powder pellet with no further treatment in order to ensure that the process of resin mounting did not modify the clay mineralogy or REE coordination. Details of the sample materials used are provided in Supplementary Data 1.

Analytical standards and blanks measured during the XAS studies were prepared as powders from natural and synthetic REE minerals in which the REEs occupy different coordination states (Supplementary Data 1). Microcrystalline Y-doped NdPO4 was synthesised at the University of St. Andrews following procedures described in Borst et al. All analytical standards were ground under ethanol in an agate mortar and checked for phase purity by powder XRD (Philips 1050 XRD instrument with monochromated Co-Kα-radiation, University of St. Andrews) prior to X-ray absorption measurements.

Single cation Y and Nd solutions were prepared from the oxide in 5% nitric acid (HNO3) (Inorganic Ventures COY1–1000 p.p.m. Y in nitric acid, and CGN1–1000 p.p.m. Nd in nitric acid), alongside a synthesised REE-bearing kaolinite standard at the University of Brighton (UK). The kaolinite was prepared using IMERYS reagent grade “light kaolinite”, which was analysed by inductively coupled plasma mass spectrometry (ICP-MS) prior to experiments to identify any initial REE content. The exchangeable REE fraction was then leached with ammonium sulfate to remove any surface adsorbed cations, and then saturated for 16 h with 30 p.p.m. REE solution with 0.1 M NaNO3 (prepared from Agilent 8500–6944 100 p.p.m. REE oxides in 5% HNO3) and dried. A split from the re-adsorbed kaolinite sample was leached with ammonium sulfate, and the bulk material was fused with lithium borate and digested in nitric acid to confirm the mineral framework REE content, and ion-exchangeable REEs adsorbed to the mineral surfaces. The leach and experimental solutions were analysed for REE contents by ICP-MS (Agilent 7900) at all intermediate stages. The octopole reaction system was operated in He mode to reduce polyatomic interferences. The samples and a matrix-matched blank solution were diluted with 2% HNO3, and the blank was used to calibrate the REEs from 1 to 500 µg L−1 using the multielement calibration standard (8500–6944 Agilent). Internal standard (Rh) was added automatically to all standards, samples and blanks via the online internal standard solution and measured continuously alongside sample analysis. REE contents for each step in the IMERYS kaolinite leaching and adsorption experiments are shown in Supplementary Table 2.

Following X-ray absorption measurements, corresponding areas on the thin sections (Madagascar) and resin mount (China) were characterised and imaged by SEM at the University of Brighton using a Zeiss EVO LS 15 SEM equipped with an Oxford Instruments Max5 80 EDX spectrometer, at 20 kV acceleration voltage and 1.2 nA beam current. Samples were carbon coated to avoid charging, so all SEM analyses were carried out to confirm mineralogy of the studied areas after XAS in order to avoid sample contamination issues. Blank analyses were also acquired on areas of just glass and slide preparation resin in order to demonstrate no interference from the sample preparation media.

Clay characterisation. The clay minerals were characterised using powder XRD at the University of Brighton (UK) using a Panalytical MRD X’pert Pro High Resolution powder diffractometer in Bragg-Brentano geometry using Ni-filtered Cu-Kα radiation. Tube conditions were 40 kV and 40 mA. Randomly oriented powders were prepared by mixing ~10 g of each sample with ~400 µL of deionised water were added to the clay concentrate. Slides of well-oriented clay were made by putting a few drops of the clay suspension on glass slides, which were
then air-dried. Results for LJ316 are shown in Supplementary Fig. 2 and SEM images shown in Supplementary Fig. 3.

**Leaching experiments.** Leaching studies in support of the X-ray absorption study were conducted on four powder samples (LJ16, PIT2, MAD3241, MAD219). One gram of each sample was dried in an oven (105 ± 2 °C) until constant weight and mixed with 40 mL of 0.5 M (NH4)2SO4 solution30, adjusted to pH 4 with H2SO4 in a 50 mL centrifuge tube. The mixture was immediately shaken at 30 ± 10 r.p.m. for 1 h using a mechanical end-over-end shaker at room temperature. The extract was separated from the solid residue by centrifuging at 3000 × g for 20 min. The solution obtained was filtered through 0.22 µm syringe filters and the filter was washed with 50 mL deionised water. Samples were stored in a fridge at 4 °C prior to analysis. For each batch of 14 samples, a blank was prepared following the same procedure. No certified reference material exists for REE-leaching experiments, but repeat analyses of BCR-70 showed that leaches reproduced values within 5% precision for transition metals.

**X-ray absorption spectroscopy.** XAS data were collected at the 118 microfocus beamline at Diamond Light Source Ltd (Didcot, UK), a 3 GeV third-generation synchrotron facility typically operating at a current of 300 mA. 118 is designed for high spatial resolution analyses of heterogeneous samples within the 2–20 MeV energy range, and is set up for µSRFX mapping, µXRD and µXAS. All measurements were done by measuring the Mn K-edge (at 6539 eV) and Zr K-edge (at 17,038 eV) was done by measuring the Mn K-edge (at 6539 eV) and Zr K-edge (at 17,038 eV) from Mn and Zr metal foils, respectively. Detector count rates were measured in transmission mode. The energy range was set to include both the Mn and Zr metal foils, respectively, to yield compatible fitting parameters (ΔE0/k) supported by the data. The quality of the fit is assessed by the R-factor and the reduced χ² function calculated in Artemis. Fits of acceptable quality yield R-factors of 0.02 or below57. Refined parameters include the energy offset (ΔE0 in eV), CNs, the mean interatomic distance between the absorber and the scattering atoms (R0, R1, R2…), and mean-square relative displacement Debye–Waller factors per scatterer (σ² in Å⁻2). The amplitude reduction factor (α²) was fixed to 1, which was determined from a three-shell fit of the Y2O₃ reference powder (see ref. 48). Initial first-shell refinements with four variables were evaluated and improved iteratively and the robustness and codependence of the fitted parameters checked by systematically fixing and changing one of the variables. The final refinements of the kaolinite and Y solution spectra are fitted for two variables (CN and AR), where ΔE0 and σ² values are fixed to best-fit values obtained in the previous fits (Tables 1 and 2). The k²-weighted Y EXAFS spectra and fitted models are provided in Supplementary Data 4. Underlying Artemis files for the final fits are provided in Supplementary Data 6.

**Data availability**

The authors declare that all data supporting the findings of this study are available within the paper and its supplementary files. Unprocessed data can be accessed from the University of St Andrews Research Portal, https://doi.org/10.17635/7ce5567-063-4814-b25c-fa747cb572a984.

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