

La uptake in montmorillonite: evidence of inner-sphere complexes from XAS investigations

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Abstract

In this paper, an X-Ray Absorption Spectroscopy (XAS) study of the local structural environment of La ions hosted in a set of montmorillonites is presented. The structural location of La ions in the host phases and whether they are incorporated in the structure or adsorbed at the surface has been assessed. Two source clays from the Mineral Society repository (STx and SWy) in pristine form and a polymer-modified with a penta-etylen-hexamine of formula C₁₀H₂₈N₆ have been employed as sorbent solids. Ca montmorillonite and Na-rich montmorillonite, have been contacted with La solutions of 19 and 200 mM initial concentration. XAS results yielded La-O distances ranging between 2.57 to 2.61 ±0.02 Å, compatible with literature data for La ions in water solution, where La is coordinated by water molecules. Nonetheless, we provide evidence for the presence of a further La-Si or La-Al distance (in the range 4.11-4.18 ±0.02Å) which suggest that La may also be bonded to the oxygen atoms on the outer surfaces of the TOT layer. Such a feature may play an important role among the factors limiting the efficiency of the release process.

This paper is a further step that lays the ground for REEs recovery from Electric and Electronic wastes (WEE) via a solid-liquid process, and their re-use as secondary raw materials. Indeed, the knowledge of the ions-sorbent interaction mechanism, such as nature and strength, is a fundamental information to tailor sorbents and procedures in the practical applications, such as the solid-liquid sorption technology.

Keywords: Lanthanum, XAS, montmorillonite, incorporation, uptake, release

Introduction

REE play an essential role in several fields of applied sciences (Binnemans et al., 2013) and the recent development of the green economy is making REEs source recovery increasingly popular. REEs recovery can occur from primary (ion-adsorption type from rare earth ore) and secondary (wastes from human production processes) sources. A review on the advanced technologies for the separation and purification of REEs developed during the last ten years, together with a discussion on crucial scientific issues such as sources, distribution, leaching, extraction technology, separation efficiency, etc., has been recently published (Liu and Chen 2021). REEs, particularly heavy REEs, are concentrated in clay minerals characterized by cation exchange capacity, also referred to as ion adsorption clay minerals (Yang and Zhang 2015). As a consequence, a considerable amount of research has been focused on the extraction of REEs from ion adsorption clay minerals (Moldoveanu and Papangelakis 2016). The recovery of the REEs from non-ion adsorption clays, such as kaolinite, has been, instead, less investigated (Ji and Zhang 2021a), although different thermal and mechanical treatment of kaolinite have been recently tested to enhance the leachability of REEs from this phase (Ji and Zhang 2021b). Among clay minerals, montmorillonite proved to be very promising as host crystalline phase for REE uptake due to its peculiar structural features. Its crystal structure consists of TOT layers with a plane of Al octahedra sandwiched between two inward-pointing sheets of SiO₄ tetrahedra (Figure 1). Two-thirds of the octahedral sites are occupied by Al. Interlayer cations balance the layers' negative charge and do not fill all available sites. These latter cations are extremely mobile and can give rise to exchange processes with the environment. Given the low costs involved in the processes for La uptake in clays (Iannucelli-Zubiani et al., 2017, 2018), the incorporation of REE in the interlayer makes these kinds of materials promising for recovering REE. The pristine crystalline montmorillonite phase can also be modified by intercalation of polyamine molecules to enhance their uptake capability and the recovery of valuable metals and REEs using organo-clay based absorbents has recently led to noteworthy achievements (Iannucelli-Zubiani et al., 2015, 2017). The use of natural and modified clays as sorbents in treating aqueous wastes containing REE was recently extensively investigated (*e.g.* Cristiani et al., 2021a,b), but the uptake and release mechanisms of REE ions in the montmorillonite crystal structure still needs further investigations. Specifically, three different ion-sorbent interactions are possible: ion exchange, surface adsorption and coordination; the latter occurring when polyamine molecules are intercalated in the montmorillonite interlayer to enhance the uptake performance of the clay. Cristiani et al., 2021a, report that the prevalent mechanism involved in the uptake and release process depends both on the nature of the target ion (*i.e.* atomic radius and charge) and on the reaction environment (ion concentration, pH, etc.). As an example, the capture of La³⁺ in Ca-montmorillonites is supposed to involve both ion exchange and coordination mechanisms. Both

interactions can be affected by pH: Ca ions can be exchanged by protons [Cristiani et al., 2021b], while amino-groups can be protonated/deprotonated. As a consequence, the detailed knowledge of REE bonding environment in clay hosts is a crucial prerequisite for evaluating the feasibility of using these hosts for REE recovery from electronic waste, and for tailoring uptake and release processes in order to obtaining an efficient and environmentally friendly procedure. Recently, XAS techniques have proved to be a powerful characterization tool to understand the speciation of adsorbed metals ions, being extremely sensitive to the kind atom, to the chemical state and to the coordination environment (Luo et al., 2021; Brown et al., 2005). XAS has been frequently employed in the study of the absorption mechanisms of metal ions by novel sorbent materials providing structural information on the adsorption complexes and allowing exploration of the interaction between adsorbents and adsorbed species (Yan et al., 2017; Wang et al., 2013; Li et al., 2020; Bordiga et al., 2013; Parsons et al., 2002).

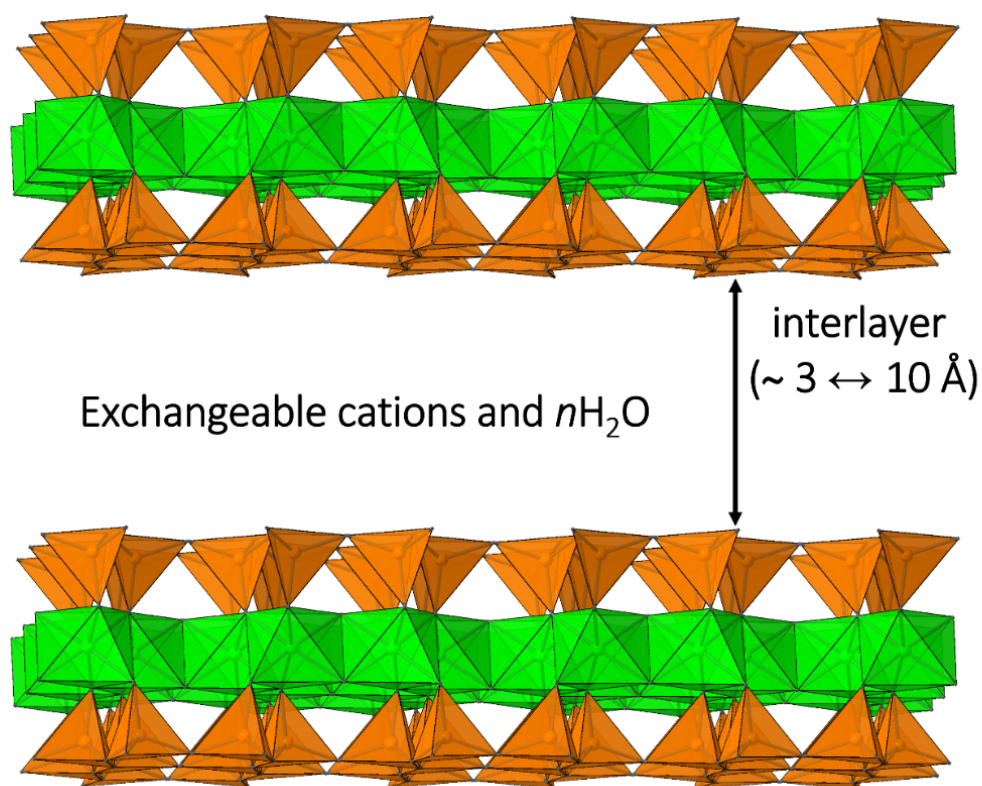


Figure 1. Crystal structure of montmorillonite, modified after Viani et al., 2002. TOT layers made of $AlO_4(OH)_2$ octahedra (green) and SiO_4 tetrahedra (orange). The layers are negatively charged and neutrality is mainly provided by intercalation of hydrated cations in the interlayer. Water adsorption and incorporation of hydrated cations lead to an expansion of the lattice along the c axis.

In order to investigate La local structural environment and to get further insights into the ion sorbent interaction mechanisms in a set of natural and modified montmorillonites previously

enriched in La, La L_{III}-edge X-ray absorption near edge structure (XANES) and Extended X-ray absorption fine structure (EXAFS) spectra have been collected on pristine smectite samples, namely a Ca-montmorillonite (STx-1b, STx in the following), and a Na-rich montmorillonite (SWy-2, SWy in the following), and on an STx sample modified by using the commercial linear pentaethylen-hexamine of formula C₁₀H₂₈N₆ (L6, in the following) as intercalating agent (STxL6, in the following).

Experimental details

Pristine clay

Two natural smectite samples were used as sorbents, namely a Ca-montmorillonite (STx-1b, which stands for “State of Texas”, **STx** in the following) and a Na-montmorillonite (SWy-2, which stands for “State of Wyoming”, **SWy** in the following) which were provided by the Clay Minerals Society. According to the suppliers datasheets, the chemical composition is: $X^{II}(Ca_{0.14}Na_{0.02}K_{0.01})^{VI}(Al_{1.21}Fe^{3+}_{0.05}Mg^{2+}_{0.36}Ti_{0.02})^{IV}Si_{4.0}O_{10}(OH)_2$ for the STx and $X^{II}(Ca_{0.11}Na_{0.16}K_{0.01})^{VI}(Al_{1.51}Fe^{3+}_{0.21}Mg^{2+}_{0.27}Mn_{0.01}Ti_{0.01})^{IV}(Si_{3.99}Al_{0.01})O_{10}(OH)_2$ for the SWy sample.

Organoclay preparation

Stx was modified upon intercalation with a C₁₀H₂₈N₆ polyamine (**L6** in the following, Sigma Aldrich, 99%). The synthesis of the organoclay (**StxL6**, in the following), was assessed elsewhere; the adopted experimental conditions allowed for the intercalation of at 0.40 mmol/g_{clay} of polyamine in its neutral form (Cristiani et al., 2019). Briefly, 2 g of STx were mixed with 50 ml of an aqueous solution of the polymer 180 mmol/L, and reacted under stirring (magnetic stirrer, 500 rpm), at 30 °C for 90 min and pH = 11, (measured by Mettler Toledo FE20/EL20 digital pH-meter). The solid-liquid separation was performed by centrifugation (13,000 rpm, 1 h, by a HETTICH 32 RotoFix centrifuge)

Capture and Release experiments

For the capture process, two contacting La³⁺ solutions, in the range 19-200 mM, were prepared starting from Lanthanum nitrate La(NO₃)₃·5H₂O 99.99% (Sigma Aldrich). In a typical capture experiment, 2 g of the pristine or modified clays were contacted with 50 mL of the La solution, under stirring at 25°C for 90 min. During the experiments, pH was measured by Mettler Toledo FE20/EL20 digital pH-meter (Mettler Toledo), but no pH correction was applied. In these conditions capture pH, for all the experiments, kept constant in the range 5-5.5. The suspensions were separated by centrifugation (13,000 rpm, 1 h; Iannicelli-Zubiani et al 2015, Cristiani et al 2021c). Samples composition is summarized in Table 1. In the table and in the text, samples are identified with a label related to the sample composition: *e.g.* StxLa-200 identifies the La-enriched Stx clay obtained upon contact of unmodified Stx with the initial ions’ solution 200 mM, as well as STxL6-19 identifies the sample obtained upon contact of the organoclay with initial ions solution 19 mM. The release tests were performed according to a previously developed

procedure which implied a contact time of 90 min, magnetic stirring (500 rpm), pH = 1 by the use of a HNO₃ solution, and a solid/liquid ratio of 0.026 g/mL. Phase separation was performed by centrifugation (13,000 rpm, 1 h). La concentration in all the liquid phases was analysed by ICP-OES inductively coupled plasma optical emission analysis (Optima 2000DV, Perkin Elmer). Captured La concentration was determined by the difference between La concentration in the initial solution and La concentration in the separated solutions after the capture processes, while released La was determined by the difference between La content in the clay-based materials and La content in the solution separated after the release process (Iannicelli-Zubiani et al 2015, Cristiani et al 2021c).

Table 1. Samples compositions, La and polyamine values correspond to the actual content in the solid

Sample	La initial concentration [mM]	Actual La content in the solid [mmol/g _{clay}]	Amine initial concentration [mM]	Actual L6 content in the solid [mmol/g _{clay}]
STxLa-200	200	1.2	-	-
STxLa-19	19	0.25	-	-
STxL6La-200	200	0.72	180	0.38
STxL6La-19	19	0.48	-	-
SWyLa-200	200	1.2	-	-
SWyLa-80	80	0.42	-	-

X-ray Absorption Spectroscopy (XAS)

XAS measurements at the La-*L*₃ edge (5482.7 eV) were performed at the LISA beamline (BM-08, d’Acapito et al., 2019) at the European Synchrotron Radiation Facility (ESRF, Grenoble – France). Measurements were taken employing a fixed exit dynamically focusing monochromator with a pair of Si (311) crystals, and a pair of Pd coated mirrors for harmonics rejection ($E_{\text{cutoff}} \approx 18$ keV). Spectra were acquired in the energy range 5283-5840 eV, corresponding to a maximum *k* value of $\sim 10 \text{ \AA}^{-1}$. The energy sampling interval in the near edge region was 0.5 eV. Powdered samples were mixed with cellulose and pressed in pellets using an amount of material such as to keep the total absorption (μ) ≤ 1.5 above the edge. Measurements were carried out in fluorescence mode by means of a 12-elements solid state (high purity Germanium) detector (Puri et al., 2019). A V (V *K*-edge= 5465.1 eV) metal foil was used to calibrate the energy. A minimum of four spectra was collected for each sample. The software ATHENA (Ravel and Newville, 2005) was used to calibrate energy (eV) and to average multiple spectra. Standard procedures (Lee et al., 1981) were followed to extract the structural EXAFS signal ($k \cdot \chi(k)$): pre-edge background removal,

spline modelling of bare atomic background, edge step normalization using a far above the edge region, and energy calibration. Model atomic clusters centred on the absorber atom were obtained by ATOMS (Ravel, 2001). Theoretical amplitude and phase functions were generated using the FEFF8 code (Ankudinov et al., 1998).

Results

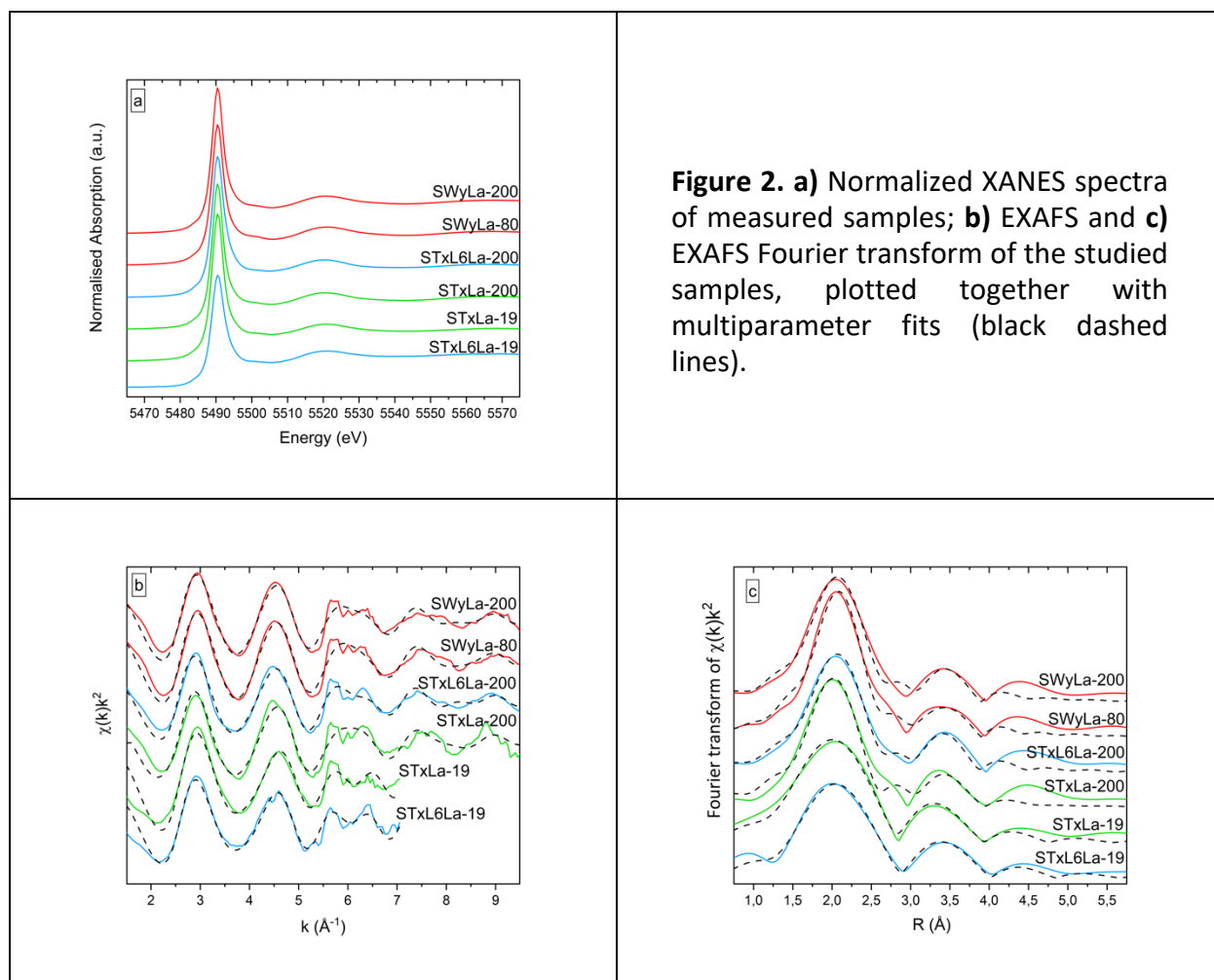
XANES spectra of the studied sample are reported in Figure 2. They display an intense white line at ca. 5490 eV, and a broad peak with a relatively low intensity at ca. 5520 eV. No significant differences can be observed among the measured samples in terms of overall shape of the spectra, peaks energy and intensity.

Table 2. EXAFS multiparameter fit results for the investigated samples.

	La-O (Å)	N (I shell)	σ^2 (Å ²)	La-Si/Al (Å)	N (II shell)	σ^2 (Å ²)	k range (Å ⁻¹)
STxLa-200	2.57(2)	10(2)	0.011(4)	4.18 (4)	6	0.012(8)	2.1-8.0
StxLa-19	2.58(2)	12(2)	0.025(5)	4.11(3)	5	-	2.1-6.4
SWyLa-200	2.60(2)	9(1)	0.013(3)	4.15(3)	5	0.009(5)	2.1-8.0
SWyLa-80	2.59(2)	9(1)	0.010(2)	4.14(4)	5	0.011(5)	2.1-9-0
STxL6La-200	2.60(2)	9(1)	0.013(3)	4.13(2)	6	0.008(4)	2.1-8.0
STxL6La-19	2.61(2)	10(1)	0.020(4)	4.16(3)	5	-	2.1-6.5

σ^2 = Debye-Waller factor, N= path degeneracy. Errors as reported in ARTEMIS. N value for the second shell was fixed to 5 or 6 depending on the samples. For samples STxLa-19 and STxL6La-19 it was not possible to refine the σ^2 value for the II coordination shell. E_0 values range from 7 to 9 eV.

The La L₃-edge EXAFS and Fourier transform of measured samples are shown in Figures 2b and 2c, respectively. The maximum k value achievable was limited by the L₂ absorption edge at ca. 5891 eV. Moreover, the shorter spectra of StxL6La-19 and STxLa-19 are due to the presence of small amounts of Ce in the sample. Main multiparameter fit results are reported in Table 2. Fits were performed in the Fourier-Transform space in the range \approx 1-4 Å. The many-body amplitude reduction factor S_0^2 was fixed to 0.8 for all samples. No systematic difference can be observed according to sample type and La concentration, suggesting that La local environment is mostly similar in all the samples. A second shell peak is clearly visible in the EXAFS Fourier-Transform. According to the multiparameter fit results, this peak is compatible with the presence of a II coordination shell with a Si and/or Al atoms. Samples StxL6La-19 and STxLa-19 show a reduced amplitude in the EXAFS region.



Discussion

As already mentioned, the spectra of the different montmorillonite samples, treated with La-rich solutions at different concentrations do not show major differences. Multiparameter fit results indicate $\langle \text{La-O} \rangle$ distances in the range 2.57-2.61 Å for all samples (Table 2, Figure 3a). Such distances suggest a large coordination number for La. According to the bond-valence theory (*e.g.* Brese and O'Keeffe, 1991; Gagné and Hawthorne, 2015) we cannot expect coordination numbers to vary much, given the short variation range of average bonding distance. Based on the parameters reported by Gagné and Hawthorne, 2015, La coordination number would span from ≈ 8.9 to ≈ 10 . Indeed the average distance found closely matches the one observed for La in a basic tricapped trigonal configuration (3+6) with O atoms such as hydrated La ions in aqueous solution and $\text{La}(\text{OH})_3$ (Zachariasen, 1948; Khidirov & Om, 1993). The above considerations are also supported by the results of X-ray Photoelectron Spectroscopy (XPS) analyses of La incorporated in montmorillonites discussed by Iannicelli-Zubiani et al., 2015.

The multiparameter fit results indicate a higher Debye-Waller parameter, which may be seen as a measure of the degree of disorder of La coordination, for the I coordination shell of La in samples StxL6La-19 and STxLa-19, which were treated with the La-poorer solutions (Table 2, Figure 3b). In Figure 3b it is also possible to notice how the I shell peaks of the same samples are broader and less intense compared to the others. La in StxL6La-19 and STxLa-19 also shows a slightly higher value of the path degeneracy (N) which, in this case, can be seen as a measure of the average coordination number; however, the coordination numbers obtained from EXAFS have low accuracy because of the correlation with other parameters affecting the amplitude of the EXAFS oscillation, specifically S_0^2 , which was fixed for this reason, and the Debye-Waller factor (σ^2). An accuracy of approximately 20% is thus typically assumed for coordination numbers and, in complex and disordered bonding environments, it is more reliable to support crystal chemical considerations on bond distances only.

XAS results evidence that Lanthanum ions allocation in the clay-based materials is independent on both polyamine presence and composition of the pristine clay. The coordination of La ions by the amino-groups of the polyamine observed by Cristiani et al. (2021c) could however be concealed by the fact that O and N x-ray scattering factors are too close to be discriminated, thus making La-O vs. La-N bonds basically equivalent unless a marked difference in La first shell coordination is involved. Therefore, the only parameter that may affect La coordination is Lanthanum content in the clay-based solid (compare spectrum of STxLa-19 with STxLa-200, spectrum of SWyLa-80 with SWyLa-200, and StxL6La-19 with StxL6La-200). Most of the studies to date explain La adsorption in clays with a purely outer-sphere model (e.g. Persson 2010, Iannicelli-Zubiani et al., 2015). In outer-sphere complexes, adsorption occurs at the interlayer sites of the clays and no direct bonds are formed between La and the sorbents. The La ions are thus easily exchangeable. Indeed, according to Trillo et al., 1992, the large value of the $\langle \text{La-O} \rangle$ distance in montmorillonite is compatible with the incorporation of hydrated La in the interlayer site. Also, according to the results obtained by Iannicelli-Zubiani et al. (2015) after a characterization performed with XRD and XPS methods on samples treated in a similar manner, La ions are captured at the clay interlayer, mainly via an ions exchange mechanism that implies the replacement of the interlayer cations with the REEs ones. However, the chemically tailored information obtained from EXAFS in this study indicates a more complex local environment for La ions. All the samples clearly show the presence of a second shell peak in the Fourier transform space that can be modelled as a La-Si/Al second coordination shell with a La-Si/Al distance ranging from 4.1 to 4.2 Å. The presence of this kind of interaction cannot be explained only with the hypothesis of La surrounded by water molecules replacing for Na/Ca in the interlayer of montmorillonite. In order to account for the short La-Si/Al distance a further incorporation mechanism must then be considered. The most likely hypothesis is that at least a part of La ions is adsorbed as inner-sphere complexes at the edges and/or at the surface of montmorillonite. This data also confirms previous literature indication on these sorbents contacted with similar

solutions (Cristiani et al., 2021c) and different solutions of different compositions (Cristiani et al., 2021a, b and 2022). Several bonding environments are possible (*e.g.* Tan et al., 2014) on octahedral and tetrahedral sites of clays; however, a corner-shared monodentate and/or bridging bidentate bindings (Fig. 4) are the only mechanism compatible with the observed La-Si/Al distances, since other mechanisms would lead to too short La-Si/Al distances.

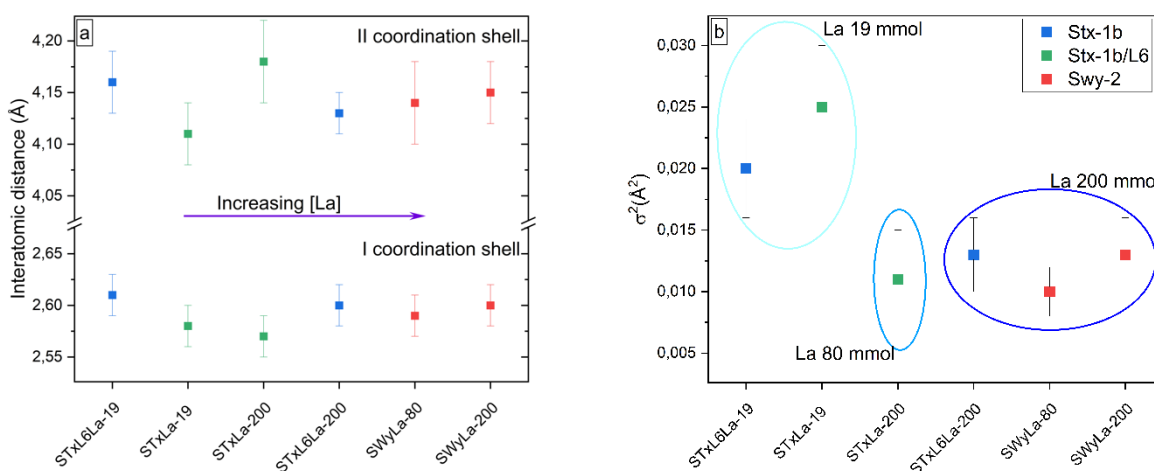


Figure 3. (a) Interatomic distances obtained from EXAFS multiparameter fit. (b) Debye-Waller factors for La I coordination shell.

The inner-sphere surface complexes are usually considered thermodynamically stable, thus making desorption more difficult compared to outer-sphere complexes; however, in the experimental condition of this work, a La release efficiency, up to 70% has been reached. This result is explained by the harsh conditions adopted in the release process, where pH=1 has been applied to assure the maximum lanthanum release via protonation of the interlayer in pristine clay and also polyamine full protonation in the case of the polymer-modified material (Iannicelli Zubiani et al. 2015, Cristiani et al. 2021 c).. In agreement with what was also found for Eu in similar systems (Kowal-Fouchard et al., 2004; Tan et al., 2014 and references therein), it is most likely that La in montmorillonite is adsorbed both via ion-exchange sites as an outer-sphere complex and onto both octahedral and tetrahedral sheets edges as mono- or bi-dentate complexes. A double uptake mechanism would also explain the higher values of Debye-Waller factors for samples StxL6La-19 and STxLa-19 with respect to the La-richer ones. The higher disorder in samples with lower La loadings could indeed be reflecting a higher ratio between inner- and outer-sphere complexes at low La uptake extent. Given the high efficiency for La release, it is evident that, as La loadings increase, the formation of outer-sphere complexes becomes the favoured uptake mechanism. The concurrent decrease of the ratio between inner- and outer-

sphere complexes is then highlighted by the reduced Debye-Waller factor for samples at higher La loadings.²⁷

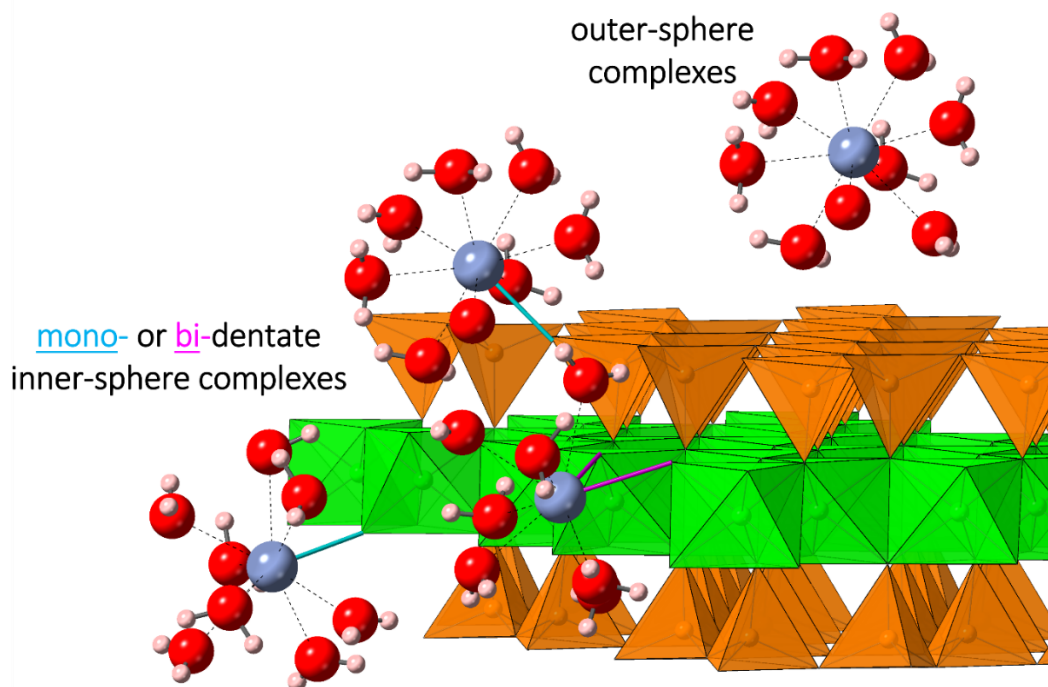


Figure 4. Example inner vs. outer complexation. Red and Blue-grey spheres are La and O atoms, respectively; light-blue and purple bars indicate corner-shared monodentate and bidentate complexes of La ions on octahedra and tetrahedra.

Conclusions

XAS results account for the presence of heterogeneous capture sites and thus different La-sorbent interaction. The $\langle \text{La-O} \rangle$ distances determined with EXAFS on all the studied samples are comprised in the 2.57-2.61 Å range, with a grand average La-O distance of 2.59 Å and a standard deviation of ± 0.015 Å. As the sigma of each distance (0.02 Å) is larger than the standard deviation of all the distances, we can deduce that there is no detectable change in the average La-O distance for these samples with respect of clay type, La concentration and the presence of polyamine. The determined $\langle \text{La-O} \rangle$ distance is in agreement with La coordinated by O atoms in a basic tricapped trigonal configuration (3+6), with an average distance of about 2.60 Å.

The La-O distance is compatible with the location of La in the interlayer of the studied samples; in particular, it is compatible with coordination of La by water molecules. However, the presence of a second shell with Si or Al indicates a more complex picture for the structural environment of La in the clay samples studied here. While La-O distance taken alone may point towards a simple cation exchange mechanism (with La coordinated by water molecules in the interlayer), the La-

Si/Al distances indicate the concurrent presence of mono- or bi-dentate inner-sphere complexes between high-coordinated La and the oxygen atoms belonging to the outer surfaces of either the tetrahedral or the octahedral sheets of the TOT layer. Moreover, the comparison between samples with different La loadings seems to indicate that the formation of inner-shell complexes is relatively favoured at lower La loadings, while outer-shell complexes become prevalent at increasing La uptake. The effect of the different La loadings may be related to a progressive saturation of different adsorption sites present in the clays, which may imply occupancy of different sites by complexes of different nature. The presence of surface complexes may act as a factor reducing the extent/efficiency of La recovery. Further investigation focused on the influence of the La-content in the sorbent clays on the efficiency of the La release are needed. In conclusion, our results shed light on the complex structural mechanisms concerning La uptake in clay minerals, providing important and accurate information for the improvement of the existing methods and for the exploration of new technologies for REEs recovery. Indeed, the comprehension of La bonding mechanisms in clay sorbents allows to design processes and sorbents characterized by improved properties, such as efficiency and selectivity. Moreover, the use of clays for the design of solid sorbents is intrinsically an environment-friendly solution, having clays low cost, good mechanical properties and excellent reusability.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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